STATE OF WASHINGTON

DRAFT DANGEROUS WASTE MANAGEMENT PERMIT

FOR CORRECTIVE ACTION

Department of Ecology

P.O. Box 477775

Olympia, Washington 98504-7775

Issued in accordance with the applicable provisions of the Hazardous Waste Management Act in Chapter 70.105 Revised Code of Washington (RCW), and the regulations promulgated thereunder in Chapter 173-303 Washington Administrative Code (WAC).

ISSUED TO:

Occidental Chemical Corporation
605 Alexander Avenue
Tacoma, Washington, 98421
And
Glen Springs Holdings, Inc.
7601 Old Channel Trail
Montague, Michigan 49437

FOR:

Occidental Chemical Corporation
605 Alexander Avenue
Tacoma, Washington, 98421

This Permit is effective as of January 6, 2020 and shall remain in effect until January 6, 2030 unless revoked and reissued, modified, or terminated under WAC 173-303-830(3) and (5) or continued in accordance with WAC 173-303-806(7).

ISSUED BY:

WASHINGTON DEPARTMENT OF ECOLOGY

Michelle Underwood, Section Manager
Department of Ecology
Hazardous Waste and Toxics Reduction Program
Southwest Regional Office

INTRODUCTION

Permittees: Occidental Chemical Inc. and Glenn Springs Holdings Inc.
I.D. Number: WAD009242314

Pursuant to Chapter 70.105 RCW, the Hazardous Waste Management Act of 1976, as amended, and regulations codified in Chapter 173-303 WAC, a permit is issued to Occidental Chemical Corporation and Glenn Springs Holidngs Inc. (jointly referred to as the Permittees) to conduct corrective action at Occidental Chemical Inc., located at 605 Alexander Avenue, Tacoma, Washington, 98401. The Permittees must comply with all the conditions of this permit.

Pursuant to RCW 70.105D.030(1)(d), the Washington State Department of Ecology (Ecology) is designated by the Washington State Legislature to carry out all State programs authorized by the United States Environmental Protection Agency (EPA) pursuant to the federal Resource Conservation and Recovery Act (RCRA), 42 U.S.C. Sec. 6901 et. Seq., as amended. Ecology has authority to issue this Permit in accordance with RCW 70.105.130 and is responsible for enforcement of all conditions of this Permit. Anyone may appeal these permit conditions or decisions by Ecology to the Pollution Control Hearings Board in accordance with WAC 173-303-845.

PART I – GENERAL CONDITIONS

I.1 The Permittees shall comply with all requirements of WAC 173-303-810, which are hereby incorporated by reference into this Permit.

I.2 Modifications to the Agreed Order Docket No. 16943, effective December 31, 2019 which is administered by Ecology shall not require a permit modification except when required by WAC 173-303-830, Appendix I (N)(5) to incorporate a substantial change requiring public comment under WAC 173-303-340-600. The Agreed Order is not appealable to the Pollution Control Hearings Board.

I.3 Compliance with the terms of this Permit does not constitute a defense to any order issued or any action brought under any other state or federal laws governing protection of public health or the environment. However, compliance with the terms of this Permit does constitute a defense to any action alleging failure to comply with the applicable standards upon which this Permit is based.

I.4 Pursuant to WAC 173-303-806(6), the Permittees shall submit a new application for a final permit 180 days prior to the expiration date of this permit, unless Ecology grants a later date provided that such date is not later than the expiration date of the Permit. This Permit and all its conditions will remain in effect beyond the Permit's expiration date until Ecology has made a final permit determination if: (1) the Permittees have submitted a timely application for a final status permit; (2) Ecology determines that the final permit application is complete as set forth in WAC 173-303-840(1)(b), and (3) Ecology has not made a final permit determination as set forth in WAC 173-303-840..

If the Permittees fail to comply with the terms and conditions of the expiring or expired permit, then Ecology may take action consistent with WAC 173-303-806(7)(b). If the Permittees fail to submit a timely complete application as required herein, then those permit conditions necessary to protect human health and the environment will remain in effect beyond the Permit's expiration date in accordance with WAC 173-303-815(2)(b)(ii), until Ecology terminates the conditions.

PART II – CORRECTIVE ACTION

II. Ecology is requiring that the Permittees fulfill corrective action responsibilities for the facility, as defined by WAC 173-303-040, using the Model Toxics Control Act (MTCA), (Chapter RCW 70.105D), as amended, and its implementing regulations (Chapter 173-340 WAC) and the Dangerous Waste Regulations [Chapter 173-303 WAC – specifically, WAC 173-303-646]. See Section III.1, *infra.* The actions taken must meet or exceed all substantive corrective action requirements of the Resource Conservation and Recovery Act (RCRA), the state Hazardous Waste Management Act, and the Dangerous Waste Regulations.

The Permittees' corrective action obligations with respect to the facility under the Agreed Order Docket No. 16943, effective December 31, 2019, are enforceable conditions of this Permit under the authority of Chapter 70.105 RCW, and its implementing regulations, Chapter 173-303 WAC.

PART III – CORRECTIVE ACTION CONDITIONS

III.1 The Agreed Order Docket No. 16943, effective December 31, 2019 and its attachments are incorporated by reference as fully enforceable under this Permit. Regardless of whether or not the Agreed order is vacated, the Permittees' corrective action obligations continue to be enforceable conditions of this Permit under the authority of the Hazardous Waste Management Act (HWMA), Chapter 70.105 RCW, and its implementing regulations, Chapter 173-303 WAC.

III.2 When Ecology selects a final cleanup remedy for Occidental Chemical Inc., this Permit will be modified as needed to include the selected remedy and incorporate by reference a consent decree or other available administrative mechanism.

STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY

In the Matter of Remedial Action by: Occidental Chemical Corporation, Glenn Springs Holdings, Inc., and Mariana Properties, Inc. For: Occidental Chemical Facility Site Facility Site No. 4326 Cleanup Site No. 1212 WAD009242314	AGREED ORDER No. DE 16943

TO: Occidental Chemical Corporation
Glenn Springs Holdings, Inc.
Mariana Properties, Inc. Attn:
Mr. Clinton Babcock
7601 Old Channel Trail
Montague, MI 49437

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I. INTRODUCTION

The mutual objective of the State of Washington, Department of Ecology (Ecology) and Occidental Chemical Corporation (OCC), Glenn Springs Holdings, Inc., and Mariana Properties Inc. (collectively referred to as potentially liable parties or PLPs under this Agreed Order (Order)) is to provide for remedial actions at a facility where there has been a release or threatened release of hazardous substances. This Order requires the PLPs to complete seasonal water level monitoring, perform a longer-term pumping test at inactive extraction well EXT-9, implement an approved Monitoring Plan to provide a baseline of groundwater quality data, and provide assistance to Ecology as requested in the development of a draft Cleanup Action Plan (dCAP). Ecology believes the actions required by this Order are in the public interest.

An Enforcement Order was issued to PRI Northwest, Inc. (PRI), F.O. Fletcher, Inc. and OCC on September 1, 1995, for the implementation of a Cleanup Action Plan at 709 Alexander Avenue. This Order shall supersede and replace the 1995 Enforcement Order No. DE95TC-S242 issued by Ecology to PRI, F.O. Fletcher, Inc., and OCC. This Order also shall supersede and replace the Administrative Order on Consent (AOC), as amended, among the United States Environmental Protection Agency (EPA), Ecology, and OCC in EPA Docket No. 10-97-0011-CERCLA (Amended AOC), attached to this Order as Exhibit B, as that Amended AOC pertains to Ecology and OCC, upon the execution by EPA, Ecology, and OCC of the second amendment of the Amended AOC providing for Ecology’s withdrawal from the Amended AOC. The status of the Amended AOC as it pertains to EPA and OCC will be addressed separately by EPA and OCC.

II. JURISDICTION

This Order is issued pursuant to the authority of the Model Toxics Control Act (MTCA), RCW 70.105D.050(1). This Order also satisfies the requirements of WAC 173-303-646 through -64630.

III. PARTIES BOUND

This Order shall apply to and be binding upon the Parties to this Order, their successors and assigns. The undersigned representative of each Party hereby certifies that he or she is fully authorized to enter into this Order and to execute and legally bind such Party to comply with the Order. The PLPs agree to undertake all the actions required by the terms and conditions of this Order. No change in ownership or corporate status shall alter the PLPs' responsibility under this Order. The PLPs shall provide a copy of this Order to all agents, contractors, and subcontractors retained to perform work required by this Order, and shall ensure that all work undertaken by such agents, contractors, and subcontractors complies with this Order.

IV. DEFINITIONS

Unless otherwise specified herein, the definitions set forth in RCW 70.105D and WAC 173-340 shall control the meanings of the terms used in this Order.

A. Agreed Order or Order: Refers to this Order and each of the exhibits to this Order. All exhibits are integral and enforceable parts of this Order. The terms "Agreed Order" or "Order" shall include all exhibits to this Order.

B. Area of Concern: Refers to any area of the Facility where a release of dangerous constituents (including dangerous waste and hazardous substances) has occurred, is occurring, is suspected to have occurred, or threatens to occur.

C. CERCLA: Refers to the Comprehensive Environmental Response, Compensation, and Liability Act, 42 U.S.C. §§ 9601–9675.

D. Cleanup Action Plan (CAP): Refers to the document prepared by and issued by Ecology under WAC 173-340-380 which selects Facility-specific corrective measures and specific cleanup standards (cleanup levels, points of compliance, and other requirements for the corrective measures).

E. Cleanup Standards: Refers to the standards promulgated under RCW 70.105D.030(2)(e) and include (1) hazardous substance concentrations (cleanup levels) that protect human health and the environment, (2) the location at the Facility where those cleanup levels must be attained (points of compliance), and (3) additional regulatory requirements that apply to a cleanup because of the type of action and/or the location of the Facility.

F. Corrective Action: Refers to any activities including investigations, studies, characterizations, and corrective measures, including actions taken pursuant to RCW 70.105D and WAC 173-340, undertaken in whole or in part to fulfill the requirements of WAC 173-303-64620.

G. Corrective Measures: Refers to any measure or action to control, prevent, or mitigate release(s) and/or potential release(s) of dangerous constituents (including dangerous waste and hazardous substances) reviewed and approved by Ecology for the Facility and set forth in a Facility-specific CAP prepared in compliance with the requirements of WAC 173-340, including WAC 173-340-360. Corrective measures may include interim actions as defined by WAC 173-340. Interim actions will not necessarily be set forth in a Facility-specific CAP.

H. Dangerous Constituent or Dangerous Waste Constituent: Refers to any constituent identified in WAC 173-303-9905 or 40 C.F.R. pt. 264, appendix IX; any constituent that caused a waste to be listed or designated as dangerous under the provisions of WAC 173-303; and any constituent defined as a hazardous substance under RCW 70.105D.020(13).

I. Dangerous Waste: Refers to any solid waste designated in WAC 173-303-070 through -100 as dangerous or extremely hazardous or mixed waste. Dangerous wastes are considered hazardous substances under RCW 70.105D.020(13).

J. Dangerous Waste Management Facility: Used interchangeably in this document with the term “Facility.”

K. Dangerous Waste Management Unit (DWMU): Refers to a contiguous area of land on or in which dangerous waste is placed, or the largest area in which there is a significant likelihood of mixing dangerous waste constituents in the same area, as defined in WAC 173-303-040.

L. Facility: Refers to the Occidental Chemical Facility, EPA ID Number WAD009242314, a site with former DWMUs located at 605 Alexander Avenue, Tacoma, Washington; all property contiguous to the former DWMUs, including 709 Alexander Avenue; and all property, regardless of control, affected by release(s) or threatened release(s) of hazardous substances, including dangerous wastes and dangerous constituents, at and from these areas.

"Facility" also includes the definition found in RCW 70.105D.020(8). "Facility" shall not include the extent of contamination caused by the release of hazardous substances originating from activities associated with historic petroleum storage and processing facilities that were operated at real properties located at 709 Alexander Avenue and at 901 and 1001 Alexander Avenue (previously known as 721 Alexander Avenue), subject to Agreed Order No. DE 9835 among Ecology, Mariana Properties, Inc., and the Port of Tacoma, and denominated as the Alexander Avenue Petroleum Tank Facilities Site. *See* Exhibit A (Facility Diagram).

M. Feasibility Study (FS): Refers to the investigation and evaluation of potential corrective measures performed in accordance with the FS requirements of WAC 173-340-350 which includes the substantive requirements for a Resource Conservations and Recovery Act (RCRA) Corrective Measures Study and a Comprehensive Environmental Response, CERCLA FS, and which is undertaken in whole or in part to fulfill the corrective action requirements of WAC 173-303-64620.

N. Parties: Refers to Ecology, OCC, Glenn Springs Holdings, Inc., and Mariana Properties Inc.

O. Potentially Liable Person (PLP): Refers to OCC, Glenn Springs Holdings, Inc., and Mariana Properties, Inc.

P. Permit or Permitting Requirement: Unless otherwise specified, refers to the requirements of WAC 173-303 for applying for, obtaining, maintaining, modifying, and terminating Dangerous Waste Management Facility permits.

Q. Property: Refers to the real property located at 605 Alexander Avenue, Tacoma, Washington, consisting of approximately 23 acres, and the real property located at 709 Alexander Avenue, consisting of approximately 4.4 acres, both currently owned by Mariana Properties, Inc.

R. RCRA: Refers to the Resource Conservation and Recovery Act, 42 U.S.C. §§ 6901–6992k.

S. RCRA Facility Assessment (RFA): Refers to the EPA conducted investigation of release(s) and potential release(s) at the Dangerous Waste Management Facility and the information contained in the report entitled RCRA Facility Assessment Report, Occidental Chemical Corporation, Tacoma, Washington dated February 26, 1988. The RCRA Facility Assessment is incorporated into this Order by reference as if fully set forth herein.

T. Release: Refers to any intentional or unintentional spilling, leaking, pouring, emitting, emptying, discharging, injecting, pumping, escaping, leaching, dumping, or disposing of dangerous waste or dangerous constituents into the environment. It also includes the abandonment or discarding of barrels, containers, and other receptacles containing dangerous waste or dangerous constituents, and includes the definition of "release" in RCW 70.105D.020(32).

U. Remedial Investigation (RI): Refers to a facility-wide investigation and characterization performed in accordance with the requirements of WAC 173-340, which includes the substantive requirements for a RCRA facility investigation and a CERCLA RI, undertaken in whole or in part to fulfill the corrective action requirements of WAC 173-303-64620, and the Amended AOC with Statement of Work (Exhibit B).

V. Site: Is used interchangeably with "Facility" and has the same definition.

W. Solid Waste Management Unit (SWMU): Refers to any discernible location at the Dangerous Waste Management Facility where solid wastes have been placed at any time, irrespective of whether the location was intended for the management of solid or dangerous waste. Such locations include any area at the Dangerous Waste Management Facility at which solid waste, including spills, have been routinely and systematically released, and include regulated unit as defined by WAC 173-303.

V. FINDINGS OF FACT

Ecology makes the following Findings of Fact, without any express or implied admissions of such facts by the PLPs.

Findings of Fact Addressing Ownership of the Facility

A. The Property is located on the eastern-most peninsula within the 12-square mile area of the Commencement Bay Nearshore/Tideflats (CB/NT) Superfund Site in Tacoma, Washington, at the southern end of the main basin of Puget Sound. The CB/NT Superfund Site includes several waterway problem areas and adjoining uplands, including the Mouth of Hylebos Problem Area where the Facility is located. The peninsula is bordered by the Hylebos Waterway on the east side and the Blair Waterway on the west. The Property includes a shoreline with the Hylebos Waterway, and is further bounded on the west, north, and south by real property formerly owned and/or operated by the United States (the United States Maritime Commission, Navy, Air Force, Naval, and Marine Corps Reserve, and/or other instrumentalities of the United States), now owned by the Port of Tacoma. On September 8, 1983, EPA placed the CB/NT Superfund Site on the National Priorities List pursuant to Section 105 of CERCLA, 42 U.S.C. § 9605.

B. The real properties which comprise the Site were undeveloped tidal mudflats prior to 1920. The area was filled with approximately 16 feet of dredge material as part of an upland expansion project between 1920 and 1936.

C. The Property located at 709 Alexander Avenue was owned and operated by F.O. Fletcher, Inc. (and predecessor and related entities) (Fletcher Oil) as a bulk petroleum fuel storage and distribution terminal from the 1930s to the 1980s. During the 1970s and 1980s, Fletcher Oil operated a tetraethyl lead plant at 709 Alexander Avenue, blending lead with gasoline. In addition, United Independent Oil operated a topping plant for crude oil distillation on the property in the 1970s and 1980s.

D. Hooker Electrochemical Company began operations at the Facility in 1929 and acquired additional adjacent parcels over time, including what is known as the North Ten Acres, acquired in 1937 from Todd Pacific Shipyards, Inc. (aka Seattle-Tacoma Shipbuilding Corp.) (Todd Shipyards). Todd Shipyards leased what is known as the North Ten Acres from Hooker Electrochemical Company from May 1941 until about June 1946. Todd Shipyards and instrumentalities of the United States including the Maritime Commission and Navy operated a salvage yard, waste incinerator and maintenance activities on this parcel during World War II. Between 1945 and 1946 a portion of the shoreline of this 10-acre parcel was used as a waste dump now known as the Navy/Todd Dump.

E. Navy Bureau of Ships entered into a contract with Todd Shipyards whereby "certain shipbuilding facilities owned by the Government" were "furnished for the use of [Todd Shipyards]." The government-owned equipment on Hooker Electrochemical Company's property (leased to Todd Shipyards) included an incinerator, a nut and bolt salvage building, salvage bins, as well as catch basins and drainage lines.

F. Defense Plant Corporation leased a portion of Hooker Electrochemical Company's Tacoma plant site and constructed Plancor 1560, an aluminum chloride plant, at the request of the War Production Board. The operation of this Plancor by Hooker Electrochemical Company was dependent on receiving chlorine, hydrogen, and steam from the adjoining Hooker Electrochemical Company plant via pipelines. The Defense Plant Corporation was a subsidiary of the Reconstruction Finance Corporation (a Depression-era United States government corporation created to fund economic recovery). The current successor of Reconstruction Finance Corporation is the General Services Administration.

G. Hooker Electrochemical Company entered into a joint venture with Detrex Inc. in 1946, forming Hooker-Detrex Inc., to manufacture tetrachloroethylene (PCE) and trichloroethylene (TCE) at the Facility. In 1958 Hooker Electrochemical Company adopted the name Hooker Chemical Corporation. By 1968 Hooker Chemical Corporation was acquired by and became a subsidiary of Occidental Petroleum Corporation. Hooker Chemical Corporation continued as a wholly-owned subsidiary of Occidental Petroleum Corporation. Hooker Chemical Corporation changed its name to OCC in 1981.

H. OCC's predecessor ceased TCE/PCE manufacturing in May of 1973. However, the Facility continued to manufacture chlorine, caustic soda, muriatic acid, and calcium chloride. In 1979 the demolition of the PCE/TCE plant was initiated.

I. The Facility was transferred by Quit Claim Deed from OCC to Occidental Chemical Corporation Tacoma, Inc. (OCC Tacoma). OCC Tacoma ". . . assumed all of the liabilities and obligations of Occidental Chemical Corporation with respect to the Tacoma Plant [Facility], including the Joint Permit, as of February 1, 1997."

J. The Facility was then sold to Pioneer Chlor-Alkali Company, Inc. (Pioneer), a Delaware corporation, on June 17, 1997. OCC Tacoma retained ownership of the groundwater treatment plant; however, Pioneer employees operated the plant on OCC Tacoma's behalf.

K. By letter dated May 9, 2001, OCC Tacoma informed Ecology and EPA of a merger of OCC Tacoma, Inc., into its parent and sole stockholder, OCC. All of OCC Tacoma's obligations, including corrective action and continued operation of the groundwater treatment plant, were transferred to OCC on June 15, 2001.

L. On December 20, 2005, Pioneer (emerging from bankruptcy as Pioneer Americas, LLC) notified Ecology and EPA that Pioneer Americas, LLC was negotiating a sale of the Facility to Mariana Properties, Inc., an affiliate of OCC. Pioneer Americas, LLC had already terminated the manufacturing of chlor-alkali and was operating the Facility solely for product storage and transfer operations. The final sale to Mariana Properties, Inc. occurred on January 5, 2006.

M. Glenn Springs Holdings, Inc., ". . . an affiliate of Occidental Chemical Corporation . . ." manages remediation projects for OCC in multiple states, including remediation of the Facility in Tacoma.

Findings of Fact Addressing Permit Status and Corrective Action

N. On November 17, 1980, a Part A permit application was submitted to EPA to operate a hazardous waste management facility under RCRA by OCC's predecessor for the Facility. An amended Part A permit application was submitted on August 12, 1982. EPA issued a letter dated April 17, 1985, acknowledging the submittal of both Part A applications. The EPA letter formally requested the submittal of a Part B application under the authority of 40 C.F.R. § 270.10(e)(4), which was submitted by OCC in October 1985.

O. In February 1988, EPA issued a RCRA Facility Assessment report identifying seventeen (17) SWMUs at the Facility.

P. On November 16, 1988, Ecology and EPA issued a joint permit for the storage of dangerous waste at the Facility. The permit authorized dangerous waste management in the following units without specific capacity limits:

1. Two railcar container storage units in areas referred to as TC1, TC2, and TC3. Wastes authorized to be stored were chlorinated hydrocarbons/sulfuric acid mixture (waste codes K073, D002), decanted chlorinated hydrocarbons (K073), decanted sulfuric acid (D002, K073), and chlorinated hydrocarbons (K073).
2. One container drum storage unit authorized to store solid residues from closure and/or spill cleanup of chlorinated hydrocarbons (K073). Spent graphite electrode "blades and butts", mastic, and dross (D008), and contaminated clothing (K073).
3. Graphite waste pile building containing spent graphite electrode "blades and butts", mastic, and dross (D008).

Q. Since 1979, corrective action was conducted with both Ecology and EPA oversight. In December 1979, a Phase I groundwater investigation was completed, and in August 1980, a Phase II groundwater investigation was completed. A Phase III investigation of chlorinated volatile organic compounds in unsaturated soils was conducted in October 1980. Additional work completed from 1980 to 1988 included the completion of a groundwater quality report and proposed corrective action (December 1980), excavation and disposal off-site of 1850 cubic yards of soils containing chlorinated volatile organic compounds from the vadose zone in the former TCE/PCE plant area and from adjacent former lime settling ponds that served the plant, evaluation of monitoring data by Conestoga-Rovers & Associates, quarterly groundwater monitoring, multiple reports on the Hylebos Waterway sediment sampling, reports assessing groundwater treatment technologies, and compilation of a groundwater data base, with an addendum.

R. Corrective action, after the permit was issued, was covered by Section V of the permit entitled "Corrective Action for Past Practices". The permit directed the continuation of investigations already underway. OCC submitted RCRA Facility Investigation I and II reports in July and October 1989, respectively.

S. Closure of the permitted units was accomplished between 1990 and 1995. In May 1990, OCC closed permitted storage areas TC1 and TC3 as well as the graphite waste pile. These units were certified by OCC to be clean closed, and Ecology approved the certifications in August of the same year. Between March 1995 and August 1995 OCC completed, and Ecology approved, the certified clean closure of the remaining units.

T. Under the Dangerous Waste Permit, the corrective action to address soil and groundwater contamination between 1990 and 2005 consisted of the removal of 750 cubic yards of contaminated soils during construction of the groundwater treatment facility, submittal of a Corrective Action Plan and a Corrective Action Monitoring Plan, analysis of Preliminary Pumping Tests, construction and start-up of the groundwater treatment facility, and the start-up of groundwater extraction and injection systems. Beginning in 1996, OCC submitted quarterly monitoring event reports under a revised Corrective Action Plan and an updated Corrective Action Monitoring Plan, approved by EPA in October 1998. After the start-up of the extraction system, OCC also submitted Annual Data and Performance Evaluations. A “Compilation of Soils and Related Data” was submitted in January 1999. Annual “Investigation Progress Reports” were submitted by OCC beginning in December 2000.

U. In 2005, Ecology required OCC to submit a Corrective Measures Study work plan. The work plan was submitted by OCC and approved by Ecology on February 1, 2005.

V. The last groundwater monitoring report under the Corrective Action Monitoring Plan was dated May 2009. Ecology formally suspended implementation of the Corrective Action Monitoring Plan in 2013 acknowledging that the plan would be revised when Ecology determined clear objectives for continued groundwater monitoring.

W. A Part B permit renewal application was received on May 20, 1998. The existing permit subsequently expired on November 16, 1998, but remained effective until April 29, 2005, when a RCRA corrective action permit was issued incorporating by reference the Amended AOC. The corrective action permit expired on April 29, 2015.

Facts Related to Contamination

X. OCC and its predecessors, formerly owned and operated a chemical plant which continuously operated from 1928 until June 1997. At various times, the plant manufactured chlorine, sodium hydroxide, calcium chloride, muriatic acid, ammonia, ammonium hydroxide, TCE, PCE, sodium aluminate, and aluminum chloride. From approximately 1929 to 1970, effluents from chlorine production operations were discharged directly to the Hylebos Waterway through the main plant outfall. Wastes from the TCE and PCE production process were discharged to the Hylebos Waterway, disposed of at a deep-water disposal site, temporarily held in on-site settling ponds, or disposed of off-site. Due to past operating practices, soil and groundwater on and under portions of the Facility contain chlorinated organic compounds. Direct discharge of sludges and wastewaters as well as the soil and groundwater are potential sources of certain organic compounds detected in the Hylebos Waterway.

Y. Todd Shipyards, via Todd Dry Dock & Construction Co., formerly owned and operated ship construction facilities which were active during World War I under the supervision of the United States Maritime Commission, the United States Navy, and/or other instrumentalities of the United States. The shipyard continued to exist after World War I and into the 1930s, but little is currently known about its activities. In 1939, Todd Shipyards under contract with the United States Maritime Commission began construction of a shipyard at the end of the Hylebos/Blair Peninsula that during World War II occupied essentially all of the peninsula north of Eleventh Street, with the exception of the chemical plant located at 605 Alexander Avenue and a petroleum storage/distribution facility located at 709 Alexander Avenue. The shipyard operated from 1939 to 1946, and its operations were supervised and controlled by instrumentalities of the United States. The North Ten Acres at 605 Alexander Avenue were used by Todd Shipyards and instrumentalities of the United States for a variety of shipyard activities, including: a "scrap disposal yard," waste incineration, vehicle maintenance (including a 2000 gallon fuel tank on the shoreline), and a sewer system that discharged to the Hylebos Waterway. Shipyard wastes were dumped on the uplands and on the shoreline of the North Ten Acres and partially pushed into the Hylebos Waterway, forming the Navy/Todd Dump. Following World War II, the United States Navy used most of the Mouth of the Hylebos Waterway area and adjacent upland properties (then called the Naval Station Tacoma) for mothballing, berthing, maintaining, and/or dismantling Navy ships. The Port of Tacoma purchased most of the Naval Station Tacoma properties from the United

States in 1960, and has since leased portions of the properties to many businesses, including several ship-related businesses. Operations at 401 Alexander Avenue (north of, and adjacent to, 605 Alexander Avenue), previously known as the Port Industrial Yard and now known as the Earley Business Center, have included ship dismantling by Zidell Dismantling (1960 to 1984), ship construction by Tacoma Boatbuilding (1969 to 1987), ship construction by AK-WA Shipbuilding (1986 to 1997), and ship-related operations of the United States Army Reserve. Other operations in the vicinity of the Property (south of, and adjacent to, 709 Alexander Avenue) have included United States Air Force petroleum storage/distribution facilities and the United States Naval and Marine Corps Reserve homeport for vessels. Due to past operating practices associated with the activities described above, soil and groundwater on and under portions of the Facility contain various hazardous substances. Direct discharge of wastes as well as the soil and groundwater are potential sources of hazardous substances detected in the Hylebos Waterway.

Z. Under a Cooperative Agreement with EPA, Ecology conducted a RI/FS of the CB/NT Superfund Site. Within the Tideflats area of the CB/NT Superfund Site, the RI/FS evaluated the nature and extent of contamination in the Sitcum, Blair, Milwaukee, Hylebos, St. Paul, Middle, Thea Foss (formerly known as City), and Wheeler-Osgood Waterways. The final RI/FS was made available for public comment in February 1989. Several chemicals were detected in the Mouth of the Hylebos Waterway sediments, including, but not limited to, polychlorinated biphenyls, hexachlorobenzene, TCE, PCE, 1,2-dichlorobenzene, 1,3-dichlorbenzene, hexachlorobutadiene, and lead. On September 29, 1989, EPA issued a Record of Decision (ROD) that selected the remedy for remediation of sediments for Operable Unit 1 (Mouth of the Hylebos and Head of the Hylebos) and sources of contamination (Operable Unit 05) in the CB/NT Superfund Site. polychlorinated biphenyls and hexachlorobenzene, were selected as chemical indicators of biological effects and human health risks at the Mouth of the Hylebos Waterway because these chemicals were found at the highest concentrations over the greatest area.

1. The ROD also determined that natural recovery will not sufficiently reduce contaminant concentrations in some areas of the Mouth of the Hylebos Waterway

within the ten (10) year period, so the ROD required active sediment cleanup with one (1) of the four (4) technology options as a component of the remedy.

2. OCC, along with five other companies or entities, performed pre-remedial design activities pursuant to the ROD on the Hylebos Waterway under an AOC, dated November 25, 1993.

AA. During pre-remedial design activities, organic compounds were detected in sediment adjacent to the Property and in the vicinity of where barges were used for sludge dewatering. This area was identified as Area 5106, and characterized as having relatively high concentrations of TCE, PCE, vinyl chloride, hexachlorobenzene, and hexachlorobutadiene above the sediment quality criteria.

BB. An investigation into the embankment area of the Facility, between +18 feet mean lower low water level and 0 feet mean lower low water level, found concentrations of contaminants significantly above the sediment quality objectives, including: DDE, a pesticide, DDT, polychlorinated biphenyls, and semi-volatile organic compounds. Intertidal sampling conducted as part of the pre-remedial design studies also identified chemicals in the intertidal area similar in composition and concentration and on the adjacent PRI Northwest embankment.

CC. On November 6, 1997, EPA and OCC entered into an AOC in EPA Docket No. 10-97-0011-CERCLA to conduct removal actions to abate an imminent and substantial endangerment to the public health, welfare, or the environment that may be presented by the actual or threatened release of hazardous substances at or from the Facility.

DD. On February 2, 2005, the 1997 AOC was amended to add Ecology as a Party, to require compliance with CERCLA, MTCA, and RCRA, and to conduct additional site characterization for both upland areas and beneath the Hylebos Waterway to determine the nature and extent of soil, groundwater, surface water, and sediment contamination; develop feasible alternatives to address the remaining contamination of all media; and develop an integrated remedy or set of remedies to be selected and designed to satisfy both EPA and Ecology's statutory requirements.

EE. The tasks required by the Amended AOC Statement of Work, the current status of each task, and each task's approval date for final products are listed in Exhibit C. The list also includes tasks performed by OCC under Ecology and EPA oversight in addition to those specified in the Amended AOC Statement of Work.

FF. According to the draft Site Characterization Report, submitted to Ecology and EPA on August 29, 2015, which included all RI data and the final Conceptual Site Model, (approved by Ecology and EPA on April 10, 2014), hazardous substances continue to be released from sources at the Facility into the environment including the Hylebos Waterway, shallow groundwater beneath and beyond the Facility and Commencement Bay, and buildings at the Port of Tacoma "Port Industrial Yard". The draft Site Characterization Report was conditionally approved by Ecology and EPA via letter dated October 11, 2016.

GG. The FS Report was submitted to Ecology for review, revised, opened for public comment on January 27, 2017, and closed to public comment on June 26, 2017. The FS Report was amended by Ecology in response to the comments and approved as amended by letter dated November 6, 2018. EPA was given the opportunity for review and comment, pursuant to the AOC.

Facts Related to Contamination at 709 Alexander Avenue

HH. From 1979 until 1983 the following spills were documented at the 709 Alexander Avenue property:

1. 1979 – Gasoline spill, 69 gallons.
2. 1981 – Safety-Kleen (aliphatic solvent) spill, quantity unspecified.
3. 1981 – Product spills from leaky valves noted, quantity unspecified.
4. 1983 – Diesel fuel spill, 300 gallons, seeped into ground, did not enter Hylebos Waterway over land.

II. In 1989, Ecology and Environment, Inc., under contract with EPA, performed a file review and inspection of 709 Alexander Avenue. Chemical constituents detected in soil and groundwater samples included chlorinated hydrocarbons such as PCE, TCE, chloroform; semi-volatile compounds such as hexachlorobutadiene; and metals such as arsenic, chromium, copper, lead, nickel, and zinc. Only arsenic and nickel were detected as dissolved constituents in more than one groundwater sample. Some soil samples contained petroleum hydrocarbons dominated by diesel-range or heavier hydrocarbons, and semi-volatile compounds.

JJ. The source of the non-petroleum chemical constituents in the soil, groundwater, and seep samples were identified as backfill debris containing graphite anodes and white fibrous sludge-like material similar in appearance to waste historically derived from industrial processes at the OCC property (605 Alexander Avenue). The vertical extent of backfill debris varies from 9 to 13 feet below grade with an average depth of 11 feet. The horizontal extent of backfill debris is approximately 210 feet with an average width of 105 feet. The depth to groundwater below the ground surface is approximately 9 feet at the contaminated areas; therefore, the backfill debris is in direct contact with the groundwater. The approximate in-place volume of the backfill debris is 9,000 cubic yards, of which approximately 2,000 cubic yards consist of white fibrous sludge-like material, graphite anodes, other industrial debris such as rubber, metal, and ceramic fragments, and concrete debris. The remaining is silty fill material.

KK. In May 1995, Ecology drafted an Agreed Order for the 709 Alexander Avenue property to support the source control program being implemented by EPA in Commencement Bay to eliminate or reduce the hazardous substance release into the Hylebos Waterway. Ecology faxed copies of the Agreed Order, and the Cleanup Action Plan, to PRI for their comments/signature. As of August 1995 Ecology has not received a response. This caused delays in implementing the site cleanup at 709 Alexander Avenue, which led Ecology to issue an Enforcement Order No. DE 95TC-S242 jointly to PRI, OCC, and F.O. Fletcher, Inc. for completing the site cleanup at 709 Alexander Avenue on September 1, 1995.

LL. Section 10 of the Amended AOC held the 1995 Enforcement Order in abeyance pending the implementation of a Consent Decree or Agreed Order implementing the selected remedies for the Property.

MM. The petroleum contamination located at 709 Alexander Avenue and at other real properties located at 901 and 1001 Alexander Avenue (previously known as 721 Alexander

Avenue) is addressed in a separate October 3, 2013, Agreed Order No. DE 9835 entered between Ecology, Mariana Properties, Inc., and the Port of Tacoma. Ecology's findings of fact regarding the history of land use, property ownership, and contamination at those real properties are set forth in Agreed Order No. DE 9835.

VI. ECOLOGY DETERMINATIONS

Ecology makes the following determinations, without any express or implied admissions of such determinations (and underlying facts) by the PLPs.

A. OCC, Glenn Springs Holdings, Inc., and Mariana Properties, Inc. are persons within the meaning of RCW 70.105D.020(24).

B. OCC is the past owner and operator of a Dangerous Waste Management Facility that received a final facility permit, subject to RCRA, 42 U.S.C. §§ 6924, 6925, and regulations promulgated thereunder, including authorized state regulations in WAC 173-303. OCC is also a past "owner or operator" as defined by RCW 70.105D.020(22) and meets the definition of a "facility" as defined by WAC 173-303.

C. Glenn Springs Holdings, Inc. is the current operator of the groundwater treatment plant.

D. Mariana Properties, Inc. is the current owner of the Facility and the Property.

E. Certain waste and constituents found at the Facility are dangerous wastes and/or dangerous constituents as defined by WAC 173-303 and in Section IV (Definitions) of this Order.

F. These dangerous wastes and dangerous constituents are considered hazardous substances within the meaning of RCW 70.105D.020(13).

G. Based on the Findings of Fact and the administrative record, Ecology has determined that release(s) and potential release(s) of hazardous substances at and/or from the Facility present a threat to human health and the environment.

H. Based on credible evidence, Ecology issued a PLP status letter to OCC dated August 27, 1998, for the Facility and Property located at 605 Alexander Avenue, pursuant to RCW 70.105D.040, .020(26), and WAC 173-340-500. By letter dated August 28, 1998, OCC voluntarily waived its rights to notice and comment and accepted Ecology's determination that OCC is a PLP under RCW 70.105D.040. On September 23, 1994, Ecology issued a PLP status letter to OCC for the Property located at 709 Alexander Avenue. By letter OCC voluntarily waived its rights to notice and comment and accepted Ecology's determination that OCC is a PLP under RCW 70.105D.040.

I. Based on credible evidence, Ecology issued a PLP status letter to Mariana Properties, Inc. dated June 8, 2015, and to Glenn Springs Holdings, Inc. also dated June 8, 2015, pursuant to RCW 70.105D.040, .020(26), and WAC 173-340-500. In separate letters, both dated July 17, 2015, Glenn Springs Holdings, Inc. and Mariana Properties, Inc. voluntarily waived their rights to notice and comment and accepted Ecology's determination that they are PLPs under RCW 70.105D.040.

J. Based on credible evidence, Ecology issued a PLP status letter to Mariana Properties, Inc., for the Property at 709 Alexander Avenue, pursuant to RCW 70.105D.040, .020(26), and WAC 173-340-500. In a letter dated April 4, 2013, Mariana Properties, Inc. voluntarily waived its rights to notice and comment and accepted Ecology's determination that it is a PLP under RCW 70.105D.040.

K. The 1995 Enforcement Order No. DE 95TC-S242 issued to PRI, OCC, and F.O. Fletcher on September 1, 1995, is hereby withdrawn and its terms are superseded and replaced by this Order.

L. This Order does not and is not intended to address the petroleum contamination located on the 709 Alexander Avenue Property and on real property located at 901 and 1001 Alexander Avenue (previously known as 721 Alexander Avenue). That is covered in the October 3, 2013, Agreed Order No. DE 9835 among Ecology, Mariana Properties, Inc., and the Port of Tacoma.

M. Pursuant to RCW 70.105D.030(1), .050(1), Ecology may require PLPs to investigate or conduct other remedial actions with respect to any release or threatened release of hazardous substances, whenever it believes such action to be in the public interest. Based on the foregoing facts, Ecology believes the remedial actions required by this Order are in the public interest.

Under WAC 173-340-430, an interim action is a remedial action that is technically necessary to reduce a threat to human health or the environment by eliminating or substantially reducing one or more pathways for exposure to a hazardous substance, that corrects a problem that may become substantially worse or cost substantially more to address if the remedial action is delayed, or that is needed to provide for completion of a site hazard assessment, RI/FS, or design of a cleanup action plan. Either Party may propose an interim action under this Order. If the Parties are in agreement concerning the interim action, the Parties will follow the process in Section VII.H. If the Parties are not in agreement, Ecology reserves its authority to require interim action(s) under a separate order or other enforcement action under RCW 70.105D, or to undertake the interim action itself.

VII. WORK TO BE PERFORMED

This Order shall supersede and replace the procedural and substantive requirements set forth in the 1995, Enforcement Order No. DE 95TC-S242 issued jointly to PRI, F.O. Fletcher, and OCC on September 1, 1995. This Order also shall supersede and replace the procedural and substantive requirements set forth in the Amended AOC in EPA Docket No. 10-97-0011-CERCLA, as that Amended AOC pertains to Ecology and OCC, upon the execution by EPA, Ecology, and OCC of the Second Amendment of the Amended AOC providing for Ecology's withdrawal from the Amended AOC. The status of the Amended AOC as it pertains to EPA and OCC will be addressed separately by EPA and OCC.

Based on the Findings of Fact and Ecology Determinations, it is hereby ordered that the PLPs take the following remedial actions and that these actions be conducted in accordance with WAC 173-340 unless otherwise specifically provided for herein.

A. Seasonal Water Level Monitoring

The PLPs shall conduct seasonal water level monitoring activities in accordance with the schedule in Exhibit D and the approved Seasonal Water Level Monitoring Plan dated September 27, 2019 in Exhibit E.

B. Monitoring Plan

In accordance with the schedule in Exhibit D, the PLPs will implement the approved Monitoring Plan dated June 11, 2019 in Exhibit F, intended to describe baseline conditions prior to future remedial measures at the Site and to provide information for remedy design.

C. Groundwater Extraction Demonstration

In accordance with the schedule in Exhibit D, the PLPs shall conduct a groundwater extraction demonstration in accordance with the approved Inactive Extraction Well EXT-9 Longer-Term Pumping Test Work Plan dated April 1, 2019 in Exhibit G.

D. Draft Cleanup Action Plan

Ecology approved as amended the FS as a final document on November 6, 2018, following review and comment by EPA. Ecology will select cleanup actions consistent with the procedures and requirements of WAC 173-340-360, -370. Ecology will prepare the draft cleanup action plan in accordance with WAC 173-340-380, for public review. Ecology agrees to provide the PLPs a reasonable opportunity to review and to comment on a preliminary draft version of the document, and to discuss the document and comments with Ecology, before the public review draft cleanup action plan is completed and issued for notice and opportunity for public comment.

E. Risk Assessments

Ecology may determine that a quantitative or ecological risk assessment of cleanup action alternatives is required under WAC 173-340. Ecology will notify the PLPs by letter that such a determination has been made and that a work plan must be submitted on a specific schedule. Once Ecology makes this determination, the work plan and schedule are an enforceable part of this Order.

F. Change in Conditions

If PLPs learn of a significant change in conditions at the Facility, including but not limited to a statistically significant increase in contaminant and/or chemical concentrations in media, e.g., soil, groundwater, surface water, air, and/or sediments, the PLPs, within seven (7) days of learning of the change in condition shall notify Ecology in writing of said change and provide Ecology with any reports or records (including laboratory analysis, sampling results) relating to the change in conditions.

G. Progress Reports

The PLPs shall submit semiannual progress reports on the fifteenth (15th) of January and July. If Ecology agrees, in writing, progress reports may be submitted at less frequent intervals. The semiannual progress reports shall include at a minimum:

1. A description of work performed or completed in accordance with the approved work completed during the reporting period.
2. A description of work activities planned for the next reporting period.
3. A description of any problems and how problems were resolved including any deviation from the approved work that Ecology and the PLPs have agreed to under Section VII (Work to be Performed) of this Order.
4. A summary of progress toward completion of the Order including work in progress, problem areas, key activities, deliverables submitted, field work and data generated, if any, subcontracting, analytical services performed, significant findings, changes in personnel, and significant contacts with all federal, state, local governments, community, and public interest groups.

H. Deliverables

All plans or other deliverables submitted by the PLPs for Ecology’s review and approval under Section VII (Work to be Performed) of this Order and the attached Schedule (Exhibit D) shall, upon Ecology’s approval, become integral and enforceable parts of this Order. All plans or other deliverables submitted by the PLPs for Ecology’s review and approval under Section VII (Work to be Performed) of this Order and the attached Schedule (Exhibit D) shall also be provided to EPA by the PLPs.

I. Interim Actions

If the Parties agree on an interim action under Section VI.N (Ecology Determinations), the PLPs shall prepare and submit to Ecology an Interim Action Work Plan, including a scope of work and schedule, by the date determined by Ecology. Ecology will provide public notice and opportunity to comment on the Interim Action Work Plan in accordance with WAC 173-340-600(16). The PLPs shall not conduct the interim action until Ecology approves the Interim Action Work Plan in writing. Upon approval by Ecology, the Interim Action Work Plan becomes an integral and enforceable part of this Order, and the PLPs are required to conduct the interim action in accordance with the approved Interim Action Work Plan.

J. SWMU and Area of Concern Identification

The PLPs shall notify Ecology's project coordinator in writing of any newly-identified SWMU(s), newly-discovered release(s) from known SWMU(s), and newly discovered Areas of Concern at the Facility no later than fifteen (15) days after discovery, and shall investigate and report on these areas as directed by Ecology's project coordinator. If required, the investigation (assessment) and reporting shall be done in accordance with Section VI.H (Delieverables).

K. Completion by Ecology

If at any time after the second exchange of written comments on drafts, Ecology determines that insufficient progress is being made in the preparation of any of the deliverables required by this section, Ecology may complete and issue a final deliverable.

VIII. TERMS AND CONDITIONS

A. Remedial Action Costs

The PLPs shall pay to Ecology costs incurred by Ecology pursuant to this Order and consistent with WAC 173-340-550(2). These costs shall include work performed by Ecology or its contractors for, or on, the Facility under RCW 70.105D, including remedial actions and Order preparation, negotiation, oversight, and administration. These costs shall include work performed both prior to and subsequent to the issuance of this Order. Ecology's costs shall include costs of direct activities and support costs of direct activities as defined in WAC 173-340-550(2). For all costs incurred subsequent to the effective date of this Order, the PLPs shall pay the required amount within thirty (30) days of receiving from Ecology an itemized statement of costs that includes a summary of costs incurred, an identification of involved staff, and the amount of time spent by involved staff members on the project. A general statement of work performed will be provided upon request. Itemized statements shall be prepared quarterly. Pursuant to WAC 173-340-550(4), failure to pay Ecology's costs within ninety (90) days of receipt of the itemized statement of costs will result in interest charges at the rate of twelve percent (12%) per annum, compounded monthly. The PLPs shall pay to Ecology costs incurred by Ecology for work performed by Keta Waters LLC and its contractors in accordance with the terms and conditions specified in Agreement No. HW9M26 between Ecology and OCC.

In addition to other available relief, pursuant to RCW 19.16.500, Ecology may utilize a collection agency and/or, pursuant to RCW 70.105D.055, file a lien against real property subject to the remedial actions to recover unreimbursed remedial action costs.

B. Implementation of Remedial Actions

If Ecology determines that PLPs have failed to make sufficient progress or failed to implement the remedial actions, in whole or in part, Ecology may, after written notice to the PLPs, perform any or all portions of the remedial actions that remain incomplete, or at Ecology's discretion allow the PLPs opportunity to correct. In an emergency, Ecology is not required to provide notice to the PLPs, or an opportunity for dispute resolution. If Ecology performs all or portions of the remedial actions because of the PLPs' failure to comply with their obligations under this Order, the PLPs shall reimburse Ecology for the costs of doing such work in accordance with Section VIII.A (Remedial Action Costs), provided that the PLPs are not obligated under this section to reimburse Ecology for costs incurred for work inconsistent with or beyond the scope of this Order. Ecology reserves the right to reinforce requirements of this Order under Section X (Enforcement).

Except where necessary to abate an emergency situation, the PLPs shall not perform any remedial actions at the Site outside those remedial actions required by this Order, unless Ecology concurs, in writing, with such additional remedial actions. In the event of an emergency, or where actions are taken as required by law, the PLPs must notify Ecology in writing of the event and remedial action(s) planned or taken as soon as practical but no later than twenty-four (24) hours of the discovery of the event.

C. Designated Project Coordinators

The project coordinator for Ecology is:

Kerry Graber
P.O. Box 4775
Olympia, WA 98504
360-407-0241

The project coordinator for the PLPs is:

Clinton Babcock
Glenn Springs Holdings, Inc.
7601 Old Channel Trail
Montague, MI 49437
972-687-7506

Each project coordinator shall be responsible for overseeing the implementation of this Order. Ecology's project coordinator will be Ecology's designated representative for the Facility. To the maximum extent possible, communications between Ecology and the PLPs, and all documents, including reports, approvals, and other correspondence concerning the activities performed pursuant to the terms and conditions of this Order shall be directed through the project coordinators. The project coordinators may designate, in writing, working level staff contacts for all or portions of the implementation of the work to be performed required by this Order.

Any Party may change its respective project coordinator. Written notification shall be given to the other Parties at least ten (10) calendar days prior to the change.

D. Performance

All geologic and hydrogeologic work performed pursuant to this Order shall be under the supervision and direction of a geologist or hydrogeologist licensed by the state of Washington or under the direct supervision of an engineer registered by the state of Washington, except as otherwise provided for by RCW 18.43, .220.

All engineering work performed pursuant to this Order shall be under the direct supervision of a professional engineer registered by the state of Washington, except as otherwise provided for by RCW 18.43.130.

All construction work performed pursuant to this Order shall be under the direct supervision of a professional engineer or a qualified technician under the direct supervision of a professional engineer. The professional engineer must be registered by the state of Washington, except as otherwise provided for by RCW 18.43.130.

Any documents submitted containing geologic, hydrologic, or engineering work shall be under the seal of an appropriately licensed professional as required by RCW 18.43, .220. The PLPs shall notify Ecology in writing of the identity of any engineer(s) and geologist(s), contractor(s) and subcontractor(s), and others to be used in carrying out the terms of this Order, in advance of their involvement at the Facility.

E. Access

Ecology or any Ecology authorized representative shall have access to enter and freely move about all property at the Facility that the PLPs either own, control, or have access rights to at all reasonable times for the purposes of, *inter alia:* inspecting records, operation logs, and contracts related to the work being performed pursuant to this Order; reviewing the PLPs' progress in carrying out the terms of this Order; conducting such tests or collecting such samples as Ecology may deem necessary; using a camera, sound recording, or other documentary type equipment to record work done pursuant to this Order; and verifying the data submitted to Ecology by the PLPs. The PLPs shall make all reasonable efforts to secure access rights for those properties within the Facility not owned or controlled by the PLPs where remedial activities or investigations will be performed pursuant to this Order. Ecology or any Ecology authorized representative shall give reasonable notice before entering any Facility property owned or controlled by the PLPs unless an emergency prevents such notice. All persons who access the Facility pursuant to this section shall comply with any applicable health and safety plan(s). Ecology employees and their representatives shall not be required to sign any liability release or waiver as a condition of Facility property access.

F. Sampling, Data Submittal, and Availability

With respect to the implementation of this Order, the PLPs shall make the results of all sampling, laboratory reports, and/or test results generated by it or on its behalf available to Ecology. Pursuant to WAC 173-340-840(5), all sampling data shall be submitted to Ecology in both printed and electronic formats in accordance with Section VII (Work to be Performed), Ecology's Toxics Cleanup Program Policy 840 (Data Submittal Requirements), and/or any subsequent procedures specified by Ecology for data submittal. If requested by Ecology, the PLPs shall allow Ecology and/or its authorized representative to take split or duplicate samples of any samples collected by the PLPs pursuant to implementation of this Order. The PLPs shall notify Ecology seven (7) days in advance of significant field activity at the Facility related to this Order. Ecology shall, upon request, allow the PLPs and/or its authorized representative to take split or duplicate samples of any samples collected by Ecology pursuant to the implementation of this Order, provided that doing so does not interfere with Ecology's sampling. Without limitation on Ecology's rights under Section VIII.E (Access), Ecology shall notify the PLPs prior to any sample collection activity unless an emergency prevents such notice.

In accordance with WAC 173-340-830(2)(a), all hazardous substance analyses shall be conducted by a laboratory accredited under WAC 173-50 for the specific analyses to be conducted, unless otherwise approved by Ecology.

G. Public Participation

RCW 70.105D.030(2)(a) requires that, at a minimum, this Order be subject to concurrent public notice. Ecology shall be responsible for providing this public notice and reserves the right to modify or withdraw any provisions of this Order should public comment disclose facts or considerations which indicate to Ecology that this Order is inadequate or improper in any respect. A Public Participation Plan is required for this Facility. Ecology shall review any existing Public Participation Plan to determine its continued appropriateness and whether it requires amendment, or if no plan exists, Ecology shall develop a Public Participation Plan alone or in conjunction with the PLPs.

Ecology shall maintain the responsibility for public participation at the Facility, but shall consult and collaborate with the PLPs in advance of all Ecology-sponsored public participation activities. The PLPs shall cooperate with Ecology, and shall:

1. If agreed to by Ecology, develop appropriate mailing list, prepare drafts of public notices, and fact sheets at important stages of the remedial actions, such as the submission of workplans, RI/FS reports, cleanup action plans, and engineering design reports. As appropriate, Ecology will edit, finalize, and distribute such fact sheets and prepare and distribute public notices of Ecology’s presentations and meetings.
2. Notify Ecology’s project coordinator prior to the preparation of all press releases and fact sheets, and before major meetings with the interested public and local governments. Likewise, Ecology shall notify the PLPs prior to the issuance of all press releases and fact sheets, and before major meetings with the interested public and local governments. For all press releases, fact sheets, meetings, and other outreach efforts by the PLPs that do not receive prior Ecology approval, the PLPs shall clearly indicate to its audience that the press release, fact sheet, meeting, or other outreach effort was not sponsored or endorsed by Ecology.
3. When requested by Ecology, participate in public presentations on the progress of the remedial actions at the Facility. Participation may be through attendance at public meetings to assist in answering questions, or as a presenter.
4. When requested by Ecology, arrange and/or continue information repositories to be located at the following locations:

a. Department of Ecology
Southwest Regional Office
300 Desmond Drive SE
Lacey, WA 98503
360-407-6300

b. Citizens for a Healthy Bay
917 Pacific Avenue, Suite 100
Tacoma, WA 98402
253-383- 2429

c. Mary Rose Kobetich Library
212 Browns Point Blvd NE
Tacoma, WA 98422
253-248-7265

At a minimum, copies of all public notices, fact sheets, and documents relating to public comment periods shall be promptly placed in these repositories. A copy of all documents related to this Facility shall be maintained by Ecology in the repository at Ecology's Southwest Regional Office in Olympia, Washington.

H. Retention of Records

During the pendency of this Order, and for ten (10) years from the date of completion of work performed pursuant to this Order, the PLPs shall preserve all records, reports, documents, and underlying data in its possession relevant to the implementation of this Order and shall insert a similar record retention requirement into all contracts with project contractors and subcontractors. Upon request of Ecology, the PLPs shall make all records available to Ecology and allow access for review within a reasonable time.

Nothing in this Order is intended to waive any right the PLPs may have under applicable law to limit disclosure of documents protected by the attorney work-product privilege and/or the attorney-client privilege. If the PLPs withhold any requested records based on an assertion of privilege, the PLPs shall provide Ecology with a privilege log specifying the records withheld and the applicable privilege. No Facility-related data collected pursuant to this Order shall be considered privileged.

I. Resolution of Disputes

In the event that the PLPs elect to invoke dispute resolution the PLPs must utilize the procedure set forth below.

1. Upon the triggering event (receipt of Ecology's project coordinator's written decision or an itemized bill statement), the PLPs have fourteen (14) calendar days within which to notify Ecology's project coordinator in writing of its dispute (Informal Dispute Notice).
2. The Parties' project coordinators shall then confer in an effort to resolve the dispute informally. The Parties shall informally confer for up to fourteen (14) calendar days from receipt of the Informal Dispute Notice. If the project coordinators cannot resolve the dispute within those fourteen (14) calendar days, then within seven (7) calendar days Ecology's project coordinator shall issue a written decision (Informal Dispute Decision) stating: the nature of the dispute; the PLPs position with regards to the dispute; Ecology's position with regard to the dispute; and the extent of resolution reached by the informal discussion.
3. The PLPs may then request regional management review of the dispute. This request (Formal Dispute Notice) must be submitted in writing to the Southwest Regional Office's Hazardous Waste and Toxic's Reduction Section Manager within seven (7) calendar days of receipt of Ecology's Informal Dispute Decision. The Formal Dispute Notice shall include a written statement of dispute setting forth: the nature of the dispute; the disputing Party's position with respect to the dispute; and the information relied upon to support its position.
4. The Section Manager shall conduct a review of the dispute and shall issue a written decision regarding the dispute (Decision on Dispute) within thirty (30) calendar days of receipt of the Formal Dispute Notice. The Decision on Dispute shall be Ecology's final decision on the disputed matter.

The Parties agree to only utilize the dispute resolution process in good faith and agree to expedite, to the extent possible, the dispute resolution process whenever it is used.

Implementation of these dispute resolution procedures shall not provide a basis for delay of any activities required in this Order, unless Ecology agrees in writing to a schedule extension.

In case of a dispute, failure to either proceed with the work required by this Order or timely invoke dispute resolution may result in Ecology's determination that insufficient progress is being made in preparation of a deliverable, and may result in Ecology undertaking the work under Section VII (Work to be Performed) or initiating enforcement under Section X (Enforcement).

J. Extension of Schedule

An extension of schedule shall be granted only when a request for an extension is submitted in a timely fashion consistent with the timeframe provided in Exhibit D, and good cause exists for granting the extension. All extensions shall be requested in writing. The request shall specify:

1. The deadline that is sought to be extended.
2. The length of the extension sought.
3. The reason(s) for the extension.
4. Any related deadline or schedule that would be affected if the extension were granted.

The burden shall be on the PLPs to demonstrate to the satisfaction of Ecology that the request for such extension has been submitted in a timely fashion and that good cause exists for granting the extension. Good cause may include, but may not be limited to:

1. Circumstances beyond the reasonable control and despite the due diligence of the PLPs including delays by unrelated third parties or Ecology such as (but not limited to) delays by Ecology in reviewing, approving, or modifying documents submitted by the PLPs.
2. Acts of God, including fire, flood, blizzard, extreme temperatures, storm, or other unavoidable casualty.
3. Endangerment as described in Section VIII.L (Endangerment).

However, neither increased costs of performance of the terms of this Order nor changed economic circumstances shall be considered circumstances beyond the reasonable control of the PLPs.

Ecology shall act upon any written request for extension in a timely fashion. Ecology shall give the PLPs written notification of any extensions granted pursuant to this Order. A requested extension shall not be effective until approved by Ecology. Unless the extension is a substantial change, it shall not be necessary to amend this Order pursuant to Section VIII.K (Amendment of Order) when a schedule extension is granted.

An extension shall only be granted for such period of time as Ecology determines is reasonable under the circumstances. Ecology may grant schedule extensions exceeding ninety (90) days only as a result of:

1. Delays in the issuance of a necessary permit which was applied for in a timely manner.
2. Other circumstances deemed exceptional or extraordinary by Ecology.
3. Endangerment as described in Section VIII.L (Endangerment).

K. Amendment of Order

The project coordinators may verbally agree to minor changes to the work to be performed without formally amending this Order. Minor changes will be documented in writing by Ecology within seven (7) days of verbal agreement.

Except as provided in Section VIII.M (Reservation of Rights), substantial changes to the work to be performed shall require formal amendment of this Order. This Order may only be formally amended by the written consent of both Ecology and the PLPs. Ecology will provide its written consent to a formal amendment only after public notice and opportunity to comment on the formal amendment.

When requesting a change to the Order, the PLPs shall submit a written request for amendment to Ecology for approval. Ecology shall indicate its approval or disapproval in writing and in a timely manner after the written request for amendment is received. If the amendment to this Order represents a substantial change, Ecology will provide public notice and opportunity to comment. Reasons for the disapproval of a proposed amendment to this Order shall be stated in writing. If Ecology does not agree to a proposed amendment, the disagreement may be addressed through the dispute resolution procedures described in Section VIII.I (Resolution of Disputes).

L. Endangerment

In the event Ecology determines that any activity being performed at the Facility is creating or has the potential to create a danger to human health or the environment on or surrounding the Facility, Ecology may direct the PLPs to cease such activities for such period of time as it deems necessary to abate the danger. The PLPs shall immediately comply with such direction.

In the event the PLPs determine that any activity being performed at the Facility is creating or has the potential to create a danger to human health or the environment, the PLPs may cease such activities. The PLPs shall notify Ecology's project coordinator as soon as possible, but no later than twenty-four (24) hours after making such determination or ceasing such activities. Upon Ecology's direction the PLPs shall provide Ecology with documentation of the basis for the determination or cessation of such activities. If Ecology disagrees with the PLPs' cessation of activities, it may direct the PLPs to resume such activities.

If Ecology concurs with or orders a work stoppage pursuant to this section, the PLPs' obligations with respect to the ceased activities shall be suspended until Ecology determines the danger is abated, and the time for performance of such activities, as well as the time for any other work dependent upon such activities, shall be extended in accordance with Section VIII.J (Extension of Schedule) for such period of time as Ecology determines is reasonable under the circumstances.

Nothing in this Order shall limit the authority of Ecology, its employees, agents, or contractors to take or require appropriate action in the event of an emergency.

M. Reservation of Rights

This Order is not a settlement under RCW 70.105D. Ecology's signature on this Order in no way constitutes a covenant not to sue or a compromise of any of Ecology's rights or authority. Ecology will not, however, bring an action against the PLPs to recover remedial action costs paid to and received by Ecology under this Order. In addition, Ecology will not take additional enforcement actions against the PLPs regarding remedial actions required by this Order, provided the PLPs comply with this Order.

Ecology nevertheless reserves its rights under RCW 70.105D, including the right to require additional or different remedial actions at the Facility should it deem such actions necessary to protect human health and the environment, and to issue orders requiring such remedial actions. Ecology also reserves all rights regarding the injury to, destruction of, or loss of natural resources resulting from the release or threatened release of hazardous substances at the Facility.

By entering into this Order, the PLPs do not admit to any liability for the Facility. Although the PLPs are committing to conducting the work required by this Order under the terms of this Order, the PLPs expressly reserve all rights available under law, including but not limited to the right to seek cost recovery or contribution against third parties, and the right to assert any defenses to liability in the event of enforcement.

N. Transfer of Interest in Property

No voluntary conveyance or relinquishment of title, easement, leasehold, or other interest in any portion of the Facility shall be consummated by the PLPs without provision for continued implementation of all requirements of this Order and implementation of any remedial actions found to be necessary as a result of this Order.

Prior to the PLPs' transfer of any interest in all or any portion of the Facility, and during the effective period of this Order, the PLPs shall provide a copy of this Order to any prospective purchaser, lessee, transferee, assignee, or other successor in said interest; and at least thirty (30) days prior to any transfer, the PLPs shall notify Ecology of said transfer. Upon transfer of any interest, the PLPs shall notify all transferees of the restrictions on the activities and uses of the property under this Order and incorporate any such restrictions into the transfer documents.

O. Compliance with Applicable Laws

All actions carried out by the PLPs pursuant to this Order shall be done in accordance with all applicable federal, state, and local requirements, including requirements to obtain necessary permits, except as provided in RCW 70.105D.090. At this time, no federal, state, or local requirements have been identified as being applicable to the actions required by the Order.

All actions carried out by the PLPs pursuant to this Order shall be done in accordance with relevant and appropriate requirements identified by Ecology. At this time, no relevant and appropriate requirements have been identified as being relevant and appropriate to the actions required by the Order.

Pursuant to RCW 70.105D.090(1), the PLPs may be exempt from the procedural requirements of RCW 70.94, 70.95, 77.55, 90.48, and 90.58 and of any laws requiring or authorizing local government permits or approvals. However, the PLPs shall comply with the substantive requirements of such permits or approvals. For permits and approvals covered under RCW 70.105.090(1) that have been issued by local government, the Parties agree that Ecology has the non-exclusive ability under this Order to enforce those local government permits and/or approvals. At this time, no state or local permits or approvals have been identified as being applicable but procedurally exempt under this section.

The PLPs have a continuing obligation to determine whether additional permits or approvals addressed in RCW 70.105D.090(1) would otherwise be required for the remedial actions under this Order. In the event either Ecology or the PLPs determine that additional permits or approvals addressed in RCW 70.105D.090(1) would otherwise be required for the remedial action under this Order, Ecology or the PLPs shall promptly notify the other Parties of such determination. Ecology shall determine whether Ecology or the PLPs shall be responsible to contact the appropriate state and/or local agencies. If Ecology so requires, the PLPs shall promptly consult with the appropriate state and/or local agencies and provide Ecology with written documentation from those agencies of the substantive requirements those agencies believe are applicable to the remedial actions. Ecology shall make the final determination on the additional substantive requirements that must be met by the PLPs and on how the PLPs must meet those requirements. Ecology shall inform the PLPs in writing of these requirements. Once established by Ecology, the additional requirements shall be enforceable requirements of this Order. The PLPs shall not begin or continue the remedial actions potentially subject to the additional requirements until Ecology makes its final determination.

Pursuant to RCW 70.105D. 090(2), in the event Ecology determines that the exemption from complying with the procedural requirements of the laws referenced in RCW 70.105D.090(1) would result in the loss of approval from a federal agency that is necessary for the state to administer any federal law, the exemption shall not apply and the PLPs shall comply with both the procedural and substantive requirements of the laws referenced in RCW 70.105D.090(1), including any requirements to obtain permits.

P. Land Use Restrictions

Restrictive covenants restricting land use on the real property located at 605 Alexander Avenue to non-residential industrial use and prohibiting the extraction, supply or use for drinking or other human consumption or domestic use of any kind of the groundwater, surface water, and subsurface water on the Property are contained and set forth in the Quit Claim Deed (Corrected) recorded on April 28, 1997, in the records of the Pierce County Auditor (Recording No. 9704280734).

Pertinent real properties owned by the Port of Tacoma are also the subject of a restrictive covenant recorded on May 5, 2003, in the records of the Pierce County Auditor (Recording No. 200305050452) prohibiting groundwater extraction, supply, or use for drinking or other human consumption or domestic use of any kind on those real properties north of Eleventh Street on the Hylebos/Blair peninsula as delineated in the restrictive covenant. Prior to any use of the groundwater on the property that is inconsistent with the terms of the restrictive covenant must be pre-approved by Ecology.

Q. Indemnification

The PLPs agree to indemnify and save and hold the State of Washington, its employees, and agents harmless from any and all claims or causes of action (1) for death or injuries to persons, or (2) for loss or damage to property to the extent arising from or on account of acts or omissions of the PLPs, its officers, employees, agents, or contractors in entering into and implementing this Order.

However, the PLPs shall not indemnify the State of Washington nor save nor hold its employees and agents harmless from any claims or causes of action to the extent arising out of the negligent acts or omissions of the State of Washington, or the employees or agents of the State, in entering into or implementing this Order

IX. SATISFACTION OF ORDER

The provisions of this Order shall be deemed satisfied upon the PLPs' receipt of written notification from Ecology that the PLPs have completed the corrective actions required by this Order, as amended by any modifications, and that the PLPs have complied with all other provisions of this Order.

X. ENFORCEMENT

Pursuant to RCW 70.105D.050, this Order may be enforced as follows:

A. The Attorney General may bring an action to enforce this Order in a state or federal court.

B. The Attorney General may seek, by filing an action, if necessary, to recover amounts spent by Ecology for investigative and remedial actions and orders related to the Facility.

C. A liable Party who refuses, without sufficient cause, to comply with any term of this Order will be liable for:

1. Up to three (3) times the amount of any costs incurred by the State of Washington as a result of its refusal to comply.
2. Civil penalties of up to twenty-five thousand dollars ($25,000) per day for each day it refuses to comply.

D. This Order is not appealable to the Washington Pollution Control Hearings Board. This Order may be reviewed only as provided under RCW 70.105D.060.

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Effective date of this Order: 12-31-2019

Occidental Chemical Corporation

Glenn Springs Holdings, Inc.

Mariana Properties, Inc.

STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY

Ava Edmonson, Section Manager
Hazardous Waste and Toxics Reduction Program
Southwest Regional Office Olympia, Washington

Second Amendment
Administrative Order On Consent For Removal Activities Embankment and Area 5106
EPA Docket No. 10-97-0011-CERCLA

Occidental Chemical Corporation ("Occidental"), the United States Environmental Protection Agency ("EPA"), and the Washington Department of Ecology ("Ecology") agree to this second amendment ("Second Amendment") of the Administrative Order on Consent for Removal Activities Embankment and Area 5106, EPA Docket No. 10-97-0011-CERCLA, as first amended by Occidental, EPA, and Ecology in 2005 ("AOC"), pursuant to Paragraph 98 of the AOC as described herein.

Whereas, the AOC pertaining to the Occidental Site ("Occidental Site")(as defined below in Paragraph #5) in Tacoma, Washington was first amended on February 1, 2005 ("First Amendment"). The First Amendment reflected agreement amongst EPA, Ecology, and Occidental that: a) additional Occidental Site characterization needed to be conducted, both in upland areas and beneath the Hylebos Waterway, to adequately determine the nature and extent of soil, ground water, surface water, and sediment contamination; b) feasible alternatives to address remaining contamination of all media needed to be developed and evaluated; and c) integrated response activities need to be selected and designed which will satisfy EPA and Ecology requirements under the Comprehensive Environmental Response, Compensation, and Liability Act ("CERCLA"), Washington Model Toxics Control Act ("MTCA"), and Resource Conservation and Recovery Act ("RCRA"), and their respective regulations including but not limited to the National Contingency Plan ("NCP"). Accordingly, the Statement of Work ("SOW") that was attached to the First Amendment included the CERCLA process elements of remedial investigation/feasibility study ("RI/FS"), remedial design ("RD"), and interim response actions.

Whereas, the SOW activities and related work accomplished by Occidental since the First Amendment all have been subject to oversight by both EPA and Ecology.

Whereas, work under the First Amendment transitioned from an investigation of the four areas of contamination pursuant to CERCLA, MTCA, and RCRA, as noted above, to a focus on soil, ground water, and surface water contamination under the lead oversight of Ecology pursuant to Ecology's MTCA and RCRA authority.

Whereas, Ecology and Occidental are simultaneously with this Second Amendment entering into an Agreed Order ("AO") for the Occidental Site pursuant to Ecology's MTCA, RCRA, and the Washington Hazardous Waste Management Act ("HWMA") authority to accomplish certain Occidental Site activities, including but not limited to Site monitoring, completion of an FS, preparation of a draft Cleanup Action Plan ("dCAP"), and related actions.

Whereas Ecology and Occidental will continue to report all AO activities to EPA, Ecology and Occidental will continue to provide EPA with opportunities to review and comment upon all AO activities as they are considered and accomplished, and Ecology and EPA will continue to coordinate AO activities.

Whereas, Ecology and EPA will review the dCAP to be prepared pursuant to the AO, Ecology will consider comments on the dCAP to be obtained from EPA and the public, and thereafter Ecology will issue a final MTCA Cleanup Action Plan ("CAP") for the soil, ground water, and surface water contamination areas of the Occidental Site, and that EPA will then evaluate pursuant to this Second Amendment whether there may be the need for additional response actions to evaluate and/or address Occidental Site sediment contamination.

ACCORDINGLY, EPA, Ecology and Occidental agree to amend the AOC as follows:

1. The First Amendment is hereby terminated, Ecology is hereby removed as a party to the AOC, and the First Amendment is hereby superseded by this Second Amendment. All additional work accomplished pursuant to the AOC and this Second Amendment, if any, shall be performed pursuant to CERCLA.

2. Five years from the date that a consent decree or order implementing a final MTCA CAP for the Occidental Site is issued, Occidental shall submit to EPA for review and approval an Occidental Site Cleanup Status Report ("Status Report"). The Status Report shall: (a) summarize the status of activities conducted at the Occidental Site since the Effective Date of this Second Amendment; (b) evaluate whether those activities have sufficiently controlled releases of hazardous substances, pollutants, or contaminants from Site contaminated soil, ground water, and surface water to Site sediments; and (c) recommend whether additional response actions are necessary to evaluate and/or address Occidental Site sediment contamination.

3. In the event that EPA's review and approval of the Status Report results in EPA's determination that additional response actions are necessary to evaluate and/or address Occidental Site sediment contamination, EPA will provide Occidental with a written determination ("EPA's Determination") which will include a proposed SOW for such additional response actions. If such additional response actions in EPA's Determination are limited to response actions that will be performed pursuant to Section 104(b)(1) of CERCLA, Occidental shall, within 60 days of Occidental's receipt of EPA's Determination, provide EPA with a written response to EPA's Determination. Occidental's written response shall include either: (1) a work plan and schedule, subject to EPA approval, for implementing the EPA proposed SOW; (2) or a written statement and explanation, subject to EPA approval, of why additional response actions are unnecessary to evaluate and/or address Occidental Site sediment contamination. EPA's review and approval, modification or disapproval of Occidental's submittal shall be subject to

the dispute resolution procedures of the AOC.

4. However, if such additional response actions in EPA's Determination are not limited to response actions that will be performed pursuant to Section 104(b)(1) of CERCLA (e.g., EPA's Determination includes additional response actions to remove, dispose, isolate treat, or destroy Occidental Site sediment contamination), Occidental and EPA shall meet and confer within 60 days of Occidental's receipt of EPA's Determination to mutually agree whether all such additional response actions in EPA's Determination will be accomplished by Occidental pursuant to another written amendment of the AOC or pursuant to a new consent decree to be issued pursuant to EPA's CERCLA authority, or absent mutual agreement, pursuant to an administrative or judicial order.

5. The following definition of the Occidental Site contained in the First Amendment's Paragraph #4 shall continue to apply to the AOC and this Second Amendment: The Site shall mean that portion of segment 5 of the Mouth of the Hylebos Waterway Problem Area and those portions of the upland properties described in the next sentence where Waste Materials have or may come to be located as a result of releases or threatened releases of Waste Materials from operations related to the production, processing, formulation or disposal of chemical materials or products. Accordingly, the Occidental Site shall include, but not be limited to the following: Area 5106; the Occidental Embankment Area; the Pioneer Property located at 605 Alexander Avenue; locations of groundwater contaminant plumes and contaminated sediments on the Port of Tacoma property located at 401 Alexander Avenue to the north of the Pioneer Property; locations of contaminated sediments and groundwater contaminant plumes on the Mariana Properties property located at 709 Alexander Avenue and the Port of Tacoma property located at 721 Alexander Avenue to the south of the Pioneer Property; and other areas of Segment 5 of the Mouth of the Hylebos Waterway Problem Area where releases of Waste Materials from such properties have come to be located and those areas necessary to stage or implement related work. The Occidental Site does not include the release of total petroleum hydrocarbon, BTEX or other constituents of concern from petroleum product storage operations currently or historically located on the 709 Alexander Avenue property or 721 Alexander property which has been identified in shallow groundwater underlying the 709 Alexander Avenue property or the 721 Alexander property and determined to be moving towards the Blair Waterway.

6. Attached to this Second Amendment is a map that generally depicts the Occidental Site.

7. The Unilateral Administrative Order (Area 5106), EPA Docket No. CERCLA 10-2002-0066 terminated by the First Amendment remains terminated.

8. Ecology Enforcement Order DE 95TC-S242, issued to PRI Northwest, Inc. and Occidental Chemical Corporation, effective September 5, 1995, and held in abeyance by the First Amendment has been superseded and replaced by the AO.

9. The AOC, as amended by this Second Amendment, contains the entire agreement among EPA, Ecology, and Occidental regarding the Occidental Site.

Occidental, EPA and Ecology have executed this Second Amendment to the AOC to signify their agreement to the foregoing, effective as of the date of EPA's execution as set forth below ("Effective Date"). This Second Amendment may be executed in counterparts, each of which shall be deemed an original, but all of which together shall constitute one and the same instrument.

AGREED for Occidental Chemical Corporation

By:

Name: Michael Anderson

Title: Vice President

Date: 12/19/2019

AGREED for Washington Department of Ecology

By:

Name: Michelle Underwood

Title: Section Manager

Date: 1/10/2020

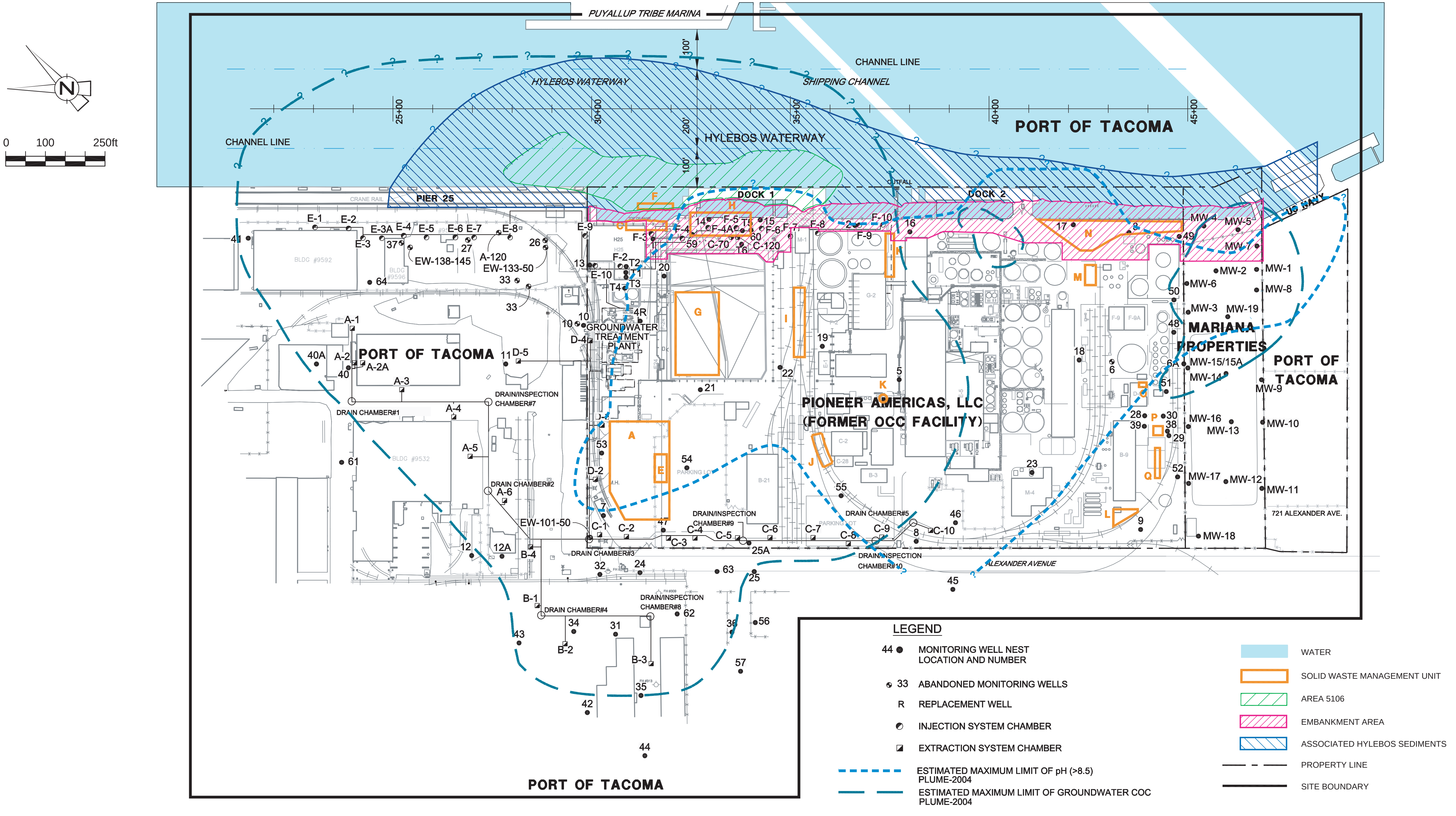
AGREED for United States Environmental Protection Agency

By:

Name: Sheila Fleming

Title: Acting Director

Date: 1/24/2020



NOTE: EXTENT OF CONTAMINATION SHOWN ON FIGURE IS FOR ILLUSTRATIVE PURPOSES ONLY.

Appendix B

OCCIDENTAL SITE PLAN
GROUNDWATER AND SEDIMENT REMEDIATION
Occidental Chemical Corporation, Tacoma, Washington

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10

IN THE MATTER OF: HYLEBOS WATERWAY OF THE COMMENCEMENT BAY NEARSHORE/TIDEFLATS SUPERFUND SITE OCC TACOMA, INC. RESPONDENT.	U.S. EPA Docket No. 10-97-0011-CERCLA
Proceeding Under Sections 106(a), 122(a), and 122(d)(3) of the Comprehensive Environmental Response, Compensation, and Liability Act as amended, 42 U.S.C §§ 9606(a), 9622(a), 9622(d)(3)).	ADMINISTRATIVE ORDER ON CONSENT FOR REMOVAL ACTIVITIES EMBANKMENT AND AREA 5106

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TABLE OF CONTENTS

I. INTRODUCTION

1. This Administrative Order on Consent (Order) is enterec into voluntarily by the United States Environmental Protection Agenc (EPA) and OCC Tacoma, Inc., (Respondent), a Delaware corporation anc a wholly-owned subsidiary of Occidental Chemical Corporation, and OCC Tacoma's, successors and assigns. The Order concerns the preparatior and performance of removal actions by Respondent and reimbursement of oversight costs. The actions to be performed by Respondent under this Order involve certain real property previously owned by Respondent located at 605 Alexander Avenue, Tacoma, Washington, (the Property), and certain adjoining property upon which releases of hazardous substances from the Property have come to be located (collectively, the Site). The Site is located within the Sediments Operable Unit (OU1) of the Commencement Bay/Nearshore Tideflats (CB/NT) Superfund Site, within the Mouth of the Hylebos Waterway problem area.

This Order requires the Respondent to conduct removal actions described herein to abate an imminent and substantial endangerment to the public health, welfare, or the environment that may be presented by the actual or threatened releases of hazardous substances at or from the Site.

II. JURISDICTION

2. This Order is issued under the authority vested in the President of the United States by Sections 106(a) and 122(a) of the Comprehensive Environmental Response, Compensation, and Liability

Act (CERCLA), as amended, 42 U.S.C. §§ 9606(a) and 9622(a). This authority was delegated to the Administrator of EPA on January 23, 1987, by Executive Order 12580, 52 Fed. Reg. 2926 (1987); further delegated to the EPA Regional Administrators on September 13, 1987, by EPA Delegation Nos. 14-14-A and 14-14B; and redelegated to Cleanup Unit Managers by Regional Redelegation Order R10 14-14-A and 14-14-B on March 25, 1996.

3. Respondent agrees to undertake all removal response actions required by the terms and conditions of this Order. In any action by EPA or the United States to enforce the terms of this Order, Respondent consents to, and agrees not to contest, the authority or jurisdiction of EPA to issue or enforce this Order, and agrees not to contest the validity of this Order or its terms.

III. PARTIES BOUND

4. This Order shall apply to and be binding upon EPA and Respondent, its directors, officers, employees, agents, successors and assigns. The signatory to this Order certifies that he/she is authorized to execute and legally bind Respondent to this Order. Changes in ownership or in corporate or other legal status, including, but not limited to, any transfer of assets or real or personal property, including the transfer of any portion of the Site owned by Respondent, or business organization, shall in no way alter Respondent's duties under this Order.

5. Respondent shall provide a copy of this Order to any subsequent owners or successors in interest of Respondent before any

controlling ownership rights, stock or assets in a corporate acquisition are transferred, if such transfer occurs before the completion of the removal actions required by this Order. Respondent shall notify EPA at least thirty (30) days prior to any such corporate transfer. Respondent shall provide a copy of this Order to all contractors, subcontractors, laboratories, and consultants retained to perform any work under this Order, within fourteen (14) days after the effective date of this Order, or the date such services are retained, whichever is later, and shall condition all contracts entered into hereunder to performance of the work in conformity with the terms of this Order. Any reference herein to the Order shall mean the Order, all Appendices thereto, any future modifications as provided by the terms of the Order as may be added hereafter, and any work plans, reports, plans, specifications, schedules, and appendices required by this Order which, upon approval of EPA, shall be incorporated into and enforceable under the Order. Notwithstanding the terms of any contract, Respondent is responsible for compliance with this Order and for ensuring that its parent company, subsidiaries, employees, contractors, consultants, subcontractors, agents, and attorneys comply with this Order.

IV. STATEMENT OF PURPOSE

6. In entering into this Order, the objectives of EPA and Respondent are: (a) to perform removal actions described herein to protect public health, welfare, or the environment, which removal actions are more specifically set forth in Section VIII, below, and

in the Scope of Work for the Embankment Area Removal Action (SOW), attached as Appendix 1 to this Order and by this reference is incorporated in and made a part of this Order, and the Area 5106 Sediment Engineering Evaluation/Cost Analysis (EE/CA) Work Plan (Work Plan), attached as Appendix 2 to this Order and by this reference is incorporated in and made a part of this Order; (b) to the extent practicable, perform such removal actions to contribute to the efficient performance of long-term remedial action of the Hylebos Waterway; and (c) provide for recovery by EPA of its response and oversight costs incurred with respect to the implementation of the removal actions and this Order. This Order does not require Respondent to implement any Removal Action Alternative for Area 5106, as defined in the Final EE/CA Report for Area 5106.

7. By entering into this Order, Respondent makes no admission of fact or liability nor does it waive any right, claim, remedy, appeal, cause of action, or defense, except as specifically described herein.

V. EPA'S <u>FINDINGS OF FACT</u>

The following paragraphs summarize the factual findings made by EPA in support of the Conclusions of Law and Determinations in this Order. Respondent neither admits nor denies the Introduction's statements, the EPA Findings of Fact or the EPA Conclusions of Law and Determinations, and reserves its rights to contest them, except in proceedings under this Order and as provided in Paragraphs 3 and 87.

8. The Hylebos Waterway is within the boundaries of the CB/NT

Superfund Site. The CB/NT Superfund Site is located in Tacoma, Washington, at the southern end of the main basin of Puget Sound. The Mouth of the Hylebos Waterway and Head of the Hylebos Waterway are two of eight problem areas that have been designated as Operable Unit One (OU1) of the CB/NT Superfund Site.

9. On September 8, 1983, EPA placed the CB/NT Site on the National Priorities List pursuant to Section 105 of CERCLA, 42 U.S.C. § 9605.

10. Under a Cooperative Agreement with EPA, the Washington Department of Ecology (Ecology) conducted a Remedial Investigation and Feasibility Study (RI/FS) of the CB/NT Site. Within the Tideflats area of the CB/NT Site, the RI/FS evaluated the nature and extent of contamination in the Sitcum, Blair, Milwaukee, Hylebos, St. Paul, Middle, Thea Foss (formerly known as City), and Wheeler-Osgood Waterways. The final RI/FS was made available for public comment in February 1989.

11. Several chemicals were detected in the Mouth of the Hylebos Waterway sediments, including, but not limited to, polychlorinated biphenyls (PCBs), hexachlorobenzene, trichloroethane, tetrachloroethane, 1,2-dichlorobenzene, 1,3-dichlorobenzene, hexachlorobutadiene, and lead, which in certain forms are known to be toxic to humans and marine life and are designated as hazardous substances under Section 102(a) of CERCLA, as reported at 40 CFR Part 302.4.

12. The RI/FS evaluated chemicals detected at the CB/NT Superfund Site to identify those that pose the greatest risk to human

health and the environment. The technical approach was to establish information relating specific chemicals to biological effects in various aquatic organisms and to quantifiable human health risks. Problem chemicals were defined as those chemicals whose concentration exceeded the low apparent effects threshold (AET) in a particular problem area. The AET was defined as the chemical concentration above which toxicity or benthic effects are always observed in a data set developed specifically for the Puget Sound using three biological effects tests: amphipod mortality, oyster larvae abnormality, and benthic infaunal depressions. Sediment Quality Objectives (SQOs) were developed as the cleanup standards for the CB/NT site based on the low AET values for chemicals other than PCBs, and based on the human health risk assessment and levels found in Puget Sound reference areas for PCBs.

13. On September 29, 1989, EPA issued a Record of Decision (ROD) that selected the remedy for remediation of sediments for OU1 and sources of contamination (Operable Unit 05) in the Commencement Bay Nearshore/Tideflats (CB/NT) Superfund Site, including the Head and Mouth of the Hylebos Waterway. PCBs and hexachlorobenzene, which were among the chemicals detected at the Mouth of the Hylebos Waterway at levels exceeding the SQOs, were selected as chemical indicators of biological effects and human health risks at the Mouth of the Hylebos Waterway because these chemicals were found at the highest concentrations relative to SQOs over the greatest area. The ROD also determined that natural recovery will not sufficiently reduce contaminant concentrations in some areas of the Mouth of the Hylebos

Waterway within the ten (10) year period, so the ROD required active sediment cleanup with one (1) of the four (4) technology options as a component of the remedy.

14. Respondent, along with five other companies or entities, is performing pre-remedial design activities pursuant to the ROD on the Hylebos Waterway under an Administrative Order on Consent, dated November 25, 1993. Respondent is also performing corrective action on volatile organic compounds in groundwater underlying the Property and certain adjoining property pursuant to Part V of its RCRA permit (No. WAD 009242314).

15. An investigation into the bank area of the Property and the adjacent PRI Northwest property, between +18 feet mean lower low water level (MLLW) and 0 feet MLLW, found concentrations of contaminants significantly above the SQOS. 4.4' DDE, a pesticide, was detected as high as 23000 ug/kg, which is 1438 times the SQO. 4,4' DDE, and 4,4' DDT were also detected at levels as high as 856 and 647 times the SQO respectively. PCBs were detected as high as 22,300 ug/kg, which is approximately 50 times the SQO, and lead as high as 150,000 mg/kg, which is 333 times the SQO. Semivolatile organic compounds (SVOCs) were also detected at high levels in an area at the south end of the Property and extending onto the adjacent PRI Northwest property. Intertidal sampling conducted as part of the pre-remedial design studies also identified chemicals in the intertidal area similar in composition and concentration and on the adjacent PRI Northwest embankment. A removal of the contaminated soils in the bank area will eliminate the imminent and substantial threat of exposure

and continuing releases into the Waterway.

16. During pre-remedial design activities referenced in Paragraph 14, organic compounds have been detected in sediments adjacent to the Property, known as the Area 5106, at concentrations exceeding those detected during the RI/FS. The organic compounds that have been found in Area 5106 include trichloroethylene, tetrachloroethylene, vinyl chloride, hexachlorobenzene, and hexachlorobutadiene. Tetrachloroethane was detected at levels as high as 3,200 mg/kg, which is approximately 56,000 times the SQO. Trichloroethane was detected at levels as high as 1,600 mg/kg for which there is no sediment cleanup criteria in the ROD. The concentrations of contaminants found in the Area 5106 poses an ongoing, substantial threat of these hazardous substances being released into the Hylebos Waterway and being exposed to wildlife and aquatic organisms in the Waterway. Preliminary analysis of sampling results from the Area 5106 sediments suggest that, natural recovery is not likely and, if excavated, these sediments/sludges would exceed the RCRA Toxicity Characteristic Leachate Procedure (TCLP) criteria and may not be appropriate for disposal with other Hylebos Waterway sediments.

17. OCC Tacoma, Inc., a subsidiary of Occidental Chemical Corporation, and its predecessors formerly owned and operated a chemical plant on thirty-three (33) acres at the Mouth of Hylebos Waterway at 605 Alexander Avenue. The plant was continuously operated from 1928 until June, 1997 by OCC Tacoma, Inc. or its predecessors . At various times, the plant manufactured chlorine, sodium hydroxide,

calcium chloride, muriatic acid, ammonia, ammonium hydroxide trichloroethylene, tetrachloroethylene, sodium aluminate, and aluminum chloride. From approximately 1929 to 1970, effluents from chlorine production operations were discharged directly to the Hylebos Waterway through the main plant outfall. Wastes from the trichloroethylene and tetrachloroethylene production process were either discharged to the Hylebos Waterway, disposed of at a deep-water disposal site, temporarily held in on-site settling ponds, or disposed of off-site. Due to past operating practices, soil and groundwater on and under portions of the Property contain chlorinated organic compounds. Direct discharge of sludges and wastewaters as well as the soil and groundwater are potential sources of certain organic compounds detected in the Hylebos Waterway.

VI. EPA'S CONCLUSIONS OF LAW AND DETERMINATIONS

Based upon the Findings of Fact in Section V and the Administrative Record, EPA makes the following Conclusions of Law and Determinations.

18. The Site is a "facility" as defined in Section 101(9) of CERCLA, 42 U.S.C. § 9601(9).

19. Substances and constituents thereof at the Site, and substances otherwise found at the Site and identified in Paragraphs 11 through 16, above, are "hazardous substance(s)" as defined in Section 101(14) of CERCLA, 42 U.S.C. § 9601(14).

20. Respondent is a "person" as defined in Section 101(21) of CERCLA, 42 U.S.C. § 9601(21).

21. Respondent is liable under Section 107(a) of CERCLA, 42 U.S.C. § 9607(a), as the "owner and operator" of the facility as defined by Section 101(20) of CERCLA, 42 U.S.C. § 9601(20), and within the meaning of Section 107(a)(1) of CERCLA, 42 U.S.C. § 9607(a)(1).

22. The conditions described in the Findings of Fact above constitute an actual or threatened "release" into the "environment," as defined by Sections 101(8) and (22) of CERCLA, 42 U.S.C. §§ 9601(8) and (22).

23. The conditions present at the facility constitute a threat to public health, welfare, or the environment based upon the factors in Section 300.415(b)(2) of the National Contingency Plan (NCP).

24. The actual or threatened release of hazardous substances from the Site may present an imminent and substantial endangerment to the public health, welfare, or the environment within the meaning of Section 106(a) of CERCLA, 42 U.S.C. § 9606(a).

25. The actions required by this Order are necessary to protect the public health, welfare or the environment, are in the public interest, are not inconsistent with CERCLA and the NCP.

VII. NOTICE TO STATE

26. EPA has notified the State of Washington through its Department of Ecology (Ecology) of this action pursuant to Section 106(a) of CERCLA, 42 U.S.C. § 9606(a).

VIII. ORDER AND WORK TO BE PERFORMED

27. Based upon the foregoing Findings of Fact, Conclusions of Law and Determinations, and the Administrative Record for this Order, it is hereby ordered and agreed that Respondent shall comply with the following provisions and perform the following actions, including, but not limited to, the attachments to this Order (if approved by EPA), all documents incorporated by reference into this Order, and all schedules and deadlines in this Order, attached to this Order, or incorporated by reference into this Order.

28. All work performed pursuant to this Order shall be under the direction and supervision of qualified persons. Within thirty (30) days after the effective date of this Order, and before any work under this Order begins at the Site, Respondent shall submit in writing the names, titles, addresses, and qualifications of all personnel, including contractors, subcontractors, laboratories, and consultants to be used in performing activities pursuant to this Order to EPA. Conestoga-Rovers & Associates has been identified as Respondent's primary contractor which EPA does not disapprove. EPA may inspect any laboratory used in performing activities pursuant to this Order to verify approved quality control procedures and protocols are maintained. If Respondent elects to use any additional contractors, subcontractors, or laboratories in performing work pursuant to this Order subsequent to commencement of activities at the Site, Respondent shall submit the information listed in this paragraph to EPA in writing at least ten (10) days prior to any such use. This Order is contingent on Respondent's demonstration to EPA's

satisfaction that Respondent is qualified to perform properly and promptly the actions set forth in this Order. EPA retains the right to disapprove of any, or all, of the contractors and/or subcontractors retained by Respondent. If EPA disapproves of a selected contractor, subcontractor, laboratory, or consultant, Respondent shall retain a replacement within fifteen (15) days following EPA's disapproval and shall notify EPA of that replacement company's or individual's name and qualifications within twenty (20) days of EPA's disapproval. If EPA subsequently disapproves of the replacement(s), EPA reserves the right to terminate this Order, conduct all or a portion of the removal and/or conduct or authorize any other response activities it deems necessary, and seek costs thereafter and take any appropriate enforcement action. During the course of the removal, Respondent shall notify EPA in writing of any changes or additions in the persons used to carry out such work, providing their names, titles and qualifications. EPA shall have the same right to approve changes and additions to personnel as it has hereunder regarding the initial notification.

29. Respondent shall conduct activities and submit deliverables for EPA review, comment, approval or modification as EPA may deem appropriate, and as provided in the SOW, attached as Appendix 1 to this Order, and as provided in the Work Plan, attached as Appendix 2 to this Order. All such work shall be conducted in accordance with the requirements of CERCLA, the NCP, and all applicable EPA guidance, including, but not limited to, Guidance on Conducting Non-Time-Critical Removal Actions Under CERCLA (EPA/540-R-

93-097), Guidance for Conducting Treatability Studies Under CERCLA (EPA/540/2-91/13a), Technology Screening Guide for Treatment of CERCLA Soils and Sludges (EPA/540/2-88/004), EPA Engineering Bulletins (series), Contaminants and Remedial Options at Solvent-Contaminated Sites (EPA/600/R-94/203), and Presumptive Remedies: Site Characterization and Technology Selection for CERCLA Sites with Volatile Organic Compounds in Soil (EPA 540-F-93-048), as well as guidances referenced therein, and guidances referenced in the SOW and the Work Plan, as such guidances may be amended or modified by EPA prior to implementation or performance of the work under this Order. Work conducted in compliance with all requirements of this Order will be deemed consistent with CERCLA and the NCP. The general activities Respondent is required to perform are identified below, including various deliverables to be submitted by Respondent for EPA review and approval. The specific tasks Respondent shall perform are described more fully in the SOW and in the Work Plan . All work performed pursuant to this Order shall be in accordance with the schedules, standards, specifications, and other requirements of this Order, including the SOW, and Work Plan, and other deliverables, as initially approved by EPA, or as may be amended or modified. For purposes of this Order, day means calendar day unless otherwise noted in the Order.

30. Embankment Area Removal Action

a. Sampling and Analysis Plan (SAP)/Quality Assurance Project Plan/Health and Safety Plan (HSP): Within fourteen (14) days after the effective date of this Order, Respondent shall submit for EPA approval a Sampling and Analysis Plan (SAP), Quality Assurance Project Plan (QAPP), and a Health and Safety Plan (HSP). Following EPA approval, or modification or revision as required by EPA, the SAP, any supplement to the SAP, the QAPP, and the HSP shall be incorporated in, and be an enforceable part of this Order.

b. Embankment Area Sampling: Within thirty (30) days after EPA approval of the SAP, QAPP and HSP, Respondent shall complete the work as outlined in the SAP. Leach tests and analyses of samples shall be completed in accordance with the schedule contained in the SAP as approved by EPA.

c. Interim Summary of Analytical Data: Within thirty (30) days after scheduled completion of SAP activities, as outlined in the SAP and approved by EPA, Respondent shall submit for EPA approval an Interim Summary of Analytical Data containing the information required in Task 3A of the attached SOW (Appendix 1).

d. Draft Embankment Area Characterization Report: Within sixty (60) days after EPA approval of the Interim Summary of Analytical Data, Respondent shall submit for EPA approval draft Embankment Area Characterization Report containing the information required in Task 3B of the attached SOW (Appendix 1).

E. Final Embankment Area Characterization Report: Within fourteen (14) days after approval of the draft Embankment Area Characterization Report, Respondent shall submit for EPA approval a final Embankment Area Characterization Report.

f. Data Gaps, Further Sampling, and Data Reporting: As necessary, and upon receipt of a written request from EPA, Respondent shall prepare addenda to the SAP and QAPP to address the potential fo further sampling in response to data gaps identified by EPA. Addend shall be submitted for EPA approval within thirty (30) days afte receipt of written request from EPA. Upon approval of the addenda b EPA in accordance with the schedule presented the in SAP addenda, a approved by EPA, Respondent shall initiate the sampling activities a outlined in the SAP and QAPP addenda. In accordance with the schedul presented in the SAP addenda, as approved by EPA, Respondent shall submit for EPA approval a Summary of Analytical Data containin information required in Task 4C of the attached SOW (Appendix 1).

g. Draft EE/CA Report. Within forty-five (45) days after EPA approval of the Embankment Area Characterization Report or completion of the work described in the SAP Addendum, whichever is later, Respondent shall submit for EPA approval a draft Engineering Evaluation/Cost Analysis (EE/CA) Report as further described in Task 5 of the attached SOW (Appendix 1).

h. Final EE/CA Report. Within fourteen (14) days after approval of the Draft EE/CA Report, Respondent shall submit for EPA approval a Final EE/CA Report. Upon approval by EPA, this Report, will be published for review during a period for public comment. Following the public comment period, EPA may: (i) select the proposed Removal Action Alternative that was published for comment; (ii) require Respondent to modify or revise the EE/CA Report and/or proposed Removal Action Alternative prior to EPA approval; or (iii) select another Removal Action Alternative. Upon approval by EPA, the EE/CA Report and the selected Removal Action Alternative shall be incorporated in, and be an enforceable part of this Order.

i. Draft Phase I Removal Action Work Plan: Within forty-five (45) days after EPA approval of the final EE/CA, Respondent shall submit for EPA approval the Draft Phase I Removal Action Work Plan containing information required in Task 6A of the attached SOW (Appendix 1).

Respondent or EPA may identify at any time the potential to conduct Time-Critical Removal Actions, prior to implementation of the "hot spot" Phase I Removal Action, if data indicate significant levels of chemicals and if implementation of such time-critical removal actions are deemed technically feasible by EPA and Respondent. If Time-Critical Removal Actions are identified and requested in writing by EPA or identified in writing by Respondent, and approved by EPA, Respondent shall submit within thirty (30) days of receipt of the written identification and request and, upon approval by EPA, shall such Time-Critical Removal Actions in accordance with said Work Plan. A Removal Action Completion Report in accordance with subparagraph t. below shall also be submitted on any Time-Critical Removal Actions performed.

j. Final Phase I Removal Action Work Plan: Within fourteen (14) days after EPA approval of the draft Phase I Removal Action Work Plan, Respondent shall submit for EPA approval a final Phase I Removal Action Work Plan.

k. Phase I Removal Action Design Documents: Respondent shall submit Phase I Removal Action design documents for EPA review and approval, as the documents are generated by Respondent and in accordance with the schedule contained in the approved Phase I Removal Action Work Plan.

l. <u>Draft Phase II Removal Action Work Plan</u>: In accordance with the schedule to be proposed in the final EE/CA by Respondent, and approved by EPA, Respondent shall submit for EPA approval the Draft Phase II Removal Action Work Plan containing information required in Task 6B of the attached SOW (Appendix 1).

m. <u>Final Phase II Removal Action Work Plan</u>: Within fourteen (14) days after EPA approval of the Draft Phase II Removal Action Work Plan, Respondent shall submit for EPA approval a final Phase II Removal Action Work Plan.

n. <u>Phase II Removal Action Design Documents</u>: Respondent shall submit Phase II Removal Action design documents for EPA review and approval, as the documents are generated by Respondent and in accordance with the approved schedule in the Phase II Removal Action Work Plan.

o. <u>Draft Long Term Monitoring and Maintenance Plan</u>: Within sixty (60) days after approval of the final Phase II Removal Action Work Plan, Respondent shall submit for EPA approval a draft Long Term Monitoring Plan containing information required in Task 8 of the attached SOW (Appendix 1).

p. <u>Final Long Term Monitoring and Maintenance Plan</u>: Within fourteen (14) days after EPA approval of the draft Long Term Monitoring and Maintenance Plan, Respondent shall submit for EPA approval the final Long Term Monitoring and Maintenance Plan.

q. <u>Monitoring Data Reports</u>: Respondent shall submit

Monitoring Data Reports for EPA review and approval according to a schedule to be proposed in the final Long Term Monitoring and Maintenance Plan as approved by EPA.

r. Implementation of Maintenance Activities: Maintenance shall be performed by Respondent as needed, as determined by EPA and Respondent, in accordance with a schedule to be determined by EPA.

s. Phase I and Phase II Removal Actions: Respondent shall complete removal actions in accordance with the activities and schedules specified in the Phase I and Phase II Removal Action Work Plans.

t. Draft Phase I and Phase II Removal Action Completion Reports. Within thirty (30) days after completion of Phase I Removal Action activities, specified in the Phase I Removal Action Work Plan, Respondent shall submit for EPA approval a draft Phase I Removal Action Completion Report containing information required in Task 7A of the attached SOW (Appendix 1). Similarly, within thirty (30) days after completion of Phase II Removal Action activities, as specified by the Phase II Removal Action Work Plan, Respondent shall submit for EPA approval a draft Phase II Removal Action Completion Report containing information required in Task 7B of the attached SOW.

u. Final Removal Action Completion Reports. Within fourteen (14) days after approval of the draft Phase I Removal Action Completion Report, Respondent shall submit for EPA approval a final Phase I Removal Action Completion Report. Similarly, within fourteen (14) days after approval of the draft Phase II Removal Action Completion Report, Respondent shall submit for EPA approval a final

Phase II Removal Action Completion Report. Upon approval by EPA, these Reports, shall be incorporated in, and be an enforceable part of this Order.

31. Area 5106 Removal Action

a. Draft Area 5106 Background Data Report: Within twenty one (21) days after the effective date of this Order, Respondent shall submit for EPA approval a Draft Area 5106 Background Data Report , containing the information required in Section 3.1.1 of the attached Work Plan (Appendix 2).

b. Final Area 5106 Background Data Report: Within fourteen (14) days after receipt of EPA approval of the draft Area 5106 Background Data Report, Respondent shall submit for EPA approval the final Area 5106 Background Data Report.

c. Draft and Final Sampling and Analysis Plan/Quality Assurance Project Plan: Within twenty-one (21) days after the effective date of this Order, Respondent shall submit for EPA approval a draft Sampling and Analysis Plan (SAP), and a draft Quality Assurance Project Plan (QAPP) containing the information required in Section 3.2.1 of the attached Work Plan (Appendix 2). Within fourteen (14) days after receipt of EPA approval of the draft SAP and the draft QAPP, Respondent shall submit for EPA approval the final SAP and the final QAAP. Following EPA approval, or modification or revision as required by EPA, the SAP, any supplement to the SAP and the QAPP shall be incorporated in, and be an enforceable part of this Order.

d. Area 5106 Sampling: Upon EPA approval of the SAP, QAPP and HSP, Respondent shall complete the work as outlined in the SAP according to the Schedule presented in the SAP.

e. Draft Area 5106 Characterization Report: Within 120 days of the effective date of this Order, Respondent shall submit for EPA approval a draft Area 5106 Characterization Report containing information required in Section 3.2 of the attached Work Plan (Appendix 2).

f. Final Area 5106 Characterization Report: Within fourteen (14) days after receipt of EPA approval of the draft Area 5106 Characterization Report, Respondent shall submit for EPA approval the final Area 5106 Characterization Report.

g. Data Gaps, Further Sampling, and Data Reporting: As necessary, and upon receipt of a written request from EPA, Respondent shall prepare addenda to the SAP and QAPP to address the potential for further sampling in response to identified data gaps by EPA. Addenda shall be submitted for EPA approval within thirty (30) days after receipt of written request from EPA. Upon approval of the addenda by EPA, Respondent shall initiate the sampling activities as outlined in the SAP QAPP addenda.

h. Draft Supplementary Characterization Report: In accordance with the schedule outlined in the SAP addendum as approved by EPA, Respondent shall submit for EPA approval a draft Supplementary Characterization Report containing information required in Section 3.2.2 of the attached Work Plan (Appendix 2).

i. Final Supplementary Characterization Report: Within fourteen (14) days after receipt of EPA approval of the draft Supplementary Characterization Report, Respondent shall submit for EPA approval the final Supplementary Characterization Report.

j. Draft Preliminary Treatment Technology Evaluation Report Within twenty-one (21) days after EPA approval of the final Area 5106 Characterization Report, or the final Supplementary Area 5106 Characterization Report, whichever is later, Respondent shall submit for EPA review and approval a draft Preliminary Treatment Technology Evaluation Report containing information required in the Section 3.4 of the attached Work Plan (Appendix 2).

k. Final Preliminary Treatment Technology Evaluation Report: Within fourteen (14) days after receipt of EPA approval of the draft Preliminary Treatment Technology Evaluation Report, Respondent shall submit for EPA approval the final Preliminary Treatment Technology Evaluation Report.

l. Draft Treatability Study Work Plan, SAP and QAPP: If required, and in accordance with the schedule presented in the final Preliminary Treatment Technology Evaluation Report as approved by EPA, Respondent shall submit for EPA review and approval a draft Treatability Study Work Plan, SAP and QAPP containing information required in Section 3.4 of the attached Work Plan (Appendix 2).

m. Final Treatability Study Work Plan, SAP and QAPP: Within fourteen (14) days of EPA approval of the draft Treatability Study Work Plan, SAP QAPP, Respondent shall submit for EPA approval the final Treatability Study Work Plan, SAP and QAPP.

n. Treatability Study: In accordance with the schedule presented in the final Treatability Study Work Plan, as approved by EPA, Respondent shall complete the treatability study.

o. <u>Treatment Standards Technical Memorandum</u>: Within fourteen (14) days after EPA approval of the final Preliminary Treatment Technology Evaluation Report, Respondent shall submit for EPA approval a Treatment Standards Technical Memorandum containing information required in Section 3.4 of the attached Work Plan (Appendix 2).

p. <u>Draft Pilot-Scale Treatment Testing Work Plan, SAP and QAPP</u>: In accordance with the schedule presented in the final Preliminary Treatment Technology Evaluation Report, as approved by EPA, Respondent shall submit for EPA review and approval a draft Treatment Work Plan, SAP and QAPP containing the information required in Section 3.4 of the attached Work Plan (Appendix 2).

q. <u>Final Pilot-Scale Treatment Testing Work Plan, SAP and QAPP</u>: Within fourteen (14) days of EPA approval of the draft Treatment Work Plan, SAP and QAPP, Respondent shall submit for EPA approval the final Treatment Work Plan, SAP and QAPP.

r. <u>Draft Final Treatment Technology Evaluation Report</u>: In accordance with the schedule presented in the final Preliminary Treatment Technology Evaluation Report, as approved by EPA, Respondent shall submit for EPA review and approval a draft Final Treatment Technology Evaluation Report containing the information required in Section 3.4 of the attached Work Plan (Appendix 2).

s. <u>Final Final Treatment Technology Evaluation Report</u>: Within 14 days after EPA approval of the draft Final Treatment Technology Evaluation Report, Respondent shall submit for EPA approval the final Final Treatment Technology Evaluation Report.

t. <u>Draft Dredging Alternatives Evaluation Report</u>: Within sixty (60) days after EPA approval of the final Area 510 Characterization Report, as approved by EPA, or the fina Supplementary Area 5106 Characterization Report, as approved by EPA, whichever is later, Respondent shall submit for EPA review an approval a draft Dredging Alternatives Evaluation Report containin the information required in Section 3.5 of the attached Work Pla (Appendix 2).

u. Final Dredging Alternatives Evaluation Report: Withi Fourteen (14) days after EPA approval of the draft Dredging Alternatives Evaluation Report or the Draft Supplementary Dredging Alternatives Report, as appropriate, Respondent shall submit for EPA approval the final Dredging Alternatives Evaluation Report.

v. Streamlined Risk Evaluation Report. Respondent shall submit for EPA approval a Streamlined Risk Evaluation Report containing information required in Section 3.7 of the attached Work Plan (Appendix 2). The draft and final versions of the Streamlined Risk Evaluation Report shall be included in, and submitted with, the draft and final EE/CA Reports.

w. Draft EE/CA Report. Within sixty (60) days after EPA approval of the final Final Treatment Technology Evaluation Report, as approved by EPA, Respondent shall submit for EPA approval a draft Engineering Evaluation/Cost Analysis (EE/CA) Report containing the information required in Section 3.10 of the attached Work Plan (Appendix 2).

x. Final EE/CA Report. Within fourteen (14) days after receipt of approval of the draft EE/CA Report, Respondent shall submit for EPA approval a final Engineering Evaluation/Cost Analysis (EE/CA) Report. Upon approval by EPA, this Report, including the proposed Removal Action Alternative, will be published for review during a period for public comment. Following the public comment period, EPA may: (i) select the proposed Removal Action Alternative that was published for comment; (ii) require Respondent to modify or revise the EE/CA Report or proposed Removal Action Alternative prior to EPA approval; or (iii) select another Removal Action Alternative.

32. EPA reserves the right to comment on, modify, and direct changes for all deliverables. At EPA's discretion, Respondent shall correct all deficiencies and incorporate and integrate all information and comments supplied by EPA either in subsequent or resubmitted deliverables. For each and every deliverable, or other item required under this Order, if EPA disapproves or requires modification or revision of any deliverable, or other item, in whole or in part, Respondent shall submit a modified or revised version thereof to EPA which is responsive to all EPA directions, comments, or requirements within thirty (30) days after receiving such directions, comments or requirements from EPA, unless a shorter or longer time is specified by EPA, or Respondent properly invokes the dispute resolution procedures set forth in Section XVII of this Order.

33. EPA reserves the right to stop Respondent from proceeding at any time, either temporarily or permanently, on any task(s), activity(s) or deliverable(s) at or relating to the Site and/or the implementation of this Order.

34. If Respondent modifies or revises any deliverable, report,

plan, or other submittal after receipt of EPA comments, directions, or requirements, and EPA subsequently disapproves the revisec submittal, or if subsequent submittals do not, in EPA's judgment, adequately address EPA's comments, directions or requirements foi changes, EPA may seek stipulated or statutory penalties fron Respondent pursuant to Section XVIII for violation of this Order; perform its own studies; complete the removal actions or any portior of one or both of the removal actions; and/or take any response actior at the Site it deems necessary, in accordance with its authority, anc seek reimbursement from Respondent for its costs therefor; and/or seek any other appropriate relief, subject to Respondent's right to invoke all remedies and defenses, including dispute resolution as provided in Section XVII.

35. In the event EPA takes over or causes others to perform some tasks, but does not remove Respondent's duty to complete the removal actions pursuant to this Order, Respondent shall incorporate and integrate information supplied by EPA as directed by EPA.

36. The absence of express EPA comment, approval or disapproval of any submission within any specified time period shall not be construed as approval by EPA. Respondent is responsible for the timely preparation of deliverables pursuant to this Order.

37. Respondent shall, prior to the shipment pursuant to this Order of hazardous substances from the Site to an out-of-state waste management facility, comply with requirements of 40 CFR § 300.440.

IX. MODIFICATION OF THE SOW OR WORK PLAN

38. If, at any time, Respondent identifies a need for additional data, Respondent shall submit a memorandum to the EPA OSC within twenty (20) days after such need has been identified explaining the need for and the nature of the data sought. EPA, in its discretion, will determine whether the additional data proposed to be collected by Respondent shall be incorporated into reports and deliverables. Additional work conducted by Respondent that is determined to be appropriate for the removal action pursuant to this Paragraph and approved by EPA, shall be deemed to be consistent with CERCLA, the NCP, and applicable EPA guidance.

39. In addition to the requirements of Section 103 of CERCLA, 42 U.S.C. § 9603, and all other applicable statutory or regulatory reporting requirements, Respondent shall immediately notify EPA and Ecology of any conditions at the Site which may pose an immediate threat to human health or welfare or the environment. If any incident, or change in site conditions, during the activities conducted pursuant to this Order causes or threatens to cause an additional release of hazardous substances from the Site or an endangerment of the public health, welfare, or the environment, the Respondent shall immediately take all appropriate action to prevent, abate or minimize such release, or endangerment caused or threatened by the release. Respondent shall also immediately notify the OSC or, in the event of his/her unavailability, shall notify the Regional Duty Officer, Emergency Response Unit, EPA Region 10, at (206) 553-1263 of the incident or site conditions. In addition to the authorities of the

NCP, EPA may modify or amend any work to be performed pursuant to thi Order or require additional work if EPA determines that suc modification or amendment is warranted by the immediate threat or i response to unanticipated conditions or changed circumstance threatening human health or the environment. Respondent shall confir its willingness to perform the modified or amended work within twent four (24) hours of notice from EPA, or in such longer period of tim that EPA may be grant. EPA reserves its right to conduct all or part of such modified or amended work with or without a notice and request to Respondent under this paragraph and to seek reimbursement of cost from Respondent, and/or to seek any other appropriate relief.

40. EPA may determine that, in addition to tasks defined i the SOW and Work Plan, other additional work may be necessary t accomplish the objectives of the removal action and this Order. EP may request Respondent to perform any such additional work or othe response activity in addition to the work initially approved o modified, if EPA determines that such actions are necessary. Any additional work requested in connection with Area 5106 and subtidal zone shall be limited to the scope of activities required for preparation of the EE/CA Report. Respondent shall confirm its willingness to perform any such additional work in writing within fifteen (15) days after receipt of the EPA request, or properly invoke the dispute resolution procedures set forth in Section XVII of this Order. Subject to the resolution of any dispute, Respondent shall implement the additional tasks EPA determines are necessary consistent with the foregoing. The additional work shall be completed according

to the standards, specifications, and schedule set forth or approved by EPA in a written modification to the SOW or Work Plan. EPA reserves the right to conduct all or part of such work itself, to seek reimbursement of costs from Respondent, and/or to seek any other appropriate relief.

X. QUALITY ASSURANCE

41. All sampling and analyses performed pursuant to this Order shall conform to EPA direction, approval, and guidance regarding sampling, quality assurance/quality control (QA/QC), data validation, and chain of custody procedures. Respondent shall ensure that the laboratory used to perform the analyses participates in a QA/QC program that complies with the appropriate EPA guidance. Respondent shall use the following documents as appropriate as guidance for QA/QC and sampling: "Quality Assurance/Quality Control Guidance for Removal Activities: Sampling QA/QC Plan and Data Validation Procedures," OSWER Dir. No. 9360.4-08. As indicated in the SOW for the Embankment Area Removal Action (Appendix 1), the Quality Assurance Project Plan (QAPP) shall be developed in accordance with EPA guidance and requirements of the EPA Contract Laboratory Program (CLP) and the Puget Sound Estuary Program (PSEP). The QAPP developed for the Hylebos Waterway pre-remedial design work, and approved by EPA, shall be utilized to the extent applicable. Upon request by EPA, Respondent shall have such a laboratory analyze samples submitted by EPA for quality-assurance monitoring. Respondent shall provide to EPA the quality assurance/quality control procedures followed by all sampling teams

and laboratories performing data collection and/or analysis. Upon request by EPA, Respondent shall allow EPA or its authorized representatives to take split and/or duplicate samples of any samples collected by Respondent while performing work under this Order pursuant to Paragraph 47 below.

XI. PROPOSED ENGINEERING ANALYSIS/COST ASSESSMENT REPORT, PUBLIC COMMENT, ADMINISTRATIVE RECORD

42. EPA retains full authority and responsibility for all aspects of public participation as set forth in CERCLA and the NCP, or as EPA may deem appropriate, including the release to the public of the proposed Embankment EE/CA Report and Area 5106 EE/CA Report. As requested by EPA, Respondent shall provide information supporting EPA's community relations programs related to the work performed pursuant to this Order, and shall participate in public meetings which may be held or sponsored by EPA to explain activities at or concerning the work performed pursuant to this Order.

43. EPA will determine the contents of the administrative record file for the selection of the removal actions. Respondent does not waive any rights or claims it may have regarding the adequacy of the administrative record. Respondent shall upon request submit documents developed pursuant to this Order to EPA upon which approval of both EE/CA Reports and Action Memoranda may be based. Upon request by EPA, Respondent shall submit copies of plans, task memoranda, including all documentation of field modifications, recommendations for further action, quality assurance memoranda and audits, raw data,

field notes, laboratory analytical reports, and other reports to EPA except those documents that are privileged. Upon request by EPA, Respondent shall also submit copies of any previous non-privileged studies conducted under state, local or other federal authorities relating to response selection under this Order, and all communications between Respondent and state, local, or other federal authorities concerning response selection. EPA shall maintain a community information repository at or near the Site to house a copy of the administrative record.

XII. PROGRESS REPORTS AND MEETINGS

44. Respondent shall make presentations at, and participate in, meetings and telephone conferences at the request of EPA during the initiation, conduct, and completion of the removal actions. In addition to discussion of the technical aspects of the removal actions, topics will include anticipated problems or new issues. Meetings and telephone conferences will be scheduled when EPA or Respondent deem it necessary .

45. In addition to the deliverables set forth in this Order, until the termination of this Order, Respondent shall provide monthly progress reports to EPA following the effective date of this Order. These progress reports shall: (1) describe the actions which have been taken to comply with this Order during the previous month; (2) list all sampling and test results and all other data reports received by the Respondent in the previous month; (3) describe all work planned for the next month with schedules relating such work to the overall

project schedule, including percentage of completion data; (4) describe all problems encountered and any anticipated problems, any actual or anticipated delays, and all solutions developed and implemented or planned to address any actual or anticipated problems or delays; and (5) include all other elements specified in the Work Plan.

During implementation of field work under both Embankment Area Work Plans, Respondent shall submit weekly progress reports containing the information required by this Paragraph and in accordance with Task 7A of the SOW (Appendix 1).

XIII. SAMPLING, ACCESS, AND DATA AVAILABILITY/ADMISSIBILITY

46. Tabular summaries of all validated results of sampling, tests, modeling or other data generated by Respondent, or on Respondent's behalf, pursuant to this Order, shall be submitted to EPA in the subsequent monthly progress report as described in Section XII of this Order. All unvalidated data, laboratory data and all laboratory analytical reports shall be submitted to EPA upon its request. EPA will make available to the Respondent validated data generated by EPA pursuant to Paragraph 47 below, and unvalidated data if relied upon by EPA for making Response action decisions.

47. Respondent shall notify EPA, Ecology, and the Trustees representatives designated in Section XIV of this Order at least fourteen (14) days prior to conducting any field events described in any approved Work Plan(s) or sampling and analysis plan. At EPA's verbal or written request, or the request of EPA's OSC or Ecology's

Project Manager or their designees, Respondent shall allow split o duplicate samples to be taken by EPA and Ecology and their authorize representatives and designees of any samples collected by th Respondent in implementing this Order. EPA will notify Respondent before conducting any sampling at the Site for purposes of this removal action. At Respondent's verbal or written request, EPA and Ecology shall allow Respondent to take split or duplicate samples of any samples collected by EPA or Ecology.

48. EPA, Ecology and the Trustees and their designated representatives, shall at all reasonable times have full access to, and authority to freely move about those portions of the Site owned by Respondent where work is to be carried out pursuant to this Order. EPA, Ecology and the Trustees and their designated representatives will comply with the Health and Safety Plan developed under this Order. EPA and Ecology and their designated representatives, also shall have such full access, including to laboratories, for purposes of inspecting conditions, activities in implementing the requirements of this Order, records, operating logs, and contracts related to work carried out under this Order; reviewing the progress of the Respondent in carrying out the terms of this Order; conducting tests as they or their authorized representatives or designees deem necessary; using a camera, sound recording device or other documentary type equipment; and verifying the data submitted to them by the Respondent. The Respondent shall allow these persons to inspect and copy all non-privileged records, files, photographs, documents, sampling and monitoring data, and other non-privileged or non-confidential writings

related to work undertaken in carrying out this Order. Copies of all other information or records created, maintained or received by Respondent or its agents, employees, accountants, contractors or consultants which are prepared pursuant to this Order, including but not limited to: contractual documents, work orders, disposal records, and any other records or documents not previously required herein shall promptly be made available to EPA on request as soon as practicable, but in any event within thirty (30) days of Respondent's receipt of EPA's request. In response to any reasonable request made by Respondent, EPA will allow Respondent to inspect or copy at their own expense non-privileged records, files, photographs, documents, sampling and monitoring data and other non-privileged writings of EPA related to the work undertaken under this Order. Nothing herein shall be interpreted as limiting or affecting EPA's right of entry or inspection authority under federal law.

49. Respondent may assert a claim of business confidentiality covering part or all of the information submitted to EPA pursuant to this Order in accordance with Section 104(e)(7) of CERCLA, 42 U.S.C. § 9604(e)(7), and 40 C.F.R. Part 2, Subpart B. This claim shall be asserted in the manner described by 40 C.F.R. 2.203(b)~~;~~. If no such claim accompanies the information when it is submitted to EPA, it may be made available to the public by EPA without further notice to Respondent. Analytical and other data specified in Section 104(e)(7)(F) of CERCLA shall not be claimed as confidential by the Respondent. EPA shall disclose information covered by a business confidentiality claim only to the extent permitted by, and by means

of, the procedure set forth at 40 C.F.R. Part 2, Subpart B.

50. Respondent reserves its right to assert privilege an work-product protections as to communications by, between or wit attorneys and their employees, consultants or agents, and as to th opinions, impressions, theories and conclusions of Respondent' employees, consultants, attorneys, or other agents that were generate at the request of or under the direction the attorney in anticipatio of litigation. In the event privilege is asserted, Respondent shal provide EPA with the date, author, recipient, or addressee, title, o description of the subject of the opinion or conclusion and the privilege asserted by Respondent.

51. For purpose of response actions contemplated by this Order, Respondent shall not object to the validity and use of any data gathered, generated, or evaluated by EPA, Ecology, or Respondent i the performance or oversight of any work which has been verifie according to the quality assurance/quality control (QA/QC) procedures required by this Order or any EPA-approved EE/CA, work plan o sampling and analysis plan, or which is contained in a report submitted by Respondent and approved by EPA under this Order. If Respondent objects to any use of any other data relating to the removal action, Respondent shall submit a report to EPA which identifies and explains Respondent's objections, describes any proposed acceptable uses of the data, and specifically identifies any proposed limitations on the use of the data. This report must be submitted to EPA within thirty (30) after such data's use is made known to Respondent, or Respondent's opportunity to object to such

data shall be waived. Notwithstanding anything to the contrary in this Paragraph, Respondent does not waive its right to dispute any conclusions or decisions made by EPA based on such data.

52. The Property was recently purchased by Pioneer Chlor Alkali Company, Inc. Respondent has an agreement with Pioneer Chlor Alkali Company, Inc., that Respondent shall have access to all portions of Property necessary for Respondent to conduct the removal actions required by this Order. If not included in its existing agreement, Respondent shall use its best efforts to obtain an agreement with Pioneer Chlor Alkali Company, Inc., to provide access for EPA, Ecology and the Trustees, and their representatives and designees, at all reasonable times and authority to freely move about the Site where work is to be carried out pursuant to this Order. EPA, Ecology and the Trustees and their designated representatives will comply with the Health and Safety Plan developed under this Order. Any such access agreement shall also specify that Respondent is not the governments' representatives with respect to any liability associated with activities required by this Order. If the Site areas that are to be used for access or are within the scope of the removal action, are owned in whole or in part by any other parties other than Respondent, Respondent shall obtain, or use its best efforts to obtain, written site access agreement(s) from the present owner(s) for Respondent, EPA, Ecology, and the Trustees not less than ninety (90) days or such shorter time period approved by EPA prior to a field sampling event that will require access. Copies or written acknowledgment of all access agreements shall be provided to EPA prior

to the initiation of any field activities. If Respondent is unable to obtain access agreements within the time referenced above, Respondent shall immediately notify EPA of their failure to obtain access. EPA may extend the schedule or modify the SAP, if deemed necessary by EPA, if delays in performance of work will result from the Respondent's inability to obtain access agreements to a location deemed necessary by EPA after Respondent has used best efforts and notified EPA in a timely manner, as specified in this Paragraph. EPA may obtain access for Respondent, or perform tasks or activities under its own authority in the event Respondent cannot obtain access agreements. In the event EPA performs any tasks or activities and does not terminate this Order, Respondent shall perform all other activities not requiring such access, and shall reimburse EPA for all costs EPA incurs in performing any tasks or activities incurred in connection to this Order. Respondent shall integrate the results of any tasks or activities undertaken by EPA into Respondent's deliverables. Furthermore, the Respondent agrees to indemnify the United States for any liability arising out of the performance of any such tasks or activities by EPA to the extent set forth in Paragraph 95 of this Order. Respondent shall also reimburse EPA for all costs and attorney fees incurred by the United States to obtain access pursuant to this Order.

XIV. <u>DESIGNATED PROJECT COORDINATOR, ON-SCENE COORDINATOR, NOTICES AND SUBMISSIONS</u>

53. Respondent has designated Alastair J. H. McGregor of Glenn Springs Holdings, Inc., an affiliate of Respondent, as its

Project Coordinator, who shall be responsible for the administratio of all of Respondent's actions under this Order. Communication between Respondent and EPA shall be directed through the Project Coordinator by facsimile and mail, with copies to such other person as EPA may designate. Communications include, but are not limited to, all documents, reports, approvals, and other correspondence submitte under this Order.

54. EPA has designated Ken Marcy of the Emergenc Response/Site Cleanup Unit 1, Environmental Cleanup Office, as its On-Scene Coordinator (OSC).

55. EPA's OSC shall have the authority lawfully vested in a On-Scene Coordinator by the NCP, and shall have the authority, i accordance with the requirements of the NCP, to halt any work require by this Order and to take any necessary response action when he or sh determines conditions at the Site may present an imminent an substantial endangerment to the public health or welfare or th environment. The absence of the EPA OSC from the area under stud pursuant to this Order shall not be cause for any stoppage or dela of any work, unless specifically directed by the OSC.

56. EPA and Respondent shall have the right to change thei designated OSC or Project Coordinator. EPA shall notify the Respondent, and Respondent shall notify EPA ten (10) days before suc a change is made. Notification may initially be made orally, but shall be followed by written notice. EPA retains the right t disapprove of any subsequent Project Coordinator named by Respondent.

57. Within thirty (30) days after the effective date of this

Order, Respondent shall submit to EPA in writing the name, title, qualifications, experience, professional affiliations, and background, of the individual selected as Respondent's Project Coordinator. EPA retains the right to disapprove of any Project Coordinator named by Respondent. If EPA disapproves of Respondent's selected Project Coordinator, Respondent shall retain another Project Coordinator and shall notify EPA of that person's name, title, qualifications, and background within ten (10) days of EPA's disapproval.

58. EPA will arrange for a qualified person to assist in its oversight and review of the conduct of the removal action, as authorized by Section 104(a) of CERCLA, 42 U.S.C. § 9604(a). The oversight assistant may observe work and make inquiries in the absence of EPA, but is not authorized to modify any work plan.

59. Documents including work plans, reports, approvals, disapprovals, and other correspondence which must be submitted under this Order, shall be sent to the individuals at the addresses specified below, unless those individuals give written notice of a change to the other parties. All notices and submissions shall be considered effective one business day after receipt by Respondent's Project Coordinator, unless otherwise provided.

a. Four (4) copies of documents to be submitted to EPA shall be forwarded to:

Ken Marcy
U.S. Environmental Protection Agency
1200 Sixth Avenue, ECL-117
Seattle, Washington 98101

b. One (1) copy of documents to be submitted to EPA shall be forwarded to:

Russell McMillan
Washington Department of Ecology
Southwest Regional Office
P.O. Box 47775
Olympia, Washington 98504

c. One (1) copy of documents to be submitted to EPA shall b forwarded to:

Robert A. Taylor
National Oceanic and Atmospheric Administration
Damage Assessment and Restoration Center
7600 Sand Point Way NW, BIN C15700
Seattle, Washington 98115

d. One (1) copy of documents to be submitted to EPA shall b forwarded to:

John Wakeman
U.S. Army Corps of Engineers
4735 E. Marginal Way South
Seattle, WA 98124

e. One (1) copy of documents to be submitted to EPA shall b forwarded to:

Larry Vanselow
Roy F. Weston, Inc.
700 Fifth Ave, Suite 5700
Seattle, WA 98104

f. Documents to be sent to the Respondent shall be forwarde to:

Alastair J. H. McGregor
Glen Springs Holdings, inc.
1795 Baseline Road
Grand Island, N.Y. 14072-1027

Frank A. Rovers
Conestoga-Rovers & Associates
2055 Niagra Falls Boulevard
Suite 3
Niagra Falls, NY 14304

Maury Wassmann
OCC Tacoma, Inc.
709 Alexander Avenue
Tacoma, WA 98412

John Wheeler
Occidental Chemical Corporation
Occidental Tower
5005 LBJ Freeway
Dallas, Texas 75244

XV. COMPLIANCE WITH OTHER APPLICABLE LAWS

60. All actions required to be taken pursuant to this Order shall be performed in accordance with the requirements of all applicable local, state, and federal laws and regulations except as provided in CERCLA Section 121(e) and 40 CFR § 300.415(i). In accordance with 40 CFR § 300.415(i), all on-site actions required pursuant to this Order shall, to the extent practicable, as determined by EPA, considering the exigencies of the situation, attain applicable or relevant and appropriate requirements (ARARs) under federal environmental, and state environmental laws. No local, state, or federal permit shall be required for any portion of any activity pursuant to this Order conducted entirely on-Site. Off-Site disposal of hazardous substances shall comply with all applicable provisions of CERCLA, RCRA, CWA, the implementing regulations respectively thereunder, and EPA guidances and policies. Respondent shall identify ARARs in the Work Plan.

XVI. RECORD PRESERVATION

61. All records and documents created by Respondent, or o Respondent's behalf, which relate to the implementation of this Order shall be preserved by Respondent for a minimum of ten (10) year following completion of the removal actions required by this Order. After this ten (10) year period, Respondent shall notify EPA at leas ninety (90) days before any records are scheduled to be destroyed. If EPA requests that the documents be saved, Respondent shall, at n cost to EPA, either maintain the documents or give EPA the non-privileged documents requested or true and accurate copies of thes documents. In addition, Respondent shall provide non-privilege records and documents retained under this section at any time befor expiration of the ten year period at the written request of EPA.

XVII. DISPUTE RESOLUTION

62. The parties to this Order shall attempt to resolve, expeditiously and informally, any disagreements concerning this Order.

63. If Respondent objects to any EPA notification or actio taken pursuant to this Order, the Respondent shall notify EPA i writing of its objection within ten (10) days of receipt of suc notification or actual notice of such action, unless the objection ha been informally resolved. Respondent's written objection required b this Section shall include, but not be limited to, any factual data, analysis, supporting documentation or legal opinion that support Respondent's position.

64. EPA and the Respondent shall have twenty (20) days fro

receipt of the notification of objection to reach agreement. This negotiation period may be extended at the sole discretion of EPA. If agreement is reached, it will be reduced to writing and will become a fully enforceable part of this Order. If agreement cannot be reached on any issue within this twenty (20) day period, the Unit Manager of the Emergency Response/Site Cleanup Unit 1, will issue a written decision to the Respondent. Respondent's obligations under this Order shall not be tolled by submission of any objection for dispute resolution under this Section, unless agreed to by EPA.

65. Respondent shall either implement EPA's decision or, within ten (10) days after Respondent's receipt of EPA's decision, submit a written appeal from the decision to the Director of the Office of Environmental Cleanup (Director). Respondent's written appeal shall include a presentation of the basis of the appeal, either legal or technical, and all supporting documentation. The Director will provide a written statement of EPA's decision reached with respect to the dispute in question. Prior to issuing the decision, the Director shall provide the Respondent with an opportunity to meet with the Director.

66. Following resolution of the dispute, as provided by this Section, Respondent shall fulfill the requirement that was the subject of the dispute in accordance with the agreement reached or with EPA's decision, whichever occurs. No EPA decision made pursuant to this Section shall constitute a final agency action giving rise to judicial review.

XVIII. STIPULATED PENALTIES

67. For each day that Respondent fails to complete a designated deliverable in a timely manner, fails to produce a designated deliverable of acceptable quality to EPA, or otherwise fails to perform in accordance with the requirements of this Order, Respondent shall be liable for stipulated penalties in accordance with this section. Penalties for late submittals shall accrue from the due date and extend until received. EPA will provide written notice for violations that are not based on timeliness. Penalties for violations that are not based on timeliness shall accrue from the date of Respondent's receipt of the written notice indicating the violation has occurred and extend through the period of correction. Where a revised submission by Respondent is required, stipulated penalties shall accrue from receipt of notice until a satisfactory deliverable is produced. Payment shall be due within thirty (30) days after receipt of a demand letter from EPA unless dispute resolution is invoked in accordance with Paragraph 72 below.

68. Respondent shall pay interest on the unpaid balance, which shall begin to accrue at the end of the thirty (30) day period, at the rate established by the Department of Treasury pursuant to 31 U.S.C. § 3717. Respondent shall further pay a handling charge of one (1) percent, to be assessed at the end of each thirty-one (31) day period, and a six (6) percent per annum penalty charge, to be assessed if the penalty is not paid in full within ninety (90) days after it is due.

69. Respondent shall make all payments by forwarding a check to:

Mellon Bank
EPA-Region 10 ATTN: Superfund Accounting
P.O. Box 360903M
Pittsburgh, Pennsylvania 15251

Checks should state the name of the Site, the Site identification number (102J), and the title and docket number of this Order. A copy of the check and accompanying transmittal letter shall be forwarded to the EPA OSC.

70. For the submission of draft and revised major deliverables described in Paragraphs 30 and 31 of this Order, stipulated penalties shall accrue in the amount of $500.00 per day, per violation, for the first seven (7) days of noncompliance; $750.00 per day, per violation, for the eighth (8th) through fourteenth (14th) day of noncompliance; $1,500.00 per day, per violation, for the fifteenth (15th) day through the thirtieth (30th) day; and $3,000.00 per day, per violation, for the thirtieth (30th) day and beyond.

71. For the monthly progress reports, and for any failure to perform in accordance with the requirements of this Order, stipulated penalties shall accrue in the amount of $250.00 per day, per violation, for the first seven (7) days of noncompliance; $500.00 per day, per violation, for the eighth (8th) through fourteenth (14th) day of noncompliance; $1,000.00 per day, per violation, for the fifteenth (15th) day through the thirtieth (30th) day; and $2,000.00 per day, per violation, for the thirtieth (30th) day and beyond.

72. Respondent may dispute EPA's right to the stated amount of penalties or interest thereon by invoking the dispute resolution procedures under Section XVII herein. Penalties shall accrue but need not be paid during a properly invoked dispute resolution period.

However, stipulated penalties shall not accrue with respect to a decision by the Director of the Office under Paragraph 65 above during the period, if any, beginning on the 21st day after the date that Respondent's written appeal is received until the date that the Director issues a final decision regarding such dispute. In any such appeal if Respondent does not prevail it may ask the Director to waive penalties that accrued during the Director's consideration of the appeal. If Respondent prevails upon resolution, no penalties or interest shall be paid.

73. In the event EPA provides for corrections to be reflected in the next deliverable and does not require resubmission of the initial deliverable, stipulated penalties, if any, on the initial deliverable shall cease to accrue on the day of such decision by EPA and will be payable in accordance with Paragraph 67 of this Order. Stipulated penalties, if any, for alleged failure to produce a deliverable of acceptable quality as an initial submission of that deliverable shall accrue from receipt of notice until the resubmission is approved by EPA in accordance with Paragraph 67 of this Order.

74. The stipulated penalties provisions of this Order do not preclude EPA from pursuing any other remedies or sanctions which are available to EPA because of the Respondent's failure to comply with this Order, including but not limited to conduct of all or part of the removal action by EPA. EPA will elect to assess either stipulated or statutory penalties for any given violation of this Order. EPA reserves its right to seek treble damages for work it may perform as provided by Section 107(c)(3) of CERCLA. If EPA elects to assess

statutory penalties, EPA and Respondent agree that the procedures in 40 C.F.R. Part 22 shall govern the assessment and judicial review of such penalties. Payment of stipulated or statutory penalties does not alter Respondent's obligation to complete performance under this Order.

XIX. FORCE MAJEURE

75. Force majeure, for purposes of this Order, is defined as any event arising from causes beyond the control of Respondent or any entity controlled by Respondent, including Respondent's agents, consultants, contractors and subcontractors, which delays the timely performance of any obligation under this Order notwithstanding Respondent's best efforts to avoid such delay. The requirement that Respondent use best efforts to avoid the delay includes using best efforts to anticipate potential force majeure events and using best efforts to address the effects of any force majeure event: (1) as it is occurring; and (2) following the potential force majeure event, such that the delay is minimized to the greatest extent practicable. Increased costs or expenses of any work to be performed under this Order, or the financial difficulty of Respondent to perform any such work shall not constitute force majeure events.

76. If any event occurs or has occurred which may delay the performance of any obligation under this Order, regardless of whether caused by a force majeure event, Respondent shall verbally notify the EPA OSC or, in his or her absence, the Unit Manager of the Emergency Response Unit, EPA Region 10, within forty-eight (48) hours after Respondent knew that any event would cause a delay. Within seven (7)

days thereafter, Respondent shall provide in writing the reasons fo the delay; the anticipated duration of the delay; all actions take or to be taken to prevent or minimize the delay; a schedule for th implementation of any measures to be taken to mitigate the effect o the delay; and a statement as to whether Respondent believes the even may cause or contribute to an endangerment to public health, welfar or the environment. Respondent shall exercise best efforts to avoi or minimize any delay and any effects of any delay. Failure to compl with the above requirements shall preclude Respondent from assertin any claim of force majeure.

77. If EPA agrees that the delay or anticipated delay is attributable to force majeure, the time for performance of the obligations under this Order that are directly affected by the force majeure event shall be extended by EPA for a period not to exceed the actual duration of the delay attributed to the force majeure event. An extension of the time for performance of the obligation directly affected by the force majeure event shall not extend the time for performance of any other unrelated obligations.

78. If EPA does not agree that the delay or anticipated delay has been or will be caused by a force majeure event, or does not agree with Respondent as to the appropriate length of any extension due to force majeure, the issue shall be subject to the dispute resolution procedures set forth in Section XVII of this Order. In dispute resolution, Respondent shall have the burden of demonstrating by a preponderance of the evidence that the delay or anticipated delay has been or will be caused by a force majeure event, that the duration of

the delay was or will be warranted under the circumstances, that Respondent did exercise or is exercising due diligence by using its best efforts to avoid and mitigate the effects of the delay, and that Respondent has complied with all of the requirements of Paragraph 74 above.

79. Should Respondent establish the existence of a force majeure event, the delay at issue shall not be deemed to be a violation of, or non compliance with, the affected obligation(s) of this Order.

XX. REIMBURSEMENT OF RESPONSE AND OVERSIGHT COSTS

80. Respondent shall reimburse EPA for all response costs paid or incurred but not yet paid by the United States in connection with this removal action prior to the effective date of this Order. Following the issuance of this Order, EPA shall submit to the Respondent on a periodic basis an accounting of all response costs incurred by the United States with respect to this Order. Response costs may include, but are not limited to: costs incurred by the United States in drafting, reviewing, and/or negotiating this Order, the SOW, and the Work Plan; overseeing Respondent's implementation of the requirements of this Order; or activities performed by the United States as part of the removal action, including any costs incurred to obtain access, conduct community relations. Additionally, costs shall include all direct and indirect costs with respect to this Order, including but not limited to, time and travel costs of EPA personnel and associated indirect costs, contractor costs, cooperative agreement

costs, compliance monitoring, including the collection and analysi of split samples, inspection of removal activities, Site visits discussions regarding disputes that may arise regarding this Order review and approval or disapproval of submissions, and costs of doin or redoing any of Respondent's tasks. Summaries, including EPA' certified Agency SCORES Reports, or such other summary as certifie by EPA, shall serve as the basis for the payments. Within ten (10) days of receipt of an EPA summary, Respondent may request supportin documentation from EPA substantiating the costs sought by EPA.

81. Respondent shall within thirty (30) days of receipt of th bill or receipt of supporting documentation, if requested pursuant t Paragraph 80, above, remit a certified or cashier's check for th amount of those costs. Interest shall accrue on the unpaid balanc from the date of receipt of the bill. The interest rate shall be th rate of interest on investments for the Hazardous Substances Superfun in Section 107(a) of CERCLA, 42 U.S.C. § 9607(a).

82. Checks in payment of Response and Oversight Costs should be made payable to the Hazardous Substances Superfund and should state the name of the Site, the Site identification number (102J), and the title and docket number of this Order. Checks should be forwarded to:

Mellon Bank
EPA-Region 10 ATTN: Superfund Accounting
P.O. Box 360903M
Pittsburgh, Pennsylvania 15251

83. Copies of the transmittal letter and check should be sent simultaneously to the EPA OSC.

84. Disputes concerning EPA's payment demands shall be made and decided in accordance with Section XVII of this Order. Respondent

agrees to limit any disputes concerning costs to accounting errors an the inclusion of costs outside the scope of this Order or no authorized by statute. Respondent shall identify any contested cost and the basis of its objection in writing. All undisputed costs shal be remitted by Respondent in accordance with the schedule set fort above. Disputed costs shall be paid into an escrow account b Respondent while any such dispute is pending. Respondent bears the burden of establishing an EPA accounting error or the inclusion of an cost outside the scope of this Order or not authorized by statute. Interest shall accrue during any cost dispute.

XXI. RESERVATIONS OF RIGHTS AND REIMBURSEMENT OF OTHER COSTS

85. EPA reserves the right to bring an action against Respondent under Section 107 of CERCLA, 42 U.S.C. § 9607, for recovery of all response costs incurred by the United States which are not reimbursed by Respondent, including past costs, any costs incurred in the event that EPA performs the removal action or any part thereof, and any future costs incurred by the United States in connection with response activities under CERCLA at the Site, or the CB/NT Superfund Site. Respondent reserves the right to bring any claim under CERCLA or any other applicable law it may have against the United States or any department, agency, instrumentality, or representative thereof, for recovery of any and all response costs or damages paid or incurred by, or on behalf of, Respondent or others with respect to the ownership and/or operation of the Site or of the CB/NT Superfund Site (collectively the "Sites") or any portions thereof and/or the

generation, storage, treatment, handling, transportation, release or disposal of any hazardous substances on the Sites, or which may have come to be located on the Sites by, or on behalf of, the United States or any department, agency, instrumentality, or representative thereof; provided, however, this reservation of rights shall not apply to any claims against the United States based on any acts or omissions by EPA.

86. EPA reserves the right to bring an action against Respondent to enforce any provision or requirement of this Order or any requirement developed pursuant to this Order, to enforce the cost reimbursement requirements of this Order, and to collect stipulated penalties assessed pursuant to Section XVIII of this Order or to seek penalties pursuant to Section 109 of CERCLA, 42 U.S.C. § 9609 if stipulated penalties were not already assessed.

87. Except as expressly provided in this Order, each party reserves all rights, claims, privileges, and defenses it may have and nothing in this Order shall affect EPA's response, enforcement or other statutory and/or regulatory authority, including the right to perform response activities or to seek injunctive relief, stipulated penalties, or statutory penalties, and/or punitive damages.

88. Following satisfaction of the requirements of this Order, Respondent shall have resolved its liability to EPA for the work performed and response costs paid by Respondent pursuant to this Order. Respondent is not released from any liability, if any, for any past response costs or response actions taken beyond the scope of this Order regarding other removals, other operable units, pre-remedial

design, remedial design and remedial action of the Hylebos Waterwa or any other problem area in the CB/NT Site, or any activitie pursuant to Section 121(c) of CERCLA, 42 U.S.C. § 9621(c).

XXII. CONTRIBUTION PROTECTION

89. With regard to claims for contribution against Respondent or its affiliates for matters addressed in this Order, the Parties hereto agree that Respondent and its affiliates are entitled to protection from contribution actions or claims to the fullest extent provided by section 113(f)(2) of CERCLA, 42 U.S.C. Sections 9613(f)(2). Nothing in this Order precludes the United States from asserting any claims, causes of action or demands against any persons not parties to this Order (except for Respondent's affiliates) for indemnification, contribution, or cost recovery. Nothing in this Order precludes Respondent from asserting any claims, causes of action or demands against any persons not parties to this Order for indemnification, contribution or cost recovery.

XXIII. DISCLAIMER

90. By signing this Order and taking actions under this Order, Respondent neither admits nor denies the Introduction's statements, the EPA Findings of Fact or the EPA Conclusions of Law and Determinations. Furthermore, Respondent's execution of and activities under this Order shall not be considered an admission of liability and is not admissible as evidence against it in any

judicial or administrative proceeding other than a proceeding by EPA or the United States to enforce this Order or any judgment relating to it. Respondent retains its right to assert claims against other potentially responsible parties and other persons with respect to the Site, and the CB/NT Superfund site. However, Respondent agrees not to contest the validity of this Order, or the procedures underlying or relating to it, in any action brought by the United States, including EPA, to enforce its provisions.

XXIV. OTHER CLAIMS

91. In entering into this Order, Respondent waives any right to seek reimbursement under Section 106(b) of CERCLA, 42 U.S.C. § 9606(b) for work covered by this Order. Respondent also waives any right to present a claim under Sections 111 or 112 of CERCLA, 42 U.S.C. §§ 9611, 9612 for work covered by this Order. Respondent further waives all other statutory and common law claims against EPA, including, but not limited to, contribution and counterclaims, relating to or arising out of conduct of the removal action. This Order does not constitute any decision on preauthorization of funds under Section 111(a)(2) of CERCLA, 42 U.S.C. § 9611(a)(2).

92. Nothing in this Order shall constitute or be construed as a covenant not to sue or release from any claim, cause of action or demand in law or equity against any person, firm, partnership, subsidiary or corporation not a signatory to this Order (other than Respondent's affiliates), including agencies of the United States other than EPA, for any liability it may have arising out of or relating in any way to the generation, storage, treatment,

handling, transportation, release, or disposal of any hazardous substances, pollutants, or contaminants at, from, or taken to the Site.

93. Respondent shall not seek to recover any costs or attorneys fees from EPA with regard to any matter connected with implementation of this Order.

XXV. FINANCIAL ASSURANCE, INSURANCE, AND INDEMNIFICATION

94. Respondent shall establish and maintain financial security for performance of the work and any other obligations required under this Order. Within thirty (30) days after the effective date of this Order and on the anniversary date of this Order thereafter until this Order is terminated under Paragraph 100 below, Respondent shall establish and maintain financial security in one or more of the following forms: (a) A surety bond guaranteeing performance of the work; (b) one or more irrevocable letters of credit equaling the total estimated cost of the work; (c) a trust fund; (d) a guarantee to perform the work required under this Order by a direct or indirect parent corporation.EPA acknowledges that a corporate guarantee from any of Respondent's parent corporations would be an acceptable financial assurance mechanism, if it can meet the requirements for a corporate guarantee under 40 C.F.R. Section 264.143.

a. Prior to commencement of any work under this Order, Respondent shall secure, and shall maintain in force for the duration of this Order, and for two (2) years after the completion of all activities required by this Order, Comprehensive General Liability ("CGL") and automobile insurance, naming as an additional insured the United States. The CGL insurance shall include Contractual Liability Insurance in the amount of $ 1 million per occurrence, and Umbrella Liability in the amount of $2 million per occurrence.

b. For the duration of this Order, Respondent shall satisfy, or shall ensure that its contractors or subcontractors satisfy, all applicable laws and regulations regarding the provision of employer's liability insurance and workmen's compensation insurance for all persons performing work on behalf of the Respondent, in furtherance of this Order.

c. If Respondent demonstrates by evidence satisfactory to EPA that any contractor or subcontractor maintains insurance equivalent to that described above, or with respect to that contractor or subcontractor Respondent need provide only that portion of the insurance described above which is not maintained by the contractor or subcontractor.

d. Prior to commencement of any work under this Order, and annually thereafter on the anniversary of the effective date of this Order, Respondent shall provide to EPA certificates or declarations of such insurance.

95. At least seven (7) days prior to commencing any work under this Order, Respondent shall certify to EPA that the required insurance has been obtained by that contractor.

96. The Respondent agrees to indemnify and hold the United

States Government, its agencies, departments, agents, and employees harmless from any and all claims or causes of action arising from or on account of acts or omissions of Respondent, its employees, agents, servants, receivers, successors, or assignees, contractors, subsidiaries and parent company and its employer agents, and servants in carrying out activities under this Order provided that this Order shall not indemnify nor hold harmless the United States or any Department, agency, instrumentality, or representative thereof which may have liability or responsibility under CERCLA for any generation, storage, treatment, handling, transportation, release or disposal of any hazardous substance on the Site or which may have come to be located on the Site by them or on their behalf. The United States Government or any agency or authorized representative thereof shall not be held as a party to any contract entered into by Respondent in carrying out activities under this Order.

XXVI. <u>EFFECTIVE DATE AND SUBSEQUENT AMENDMENT</u>

97. The effective date of this Order shall be the date it is signed by EPA. Except when expressly stated otherwise herein, all time periods referred to in this Order shall be construed as calendar days, rather than business or working days. Any time period scheduled to begin on the occurrence of an act or event shall begin on the day after the act or event. If the final day of any time period falls on a Saturday, Sunday, or legal holiday, the time period shall be extended to the next regular business day.

98. In addition to the procedures set forth elsewhere in this Order, this Order may be amended by agreement between EPA and Respondent. Amendments shall be in writing and shall be effective when signed by EPA. EPA OSCs do not have the authority to sign any amendment to this Order.

99. No informal advice, guidance, suggestions, or comments by EPA regarding reports, plans, specifications, schedules, or any other writing submitted by Respondent will be construed as relieving Respondent of its obligation to obtain such formal approval as may be required by this Order. Any deliverables, plans, technical memoranda, reports (other than monthly progress reports) specifications, schedules and attachments required by this Order or developed pursuant to this Order, are, upon approval by EPA, incorporated in, and made an enforceable part of, this Order by this reference.

XXVII. TERMINATION AND SATISFACTION

100. This Order shall terminate when either: (1) Respondent demonstrates in writing and certifies to the satisfaction of EPA that all activities required by this Order, including any additional work pursuant to paragraph 40, payment of all costs subject to reimbursement under Section XX, and any stipulated penalties demanded by EPA pursuant to Section XVIII and upheld after dispute resolution, if any, have been performed, and EPA has approved the certification set forth in Paragraph 101, below; or

(2) the obligation for any remaining work required by this Order i assumed under a different agreement with EPA that is in full force and effect. Section XXII (Contribution Protection) and Respondent's obligation to comply with Sections XVI (Record Preservation), XX (Reimbursement of Response and Oversight Costs), and XXI (Reservations of Rights and Reimbursement of Other Costs), of this Order shall remain in full force and effect without time o other limitation.

101. The following certification shall be signed by a responsible official on behalf of Respondent:

> In accordance with 28 U.S.C. § 1746, I certify under penalty of perjury under the laws of the United States that to the best of my knowledge, after appropriate inquires of all relevant persons involved in the preparation of information contained in and accompanying this certification, the information contained in and accompanying this certification is true, accurate, and complete. Dated this __ day of ________, 199_.

For purposes of this Order, a responsible official is a corporate official in charge of a principal business function.

IT IS SO ORDERED, this 6 day of November, 1997

UNITED STATES ENVIRONMENTAL
PROTECTION AGENCY

By: ______________________________
Chris Field, Manager
Emergency Response/Site Cleanup
Unit 1
EPA Region 10

RESPONDENT hereby consents to the issuance of this ORDER, and agre to abide by each and every provision herein, and to perform each and every task or requirement herein.

BY: Keith C. McDole
Title: Sr. Vice President and Secretary

DATE: October 30, 1997

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EPA--REGION 10

Amendment
Administrative Order On Consent For Removal Activities Embankment and Area 5106
EPA Docket No. 10-97-0011-CERCLA

Occidental Chemical Corporation ("Occidental"), the United States Environmental Protection Agency ("EPA"), and the Washington Department of Ecology ("Ecology") agree to amend the Administrative Order on Consent for Removal Activities Embankment and Area 5106, EPA Docket No. 10-97-0011-CERCLA ("AOC") pursuant to Paragraph 98 of the AOC as follows.

This amendment reflects agreement amongst EPA, Ecology, and Occidental that A) additional site characterization needs to be conducted, both in upland areas and beneath the Hylebos Waterway, to adequately determine the nature and extent of soil, ground water, surface water, and sediment contamination; B) feasible alternatives to address remaining contamination of all media need to be developed and evaluated; and C) an integrated remedy or set of remedies needs to be selected and designed which will satisfy EPA and Ecology requirements under CERCLA, MTCA, and RCRA. Accordingly, the attached SOW includes the CERCLA remedial process elements of RI/FS, RD, and interim response actions.

1. Pursuant to Paragraph 40 of the AOC, Occidental shall implement the attached Statement of Work ("SOW"). The SOW is attached to this Amendment as Attachment A and and provides for environmental investigation, alternatives analyses, interim response actions to address pH contaminated groundwater, response action selection, and remedial design. All work plans, schedules and other tasks required by the SOW shall be performed pursuant to the terms and conditions of the AOC and subject to approval by EPA and/or Ecology. In addition, all work plans, schedules and other tasks required by the SOW shall be conducted consistent with the Model Toxics Control Act ("MTCA"), Resource Conservation and Recovery Act ("RCRA"), and the Comprehensive Environmental Response, Compensation and Liability Act ("CERCLA").

2. EPA and Ecology have entered into a Memorandum of Understanding ("MOU") that provides a framework for coordination and cooperation between the two agencies. The MOU designates the "lead agency" for particular activities that will be performed pursuant to this Amendment, and explains how decision-making responsibilities will be allocated. EPA and Ecology expect that implementation and oversight of this Amendment will be consistent with the MOU. Nothing in this Amendment is intended to provide Occidental or any other third-party with any rights or obligations regarding the MOU.

3. Until the AOC, as amended, is superceded by another legal mechanism (e.g., a consent decree) requiring implementation of recommended alternatives to be developed under the SOW, Occidental shall continue to maintain and operate the Groundwater Treatment System according to the current Corrective Action Plan

and current Corrective Action Monitoring Plan which has been developed under the expired RCRA permit No. WAD00924314. Occidental shall continue to monitor and report hydraulic responses of injection and extraction wells according to the procedures and schedule specified in the Corrective Action Monitoring Plan. Occidental shall continue to redevelop or replace injection and extraction wells with new wells as necessary according to the criteria specified in the Corrective Action Monitoring Plan.

4. The definition of the Site contained in Paragraph 1 of the AOC shall be changed to the following:

> The Site shall mean that portion of segment 5 of the Mouth of the Hylebos Waterway Problem Area and those portions of the upland properties described in the next sentence where Waste Materials have or may come to be located as a result of releases or threatened releases of Waste Materials from operations related to the production, processing, formulation or disposal of chemical materials or products. Accordingly, the Occidental Site shall include, but not be limited to the following: Area 5106; the Occidental Embankment Area; the Pioneer Property located at 605 Alexander Avenue; locations of groundwater contaminant plumes and contaminated sediments on the Port of Tacoma property located at 401 Alexander Avenue to the north of the Pioneer Property; locations of contaminated sediments and groundwater contaminant plumes on the Mariana Properties property located at 709 Alexander Avenue and the Port of Tacoma property located at 721 Alexander Avenue to the south of the Pioneer Property; and other areas of Segment 5 of the Mouth of the Hylebos Waterway Problem Area where releases of Waste Materials from such properties have come to be located and those areas necessary to stage or implement related work. The Occidental Site does not include the release of total petroleum hydrocarbon, BTEX or other constituents of concern from petroleum product storage operations currently or historically located on the 709 Alexander Avenue property or 721 Alexander property which has been identified in shallow groundwater underlying the 709 Alexander Avenue property or the 721 Alexander property and determined to be moving towards the Blair Waterway. Attachment B to this Amendment is a map that generally depicts the Site.

5. Ecology shall be added as a party to the AOC. Ecology shall have the authority to enforce the terms and conditions of the AOC as appropriate as such relate to the work performed pursuant to this Amendment. The terms and condition of the AOC applicable to EPA shall be applicable to Ecology.

6. Consistent with Section XVIII of the AOC ("Stipulated Penalties"), Ecology shall also have the authority to assess and collect stipulated penalties . However, in no event will Occidental be required to pay duplicative stipulated penalties to EPA

and Ecology. Payments of stipulated penalties owed, if any, to the State shall be mailed to the Department of Ecology, Cashiering Section, P.O. Box 5128, Lacey, WA 98509-5128.

7. Consistent with Section XX of the AOC ("Reimbursement of and Oversight Response Costs"), Occidental shall also reimburse the State for all response costs paid or incurred by the State in connection with this Amendment. Occidental shall pay the required amount of such response costs within thirty (30) days of receiving from Ecology an itemized statement of such costs that includes a summary of costs incurred, an identification of involved staff, and the amount of time spent by involved staff members on the project. A general description of the work pertinent to such costs will be provided if requested by Occidental. Ecology will prepare and provide Occidental with itemized statements on a quarterly basis. In addition, within ninety (90) days of the effective date of this Amendment, Occidental shall pay the State $458,259.17 in reimbursement of response costs that the State has incurred in connection with the Occidental Site prior to June 30, 2004. Failure to pay response costs within thirty (30) days of receipt of the itemized statement will result in interest charges in accordance with WAC 173-340-550. All payments owed to the State pursuant to this Amendment will be sent to the Department of Ecology, Cashiering Section, P.O. Box 5128, Lacey, WA 98509-5128.

8. Consistent with Section XVII of the AOC ("Dispute Resolution"), in the event that Occidental objects to notification provided by or action undertaken by Ecology, the Section Supervisor for Hazardous Waste and Toxic Reduction for the Southwest Regional Office shall resolve the initial dispute related to such objection. Any subsequent and timely written appeal of such initial dispute decision shall be resolved by the Program Manager of Ecology's Hazardous Waste and Toxics Reduction Program.

9. The Unilateral Administrative Order (Area 5106), EPA Docket No. CERCLA 10-2002-0066 (the "UAO") is hereby terminated. Remaining additional response actions, required by EPA on March 25, 2003 under authority of the UAO, have been incorporated into the attached Occidental Site SOW. Occidental reserves any defenses it may have to any subsequent action brought by EPA, except for those based upon principles of waiver, res judicata, collateral estoppel, issue preclusion, claims-splitting, or other defenses based upon any contention that the claims raised by EPA in the subsequent proceeding are barred by the termination of the UAO

10. Ecology Enforcement Order DE 95TC-S242, issued to PRI Northwest, Inc. and Occidental Chemical Corporation, effective September 5, 1995, is held in abeyance until a consent decree or administrative order implementing the selected remedies for the Mariana property takes effect.

11. Unless expressly modified by this Amendment, the terms and conditions of the AOC shall apply to all work or other activities required by the Amendment.

12. The AOC as modified by this Amendment contains the entire agreement between EPA, Ecology and Occidental. No statements, promises or inducements made by any party or its representatives that are not contained in this Amendment shall be valid or binding.

Occidental, EPA and Ecology have executed this document to signify their agreement to the foregoing effective as of the date of EPA's execution as set forth below. This agreement may be executed in counterparts, each of which shall be deemed an original, but all of which together shall constitute one the same instrument.

AGREED for Occidental Chemical Corporation

By:________________

Name:________________

Title:________________

Date:________________

AGREED for Washington Department of Ecology

By: K Seiler

Name: K SEILER

Title: SWRO HWTR Section Manager

Date: 1/28/05

AGREED for United States Environmental Protection Agency

By:________________

Name:________________

Title:________________

Date:________________

12. The AOC as modified by this Amendment contains the entire agreement between EPA, Ecology and Occidental. No statements, promises or inducements made by any party or its representatives that are not contained in this Amendment shall be valid or binding.

Occidental, EPA and Ecology have executed this document to signify their agreement to the foregoing effective as of the date of EPA's execution as set forth below. This agreement may be executed in counterparts, each of which shall be deemed an original, but all of which together shall constitute one the same instrument.

AGREED for Occidental Chemical Corporation

By: JoEllen Drisko

Name: JO ELLEN DRISKO

Title: VICE-PRESIDENT

Date: 19 JANUARY 2005

AGREED for Washington Department of Ecology

By:________________________

Name:________________________

Title:________________________

Date:________________________

AGREED for United States Environmental Protection Agency

By:________________________

Name:________________________

Title:________________________

Date:________________________

11. Unless expressly modified by this Amendment, the terms and conditions of the AOC shall apply to all work or other activities required by the Amendment.

12. The AOC as modified by this Amendment contains the entire agreement between EPA, Ecology and Occidental. No statements, promises or inducements made by any party or its representatives that are not contained in this Amendment shall be valid or binding.

Occidental, EPA and Ecology have executed this document to signify their agreement to the foregoing effective as of the date of EPA's execution as set forth below. This agreement may be executed in counterparts, each of which shall be deemed an original, but all of which together shall constitute one the same instrument.

AGREED for Occidental Chemical Corporation

By:______________________________

Name:___________________________

Title:____________________________

Date:____________________________

AGREED for Washington Department of Ecology

By:______________________________

Name:___________________________

Title:____________________________

Date:____________________________

AGREED for United States Environmental Protection Agency

By: Sheila M Eckman

Name: Sheila M. Eckman

Title: Unit Manager, Environmental Cleanup Office

Date: 2/1/05

Glenn Springs Holdings, Inc.
A Subsidiary of Occidental Petroleum Corporation

Clint Babcock
Director Operations
Direct Dial (972) 687-7506

7601 Old Channel Trail
Montague, MI 49437-9281
Facsimile (231) 894-4033

October 31, 2019

Reference No. 11191376

VIA EMAIL

Ms. Kerry Graber
Washington Department of Ecology
300 Desmond Drive
Olympia, WA 98504-7775

Mr. Joe Wallace, Regional Project Manager/OSC
United States Environmental Protection Agency
Region 10 ECL-111
1200 Sixth Avenue, Suite 900
Seattle, WA 98101

Dear Ms. Graber and Mr. Wallace:

Re: Progress Report for July - September 2019
Administrative Order on Consent for Removal Activities
USEPA Docket No. 10-07-0011-CERCLA
Groundwater and Sediment Remediation
Commencement Bay Nearshore/Tideflats Superfund Site
Tacoma, Washington

This progress report is submitted pursuant to Section XII of the Administrative Order on Consent (AOC) for Removal Activities, Commencement Bay Nearshore/Tideflats (CB/NT) Superfund Site (EPA Docket No. 10-07-0011 CERCLA). This progress report summarizes the activities performed by Occidental Chemical Corporation (OCC or "Respondent") during the reporting period of July 1 through September 30, 2019.

As set forth in the AOC, this progress report is divided into the following subject areas:

i) Description of Actions Taken During Reporting Period
ii) Listing of New Sampling and Testing Reports Generated or Received
iii) Summaries of New Deliverables
iv) Description of Work Planned for Next Reporting Period
v) Project Schedule and Estimates of Percentage of Work Completed
vi) Discussion of Problems Encountered, Anticipated Problems or Delays, and Solutions to Address Problems or Delays

DESCRIPTION OF ACTIONS TAKEN DURING REPORTING PERIOD

GENERAL

- Submitted the progress report for the reporting period of April 1 through June 30, 2019 on July 31, 2019 via email.
- The OCC and Agency Technical Teams participated in July 17 and 19, 2019 conference calls to discuss the draft Agreed Order (AO), Monitoring Plan, remedial alternatives, and the draft Cleanup Action Plan (dCAP).
- The OCC and Agency Technical Teams participated in an August 29, 2019 meeting to discuss the Seasonal Water Level Monitoring Work Plan locations, Inactive Extraction Well EXT-9 Longer-Term Pumping Test Work Plan (EXT-9 Pumping Test Work Plan) implementation and duration, access for proposed monitoring well locations, and dCAP.
- Received Ecology September 25, 2019 revised draft AO.

TASK A6 – PREPARE CHARACTERIZATION REPORT

- Received Ecology August 22, 2019 redlined text description of high pH areas (VOC source area mass reduction by strategic groundwater pumping).
- Submitted list of final monitoring locations for Seasonal Water Level Monitoring Work Plan on September 12, 2019.

TASK B4 – IMPLEMENT PH PILOT STUDY

- No actions taken during this period.

TASK C2/D2 – EVALUATE REMEDIAL ALTERNATIVES

- Submitted proposed redline edits to the June 20, 2019 draft cleanup action description and the June 20, 2019 draft disproportionate cost analysis (DCA) on July 26, 2019.

TASK E2 – 3D MODEL CONSTRUCTION AND CALIBRATION

- No actions taken during this period.

TASK M2 – RISK ASSESSMENT

- No actions taken during this period.

INTERIM MEASURES

- Continued with commissioning, testing, and finalizing substantive requirements for permitting of the new regenerative thermal oxidizer (RTO) system at the OCC Tacoma groundwater treatment plant (GWTP).

- Continued process to design and procure cooling tower components to replace the existing GWTP seawater pump and cooling system.

LISTING OF NEW SAMPLING AND TESTING REPORTS GENERATED OR RECEIVED

- See the new deliverables below.

SUMMARIES OF NEW DELIVERABLES

GENERAL

- Submitted the progress report for the reporting period of April 1 through June 30, 2019 on July 31, 2019 via email.

TASK A6 – PREPARE CHARACTERIZATION REPORT

- Submitted list of final monitoring locations for Seasonal Water Level Monitoring Work Plan on September 12, 2019.

TASK B4 – IMPLEMENT PH PILOT STUDY

- No new deliverables during this period.

TASK C2/D2 – EVALUATE REMEDIAL ALTERNATIVES

- Submitted proposed redline edits to the June 20, 2019 draft cleanup action description and the June 20, 2019 draft DCA on July 26, 2019.

TASK E2 – 3D MODEL CONSTRUCTION AND CALIBRATION

- No new deliverables during this period.

TASK M2 – RISK ASSESSMENT

- No new deliverables during this period.

INTERIM MEASURES

- No new deliverables during this period.

DESCRIPTION OF WORK PLANNED FOR NEXT REPORTING PERIOD

GENERAL

- Comply with various requirements of the AOC.
- Submit the progress report for the reporting period of October 1 through December 31, 2019 by January 31, 2020.
- Continue conference calls and face-to-face meetings with Agencies and stakeholders, as needed.
- Continue development of the Draft AO.
- Obtain final approvals for AOC Amendment #2 upon finalization and approvals of Draft AO.

TASK A6 – PREPARE CHARACTERIZATION REPORT

- Begin seasonal water level monitoring.
- Potentially begin the EXT-9 pumping test, subject to air permitting and GWTP status.

TASK B4 – IMPLEMENT PH PILOT STUDY

- No work planned during the period.

TASK C2/D2 – EVALUATE REMEDIAL ALTERNATIVES

- Support Agency's development of a dCAP and materials for a public meeting.

TASK E2 – 3D MODEL CONSTRUCTION AND CALIBRATION

- No work planned during the period.

TASK M2 – RISK ASSESSMENT

- No work planned during the period.

INTERIM MEASURES

- Complete process commissioning and finalizing substantive requirements for permitting of the RTO system installed at the OCC Tacoma GWTP.
- Finalize design and procurement of cooling tower components to replace the existing GWTP seawater pump and cooling system.
- Continue discussions for access to install new and replacement monitoring wells.

PROJECT SCHEDULE AND ESTIMATES OF PERCENTAGE OF WORK COMPLETED

- The current status of major ongoing items is summarized below.

Task	**Estimated Completion Schedule**
MTCA AO Finalization	TBD
dCAP	TBD
Complete RTO System Commissioning and Finalize Substantive Requirements for Permitting	October 2019
Install and Commission GWTP Cooling Tower	October 2019

- Table 1 presents the current status of the SOW deliverables.

DISCUSSION OF PROBLEMS ENCOUNTERED, ANTICIPATED PROBLEMS OR DELAYS, AND SOLUTIONS TO ADDRESS PROBLEMS OR DELAYS

No problems or delays are currently anticipated.

If you have any questions regarding this progress report, please contact us at (972) 687-7506 or (519) 241-8856, respectively.

Yours truly,

Glenn Springs Holdings, Inc.

Clinton J. Babcock
Director Operations
Glenn Springs Holdings, Inc.
(for Respondent)

Ian K. Richardson P.E.
Project Manager
GHD
(for the Supervising Contractor)

CJB/IKR/kf/3

Encl.

cc:
Dominic Giaudrone, CDM Smith
J. Massmann, Keta Waters
J. Lehto, NOAA
T. Yackulic, Esq., USEPA
Charles San Juan, Ecology
Charles Hoffman, Ecology
R. Bakemeier, Esq.
F. Parigi., GSH
R. Healy, Port of Tacoma
M. Malott, CHB
C. Naylor, Puyallup Tribe
Allyson Bazan, Ecology

Table 1

Status of SOW Deliverables
Groundwater and Sediment Remediation
as of September 30, 2019

		OCC	Agency	
Task	**Description**	**Date Submitted (Projected)**	**Date Comments Received by OCC**	**Date Approval Received by OCC**
	<u>Prepare/Finalize Statement of Work (SOW)</u>			
	Draft Work Plan	23-Dec-03	2-Feb-04	-
	Draft Work Plan (revised)	31-Mar-04	26-Apr-04	-
	Draft SOW	18-May-04	21-Jul-04	-
	Draft SOW (revised)	3-Sep-04	18-Oct-04	
	Draft SOW (redline for meeting)	26-Oct-04	28-Oct-04	
	Draft SOW (revised redline)	5-Nov-04	23-Nov-04	
	Additional Agency Revisions (following discussions)	-	29-Dec-04	
	Draft SOW (revised redline)	7-Jan-05	13-Jan-05	
	Final SOW	17-Jan-05	-	
	Final SOW (corrected)	28-Jan-05	-	
	AOC Amendment Executed	-	-	1-Feb-05
Task A - Site Characterization				
A3	**<u>Perform Supplemental Field Investigations</u>**			
	SAP/QAPP	23-Dec-03	2-Feb-04	-
	SAP/QAPP (revised)	31-Mar-04	26-Apr-04	
	SAP/QAPP (revised)	17-May-04	-	28-May-04
	SAP/QAPP (final)	21-Jun-04	-	-
	Memo - Delineation of Northern Extent of Groundwater COC Plume	15-Jun-04	18-Jun-04	-
	Letter - Preliminary Appendix IX Analytical Results	28-Jun-04	-	21-Jul-04
	Draft SAP/QAPP for Additional Supplemental Investigations	9-Feb-05	10-Mar-05	
	Revised Draft SAP/QAPP for Additional Supplemental Investigations	14-Apr-05	-	25-Oct-05
	Partial Approval of SAP/QAPP for Additional Supplemental Investigations	-	-	23-May-05
	Partial Approval of SAP/QAPP for Additional Supplemental Investigations	-	-	8-Jun-05
	Conditional Approval of SAP/QAPP for Additional Supplemental Investigations	-		25-Oct-06
	Final SAP/QAPP for Additional Supplemental Investigations		-	
	<u>709/721 Alexander Investigation</u>			
	Draft Work Plan - 709/721 Alexander Investigation	25-May-04	10-Jun-04	-
	Draft Work Plan - 709/721 Alexander Investigation (revised)	18-Jun-04	-	26-Jul-04
	<u>Focused Investigation of CDD/F and PCBs</u>			
	PCDD, PCDF, and PCB Congener Characterization Analytical Results	15-May-06	1-Sep-06	
	Draft SAP/QAPP for Focused Investigation of PCDD/F and PCBs	5-Oct-06	30-Oct-06	-
	Final SAP/QAPP for Focused Investigation of PCDD/F and PCBs	20-Nov-06	-	8-Jan-07

Table 1

Status of SOW Deliverables
Groundwater and Sediment Remediation
as of September 30, 2019

Task	Description	OCC Date Submitted (Projected)	Agency Date Comments Received by OCC	 Date Approval Received by OCC
A4/A5	**Subtidal/Hydraulic Investigation**			
	Scope of Work (by USEPA/Ecology)	-	21-Oct-04	
	Preliminary Scope of Subtidal/Upland Investigations	10-Nov-04	29-Dec-04	
	Draft SAP/QAPP for Subtidal/Hydraulic Investigation	11-Feb-05	13-Apr-05	
	Revised Draft SAP/QAPP for Subtidal/Hydraulic Investigation	6-May-05	-	20-May-05
	Final SAP/QAPP for Subtidal/Hydraulic Investigation	23-Jun-05	-	-
	Geophysical Investigation			
	Draft Scope of Work for Geophysical Investigation	5-Apr-06	5-Apr-06	
	Finalized Scope of Work for Geophysical Investigation	11-Apr-06	-	-
A6	**Prepare Characterization Report**			
	Letter - Interim GW Analytical Data Summary - 709/721 Alexander Investigation	18-Aug-04	25-Aug-04	
	Draft Geophysical Investigation Report	15-Jun-06	24-Jul-06	
	Final Geophysical Investigation Report	1-Dec-06	-	(a)
	Draft Seepage Meter Monitoring Report (CMA)	5-Dec-06	20-Apr-07	
	Preliminary PCDD/F and PCB Data Report	6-Jun-07	-	
	Preliminary PCDD/F and PCB Data Report (updated)	13-Aug-07	-	
	Hydrogeologic Characterization			
	Interim Deliverable 3.1 - Confirmation of Groundwater Recovery Following Shutdown of Extraction Wells			
	Initial Draft	6-Jul-06	13-Jul-06	
	Revision 1	19-Jul-06	21-Jul-07	
	Final Draft	30-Aug-07	-	(a)
	Interim Deliverable 4.1 - Procedure for Computing Average Pressure for 72-Hour Event			
	Initial Draft	6-Jul-06	13-Jul-06	
	Revision 1	19-Jul-06	21-Jul-07	
	Final Draft	30-Aug-07	-	(a)
	Interim Deliverable 4.2 - Methodology Presentation			
	Initial Draft	28-Jul-06	3-Aug-06	
	Revision 1	6-Sep-06	19-Sep-07	
	Final Draft	23-Oct-06	-	(a)
	Interim Deliverable 4.3 - Final Conductivity vs. Specific Gravity Relationship			
	Initial Draft	4-Oct-06	5-Oct-07	
	Revision 1	13-Oct-06	17-Oct-06	
	Final Draft	19-Oct-06	-	(a)
	Interim Deliverable 4.4 - Presentation of Adjusted Pressure Transducer Data			
	Initial Draft	8-Nov-06	15-Nov-06	
	Revision 1	30-Jan-07	28-Feb-07	
	Final Draft	15-Jun-07	-	(a)

Table 1

Status of SOW Deliverables
Groundwater and Sediment Remediation
as of September 30, 2019

Task	Description	OCC	Agency	
		Date Submitted (Projected)	Date Comments Received by OCC	Date Approval Received by OCC
	Interim Deliverable 4.5 - Density Distribution			
	Initial Draft	2-Nov-06	3-Nov-06	
	Revision 1	8-Nov-06	16-Nov-06	
	Final Draft	5-Dec-06	-	
	Final Draft - Revision 1	13-Mar-07	15-Mar-07	
	Final Draft - Final	19-Mar-07	-	(a)
	Interim Deliverable 4.6 - Presentation of Hydraulic Data from 709/721 Alexander Investigation			
	Initial Draft	22-Feb-07	22-Mar-07	
	Revision 1	29-Mar-07	10-Apr-07	
	Final Draft	11-Apr-07	-	(a)
	Interim Deliverable 6.1 - Calculation of FEH and ENV			
	Initial Draft	4-Aug-06	10-Aug-06	
	Revision 1	17-Aug-06	31-Aug-06	
	Revision 2	8-Sep-06	17-Oct-07	
	Final Draft	24-Oct-06	-	(a)
	Interim Deliverable 6.1a - Calculation of Gradients from FEHs and ENVs			
	Initial Draft	19-Oct-06	19-Oct-06	
	Revision 1	26-Oct-06	16-Nov-06	
	Final Draft	4-Jan-07	-	(a)
	Interim Deliverable 6.2 - Presentation of FEH and ENV (Events 1 & 2)			
	Initial Draft	11-Dec-06	13-Dec-06	
	Revision 1	30-Jan-07	23-Mar-07	
	Revision 2	10-May-07	14-Jun-07	
	Final Draft	15-Jun-07	-	(a)
	Interim Deliverable 6.2a - Re-Assessment of FEHs for Subtidal Transducers			
	Initial Draft	12-Jan-09	22-Jan-09	
	Final Draft	TBD		
	Interim Deliverable 6.3 - Transient Analysis of Groundwater Flow Vectors			
	Initial Draft	21-May-07	5-Jun-07	
	Final Draft	31-Oct-07		(a)
	Interim Deliverable 7.1 - Preliminary Characterization of Site Natural Attenuation			
	Initial Draft	25-Jan-07	31-Jan-07	
	Revision 1	13-Feb-07	28-Feb-07	
	Final Draft	22-Mar-07	-	(a)

Table 1

Status of SOW Deliverables
Groundwater and Sediment Remediation
as of September 30, 2019

Task	Description	OCC Date Submitted (Projected)	Agency Date Comments Received by OCC	Date Approval Received by OCC
	Interim Deliverable 8.2 - Presentation of Draft Conceptual Hydrogeologic Model			
	Initial Draft	25-Sep-07	4-Oct-07	
	Revision 1	23-Oct-07	1-Nov-07	
	Revision 2	20-Nov-07	27-Dec-07	
	Final Draft	18-Jan-08	-	(a)
	Assessment of Former Production Well			
	Memorandum - Former Production Well Investigation	3-Dec-09	28-Jan-10	
	Work Plan - Additional Production Well Investigation - Existing Well Geochemical Evaluation (Phase I)			
	Draft	17-Feb-10	5-Mar-10	
	Final	11-Mar-10	-	16-Mar-10
	Phase I Data Report	29-Apr-10	-	-
	Work Plan - Additional Production Well Investigation - Phase II			
	Draft	29-Mar-10	12-Apr-10	
	Revised Draft	30-Apr-10	12-May-10	
	Final	18-May-10	-	20-May-10
	Production Well Investigation Report			
	Draft Production Well Investigation Report	15-Oct-10	10-Jun-11	
	Revised Draft Production Well Investigation Report	5-Jul-11	11-Aug-11	
	Revised Draft Production Well Investigation Report	31-Aug-11	-	6-Jan-12
	Assessment of Stratigraphy			
	Stratigraphic Pick Table and Glacial Till Figures/Tables	7-Oct-09	-	
	Revised Site Stratigraphic Model	7-Dec-09	-	10-Dec-09
	Assessment of Geochemical Data			
	Geochemical Evaluation (Data Figures)	7-Apr-10	-	-
	Groundwater Density Distribution Report			
	Revised Groundwater Density Distribution Memorandum	17-Feb-10	24-Mar-10	
	Draft Final Groundwater Density Distribution Report	12-May-10	10-Jun-11	
	Revised Draft Final Groundwater Density Distribution Report	12-Jul-11	23-Sep-11	
	Revised Draft Final Groundwater Density Distribution Report	7-Nov-11	22-Dec-11	
	Interim Deliverable Groundwater Density Distribution (Draft)	12-Jan-12	30-Jan-12	
	Interim Deliverable Groundwater Density Distribution (Draft)	14-Feb-12		23-Apr-12

Table 1

Status of SOW Deliverables
Groundwater and Sediment Remediation
as of September 30, 2019

Task	Description	OCC Date Submitted (Projected)	Agency Date Comments Received by OCC	Agency Date Approval Received by OCC
	Assessment of Data Gaps			
	Examples of 3D EVS Visualizations and 2D Data Figures	29-Sep-10	17-Mar-11	
	Revised 3D Visualizations and 2D Data Figures			
	Groundwater 4DIMS - Group 1, 2 (part 1), 3	31-Mar-11	-	-
	Groundwater 4DIMS - Group 2 (part 2)	5-Apr-11	-	-
	Soil 4DIMS - Group 1, 2 (part 1)	8-Apr-11	-	-
	Soil 4DIMS - Group 2 (part 2), 3	12-Apr-11	-	-
	2D Data Figures (Google Earth) and Cross-Sections	29-Apr-11	-	-
	709/721 Data Summary Report	29-Oct-11	23-Dec-11	
	Evaluation of Potential DNAPL Source Areas	Nov/Dec-11	Nov/Dec-11	
	709/721 Data Summary Report	27-Jan-12	4-Apr-12	
	709/721 Data Summary Report	11-Apr-12	4-Sep-12	
	709/721 Data Summary Report	12-Sep-12		28-Sep-12
	Need for Step-Out Borings - DNAPL and LNAPL Source Areas	6-Dec-12	7-Feb-13; 22-Mar-13	
	Data Gap Evaluation Report			
	Draft Data Gap Evaluation for Site Characterization	11-Apr-11	1-Aug-11; 20, 22, 23-Sep-11; 28-Oct-11	
	Draft Data Gap Evaluation for Site Characterization	5-Dec-11	1-Feb-12; 17-Feb-12	
	Draft Data Gap Evaluation for Site Characterization	5-Mar-12	16-Mar-12	
	Draft Data Gap Evaluation for Site Characterization	27-Mar-12	4-Apr-12	
	Comprehensive Supplemental Investigation (CSI) Work Plan			
	Preliminary Draft Work Plan for Monitoring Event 3	28-Jul-11	23-Sep-11	
	Monitoring Event 3 - Work Plan for Additional Monitoring Well Installation and Data Collection	21-Oct-11	-	
	Draft CSI Work Plan	5-Dec-11	23-Dec-11	
	Draft CSI Work Plan - Advanced Well Installation	17-Jan-12	1-Feb-12; 17-Feb-12	
	Draft CSI Work Plan	5-Mar-12	16-Mar-12	
	Draft CSI Work Plan	27-Mar-12	4-Apr-12	
	CSI Work Plan	11-Apr-12	16-Apr-12	
	CSI Work Plan QAPP	14-May-12	29-Jun-12	
	CSI Work Plan QAPP	20-Jul-12	25-Jul-12	
	CSI Work Plan QAPP	26-Jul-12		26-Jul-12
	Updated Conceptual Site Model			
	Conceptual Site Model Report	14-Mar-13	13-May-13	
	Revised Conceptual Site Model Report	30-Sep-13	22-Nov-13; 6-Dec-13	
	Revised Conceptual Site Model Report	17-Jan-14	24-Feb-14	
	Revised Conceptual Site Model Report	24-Mar-14		10-Apr-14
	Final Conceptual Site Model Report	16-Apr-14		

Table 1

Status of SOW Deliverables
Groundwater and Sediment Remediation
as of September 30, 2019

		OCC	Agency	
Task	Description	Date Submitted (Projected)	Date Comments Received by OCC	Date Approval Received by OCC
	Sediment and Porewater Investigation			
	Sediment Conceptual Site Model Technical Memorandum	9-Mar-15		
	Sampling and Quality Assurance Project Plan	4-Sep-15	4-Feb-16	
	Revised Sampling and Quality Assurance Project Plan	17-Mar-16	23-May-16	
	Data Summary Report	1-Nov-16		
	Site Characterization Report			
	Preliminary Draft Site Characterization Report	31-Mar-08	13-Nov-08	
	Draft Site Characterization Report	7-Jul-08	-	
	Updated Draft Site Characterization Report	11-Apr-11	-	
	Draft Comprehensive Site Characterization Report	5-Aug-14		1-May-15; 24-Sept-15
	Revised Site Characterization Report	29-Aug-15		11-Oct-16
	Vapor Investigation			
	Draft Soil Vapor Evaluation Work Plan	26-Oct-11	29-Nov-11	
	Vapor Investigation Work Plan	14-Dec-12	24-Jan-13	
	Vapor Investigation Work Plan	14-Feb-13		22-Feb-13
	Vapor Investigation Work Plan - Addendum	14-Mar-13		
	Vapor Investigation Report	4-Jun-13	19-Jul-13	
	Vapor Investigation Report	30-Aug-13	22-Nov-13	
	Revised Vapor Investigation Report and Work Plan Addendum	17-Dec-13	23-Jan-14; 3-Mar-14	
	Revised Vapor Investigation Work Plan Addendum	5-Mar-14		6-Mar-14
	Final Vapor Investigation Work Plan Addendum	12-Mar-14; 8-Apr-15		
	Vapor Investigation Report	22-May-14		
	Revised Vapor Investigation Report	17-Mar-16	TBD	
Task B - pH Source Control				
B1	**Finalize Rapid pH Assessment Report**			
	Draft Rapid pH Assessment Report	12-May-04	11-Jun-04	
	Draft Rapid pH Assessment Report (revised)	2-Jul-04	-	22-Sep-05
	Final Rapid pH Assessment Report	-	-	
B2	**Treatability Study**			
	Treatability Study Report	7-Jun-04	26-Jul-04	
	Final Treatability Study Report	9-Aug-04	-	18-Oct-04
B3	**Prepare Work Plan for pH Pilot Study**			
	Draft Work Plan for pH Pilot Study	8-Feb-05	14-Mar-05	
	Revised Draft Work Plan for pH Pilot Study	18-Apr-05	-	20-Jun-05
	OCC Requests Clarification of One (1) Condition for Approval	28-Jun-05	29-Aug-05	
	Final Work Plan for pH Pilot Study	-	-	-
B4	**Implement pH Pilot Study**			
	Phase II			
	Draft Work Plan for Phase II	11-Sep-08	25-Sep-08	
	Revised Draft Work Plan for Phase II	2-Oct-08	-	14-Nov-08
	Final Work Plan for Phase II	Dec-09	-	
	Preliminary Data Report for Phase II	17-Mar-09	7-Apr-09	

Table 1

Status of SOW Deliverables
Groundwater and Sediment Remediation
as of September 30, 2019

		OCC	Agency	
Task	**Description**	**Date Submitted (Projected)**	**Date Comments Received by OCC**	**Date Approval Received by OCC**
	Phase III			
	Draft Work Plan for Phase III	20-Nov-08	3-Dec-08	
	Draft Work Plan for Phase III (redline)	11-Dec-08	-	18-Dec-08
	Final Work Plan for Phase III	20-Jan-09	-	
	Preliminary Data Report for Phase III	17-Feb-10	-	-
	pH Pilot Study Report			
	Draft pH Pilot Study Report	10-Jun-08	7-Jul-08	
	Revised Draft pH Pilot Study Report	13-Jan-11	6-Nov-13	
Task C/D - Groundwater/Sediment Remediation				
C1	**Evaluate Existing Containment/Treatment System**			
	Work Plan for Evaluation of Existing Containment and Treatment System			
	Draft Work Plan for Evaluation of Existing Containment and Treatment	9-Dec-11	4-May-12	
	Engineering Evaluation			
	Draft Engineering Evaluation Work Plan for Existing Groundwater Containment and Treatment Systems	24-May-12	30-Jul-12	
	Draft Engineering Evaluation Work Plan for Existing Groundwater Containment and Treatment Systems	21-Aug-12	28-Sep-12	
	Draft Engineering Evaluation Work Plan for Existing Groundwater Containment and Treatment Systems	19-Oct-12	8-Nov-12	
	Draft Engineering Evaluation Work Plan for Existing Groundwater Containment and Treatment Systems	14-Nov-12		16-Nov-12
	Final Engineering Evaluation Work Plan for Existing Groundwater Containment and Treatment Systems	30-Nov-12	-	
	Engineering Evaluation Report	5-Feb-13		25-Mar-13
	Capture Zone Analysis			
	Draft Capture Zone Analysis Conceptual Approach	20-Jun-12	30-Aug-12	
	Draft Capture Zone Analysis Conceptual Approach	24-Sep-12	15-Nov-12	
	Revised Capture Zone Analysis Conceptual Approach	28-Nov-12		8-Feb-13
C2/D2	**Evaluate Groundwater/Sediment Remedial Alternatives**			
	Preliminary Evaluation of Potential Remedial Technologies			
	Memorandum - Preliminary Evaluation of Potential Remedial Technologies (GW & Sediment)	29-Mar-10	20-Mar-13	
	Memorandum - Preliminary Evaluation of Potential Remedial Technologies (Step 1 Evaluation)	3-May-13	3-Jun-13	-
	Potential Remedial Technologies Table	2-Aug-13	19-Sep-13	
	Evaluation of Remedial Technologies Report			
	Draft Evaluation of Remedial Technologies Report	18-Oct-13	13-Mar-14	
	Draft Evaluation of Remedial Technologies Report	27-Jun-14	4-Sep-14	
	UW K_d and pH/Si Precipitation Testing Work Plan			
	UW K_d and pH/Si Precipitation Testing Work Plan	30-Apr-14		
	UW K_d and pH/Si Precipitation Testing Work Plan	27-Oct-14		

Table 1

Status of SOW Deliverables
Groundwater and Sediment Remediation
as of September 30, 2019

		OCC	Agency	
Task	Description	Date Submitted (Projected)	Date Comments Received by OCC	Date Approval Received by OCC
	Memorandum - Recommended Remedial Alternatives			
	Draft Memorandum - Recommended Remedial Alternatives			
	Final Memorandum - Recommended Remedial Alternatives			
	Evaluation Report for Remedial Alternatives			
	Draft Evaluation Report for Remedial Alternatives			
	Revised Evaluation Report for Remedial Alternatives			
	Memorandum - Soil Flushing Treatability Study			
	Soil Flushing Treatability Study Memorandum	13-Jun-13	TBD	
	UW Draft Final Effects of pH/Redox Potentials Report			
	Effects on the Partition Coefficients Characterizing Heavy Metal Release from Site Soils Report	4-May-15		
	Feasibility Study Report			
	Draft Feasibility Study Report	4-May-15	5-Jan-16	
	Draft Feasibility Study Report	13-Jun-16		
	Revised Feasibility Study Report	9-Dec-16	15-Dec-16, 18-Jan-17	
	Revised Feasibility Study Report	25-Jan-17	TBD	
D1	**Drain Tile/Embankment Cap Modeling**			
	Memo - Summary of Modeling Methodology Discussions	30-Dec-03	21-Jan-04	
	Memo - Qualitative Analysis of Density Effects	21-Jan-04	-	4-Feb-04
	Draft Modeling Plan	26-Feb-04	22-Mar-04	
	Draft Modeling Plan (revised)	15-Apr-04	-	4-May-04
	Final Modeling Plan	12-May-04		
	Memo - Existing Conditions Model	6-Jul-04	20-Jul-04	
	Memo - Existing Conditions Model Final	9-Aug-04	25-Aug-04	
	Draft Modeling Report	2-Nov-04	15-Mar-05	
	Final Modeling Report	-	-	
Task E - 3D Groundwater Flow Modeling				
E1	**Develop Modeling Plan**			
	Preliminary Modeling Plan	5-Nov-04	-	29-Nov-04
	Draft Modeling Plan	16-Dec-04	-	17-Jan-05
	Final Modeling Plan	-	-	
E2	**3D Model Construction and Calibration**			
	Technical Memorandum - Density Effects Evaluation and Simulation Program Selection	10-Feb-05	-	12-Apr-05
	Interim Deliverable 10.1 - Model Construction			
	Initial Draft	23-Jan-08	verbal	
	Revision 1	13-Feb-08	verbal	26-Feb-08
	Final Draft	26-Feb-08	-	
	Interim Deliverable 11.1 - Calibration Progress Memo/Meeting			
	Initial Draft for Presentation	8-Apr-08	-	-

Table 1

Status of SOW Deliverables
Groundwater and Sediment Remediation
as of September 30, 2019

		OCC	Agency	
Task	Description	Date Submitted (Projected)	Date Comments Received by OCC	Date Approval Received by OCC
	Interim Deliverable 14.1 - Density Equation of State			
	Initial Draft	2-Feb-07	28-Feb-07	
	Revision 1	9-Apr-07	19-Apr-07	
	Final Draft	24-Apr-07	-	(a)
	Model Peer Review Memos	10-Aug-10	15-Nov-10	-
	Peer Reviewer Responses to Agency Questions	4-Jan-11	-	-
	Model Calibration Report			
	Preliminary Draft Model Calibration Report	6-Jul-09	27-Aug-09	
	Draft Model Calibration Report	19-Jul-10	3-Aug-11	
	Revised Draft Model Calibration Report	31-Oct-11	14-Aug-12	
	Revised Draft Model Calibration Report	1-May-13	-	
	Draft Model Calibration Report	29-Aug-14		TBD
	Work Plan for Contaminant Transport Model (CTM)			
	Memorandum - CTM Conceptual Approach	11-Jul-11	22-Sep-11	
	CTM Pre-Work Plan	5-Dec-11	-	
	CTM Pre-Work Plan	20-Jan-12	22-Feb-12	
	Draft CTM Work Plan	15-May-12	9-Apr-13; 25-Nov-13	
E3	**Modeling of Remedial Alternatives**			
	Model Application Report			
	Draft Model Application Report			
	Final Model Application Report			
Interim Measures				
	Vapor Intrusion Pathway Mitigation			
	Draft Vapor Intrusion Pathway Mitigation Work Plan	25-May-12	20-Jul-12	
	Draft Vapor Intrusion Pathway Mitigation Work Plan	4-Sep-12	5-Nov-12	
	Cancelled November 13, 2012			
	Vapor Mitigation Work Plan	24-Dec-13		
	Vapor Mitigation Design Plan	4-Mar-14	4-Apr-14	
	Revised Draft Vapor Mitigation Design Plan	25-Apr-14		14-Jun-14
	Vapor Mitigation Design Plan	8-Jul-14		
	Groundwater Treatment Plant Replacement			
	Groundwater Treatment Plant - Replacement Design Approach	24-Jan-13	7-Feb-13	
	Draft Extraction Well Pilot Test Installation Work Plan	15-Feb-13	20-Mar-13	
	Interim Action Work Plan for Groundwater Treatment Plant Replacement and Extraction System Enhancement	6-Mar-13	3-Jun-13	
	Draft Extraction Well Pilot Test Installation Work Plan	9-Apr-13	30-Apr-13	
	Revised Draft Extraction Well Pilot Test Installation Work Plan	23-May-13	6-Jun-13; 14-Jun-13	
	Revised Draft Extraction Well Pilot Test Installation Work Plan	13-Jun-13; 17-Jun-13		18-Jun-13

Notes:

(a) Agency comments or approval have not been received

☐ Deliverable in Progress - Anticipated Submittal Date or Deliverable Due Date

TBD Date To Be Determined

EXHIBIT D

Schedule of Work to Be Performed

1. **Seasonal Water Level Monitoring.** Monitoring shall begin within thirty (30) calendar days of the effective date of Agreed Order DE 16943.

2. **Monitoring Plan.** A single groundwater quality and soil vapor monitoring event will be performed prior to implementation of the remedy. Within one-hundred-twenty (120) days of the effective date of Agreed Order DE 16943, the Ecology-approved Monitoring Plan (Exhibit F) will be implemented.

3. **Groundwater Extraction Demonstration.** The demonstration will be performed in accordance with the Ecology-approved Inactive Extraction Well EXT-9 Longer-Term Pumping Test Work Plan (Exhibit G). Implementation of the demonstration will begin as soon as possible after the groundwater treatment plant improvements are completed and the plant is fully operational. Once the groundwater treatment plant is fully operational the PLPs will notify Ecology in writing within seven (7) days that the plant is ready to resume operations. The demonstration will begin within thirty (30) days of the date of the written notice.

4. **Progress Reports**. Submit written progress reports semi-annually on the 15th of January and July, beginning January 15, 2020, until the termination of Agreed Order DE 16943.

5. **Draft Cleanup Action Plan.** If Ecology directs, the PLPs will assist Ecology with drafting of the cleanup action plan in whole or in part, which shall be submitted within ninety (90) days of Ecology's written request. Ecology will review and comment on the PLPs' submittal. The PLPs shall submit the revised draft, and any subsequent drafts, to Ecology within thirty (30) calendar days of receipt of Ecology's written comments.

6. **Requests for Extension.** The PLPs may submit a written request for extension for any of the required activities and deliverables in this schedule. The PLPs shall submit the request to Ecology in writing a minimum of ten (10) calendar days prior to the deadline.

Seasonal Water Level Monitoring Plan

Occidental Chemical Corporation
605 Alexander Avenue
Tacoma, Washington

Objective and Background

The objective for the water level monitoring activities described in this work plan is to collect data that describe seasonal changes in water levels at selected existing monitoring wells on the Occidental site (Site). These data will be used to describe water levels and water level fluctuations prior to remedy design and implementation.

The continuous water level data that have been collected at the Site to date have focused on several intensive, short-term events aimed at assessing the hydraulic effectiveness of the existing extraction system. Events 1 and 2 were used to collect data from May to June in 2006 and Event 3 was used to collect data from August to December of 2012. None of these events describe the seasonal fluctuation in water levels over an annual cycle.

Continuous water level data have been collected for an annual cycle at shallow monitoring wells located at the southern end of the 605 Alexander Avenue property and on the 709 Alexander Avenue property. These data were conducted from December 2011 to December 2012 at five 15-ft zone monitoring wells (49-15, 50-15, 52-15, 709-MW5-15, and 709-MW6-15) and three 25-ft zone monitoring wells (9-25, 18-25, and 709-MW20-25). Representative results are shown on Figure 1.

The minimum pressure in the two wells shown on Figure 1 occurs in mid-October 2012 following the dry period extending from June to mid-October 2012. The maximum pressure in the shallow well (52-15) occurs in early April 2012 after heavy rainfall events in mid- and late March 2012. The maximum pressure in the deeper well (18-25) occurs in December 2012 after the significant rainfall events that took place in November and early December 2012. The difference between maximum and minimum water levels during the one-year monitoring period was 3.0 feet of water (1.3 pounds per square inch (psi)) in well 52-15 and 2.1 feet of water (0.92 psi) in well 18-25.

The water level fluctuations shown in Figure 1 have potentially important implications in terms of assessing the performance of a hydraulic containment system. For example, seasonal increases in water level during late fall may mask drawdowns that result from the containment system. Or drawdowns measured in late March may be different from drawdowns measured in June or July.

Data describing seasonal water level fluctuations in shallow wells have not been collected near the vicinity of the hydraulic control boundaries.[1] Data describing seasonal water level

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[1] The hydraulic control boundaries were provided by the Agencies for the 25 foot (ft), 50 ft, 75 ft, 100 ft, 130 ft, and 160 ft zones or zone-grouping planes on Figures 1 to 6, respectively, of the Agencies' email correspondence to

fluctuations below the 25-foot zone have not been collected anywhere on the site. It is not known at this point if there are significant seasonal effects below the 25-foot zone.

Data describing the seasonal fluctuation at selected locations and depths will be used to help identify critical conditions and to inform the design of a containment system that is robust and reliable across the range of anticipated water levels. The seasonal data that will be collected as part of this plan will reduce the need to perform multiple hydraulic effectiveness events during different seasons. These hydraulic effectiveness events are much more resource- and labor-intensive than the seasonal monitoring activities that will be conducted as part of the water level monitoring plan.

The water level data collected as part of this monitoring plan will also support the data collection and modeling efforts that will eventually be needed to evaluate the hydraulic containment system. It is anticipated that the monitoring locations for this seasonal program will be a subset of the performance monitoring program that will be implemented after the containment system is constructed.

Monitoring Activities

Water level monitoring activities will include collecting water level data continuously using dedicated and calibrated pressure transducers. The proposed locations for monitoring seasonal water levels are included in Table 1. Where possible, the monitoring locations are located in clusters selected to obtain data from various zone-grouping planes (ZGPs).

The pressure transducer calibration approach is described in the Field Sampling Plan (FSP).[2] The groundwater level monitoring locations in each ZGP are depicted on Figures 2.1 to 2.6 of the Draft Monitoring Plan, which also show the hydraulic control boundaries provided by the Agencies.

The groundwater level monitoring network consists of 20 existing standard wells, all to be equipped with calibrated pressure transducers and data loggers. In addition, a pressure transducer will be installed in the Hylebos (continually submersed in surface water within a screened casing strapped to Dock 1 adjacent to the 605 Alexander Avenue property as shown on Figure 2.1 of the Draft Monitoring Plan) to measure surface water levels coincident with the groundwater level measurements.

The pressure transducer data will be downloaded on a quarterly basis and checked for accuracy. Following completion of the 1-year monitoring period, groundwater level hydrographs for each monitoring well will be prepared. Hylebos surface water levels also will be presented on the hydrographs since groundwater level fluctuations at the Site have been observed to closely correlate to surface water level fluctuations in the Hylebos, Blair Waterway, and Commencement

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[2] Appendix A of Draft Monitoring Plan, Glenn Springs Holdings, Inc.

Bay that surround the Site peninsula. In addition, precipitation data from the National Oceanic and Atmospheric Administration (NOAA) will be presented on the hydrographs.[3]

Table 1. Proposed locations for monitoring seasonal water levels

		Screen Interval	
Location	**Grouping**	**Bottom (ft BGS)**	**Top (ft BGS)**
35-25	25 ft	25	20
55-25	25 ft	23.5	18.6
61-25	25 ft	23.5	18.5
14-25R	25	24.5	19.5
5-50	50 ft	50	45
14-50R	50 ft	51.53	46.53
35-50	50 ft	44.74	39.74
61-50	50 ft	48	43
5-75	75 ft	74.2	69.2
34-75 (34-75R)	75 ft	74.3	69.3
PZ-SHI-002-075	75 ft	59.5	54.5
5-100	100 ft	100	95
77-100	100 ft	100	95
34-100	100 ft	100	95
41-100	100 ft	99.3	94.3
77-140	130 ft	140	135
41-138	130 ft	127	122
12-160	160 ft	160	150
MW-F-DEEP	160 ft	176	171
MW-G-INT	160 ft	171	166

Notes:
ft NGVD - feet National Geodetic Vertical Datum
ft BGS - feet below ground surface

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[3] https://www.ncdc.noaa.gov/cdo-web/datasets/GHCND/stations/GHCND:USC00458278/detail, Network ID GHCND:USC00458278

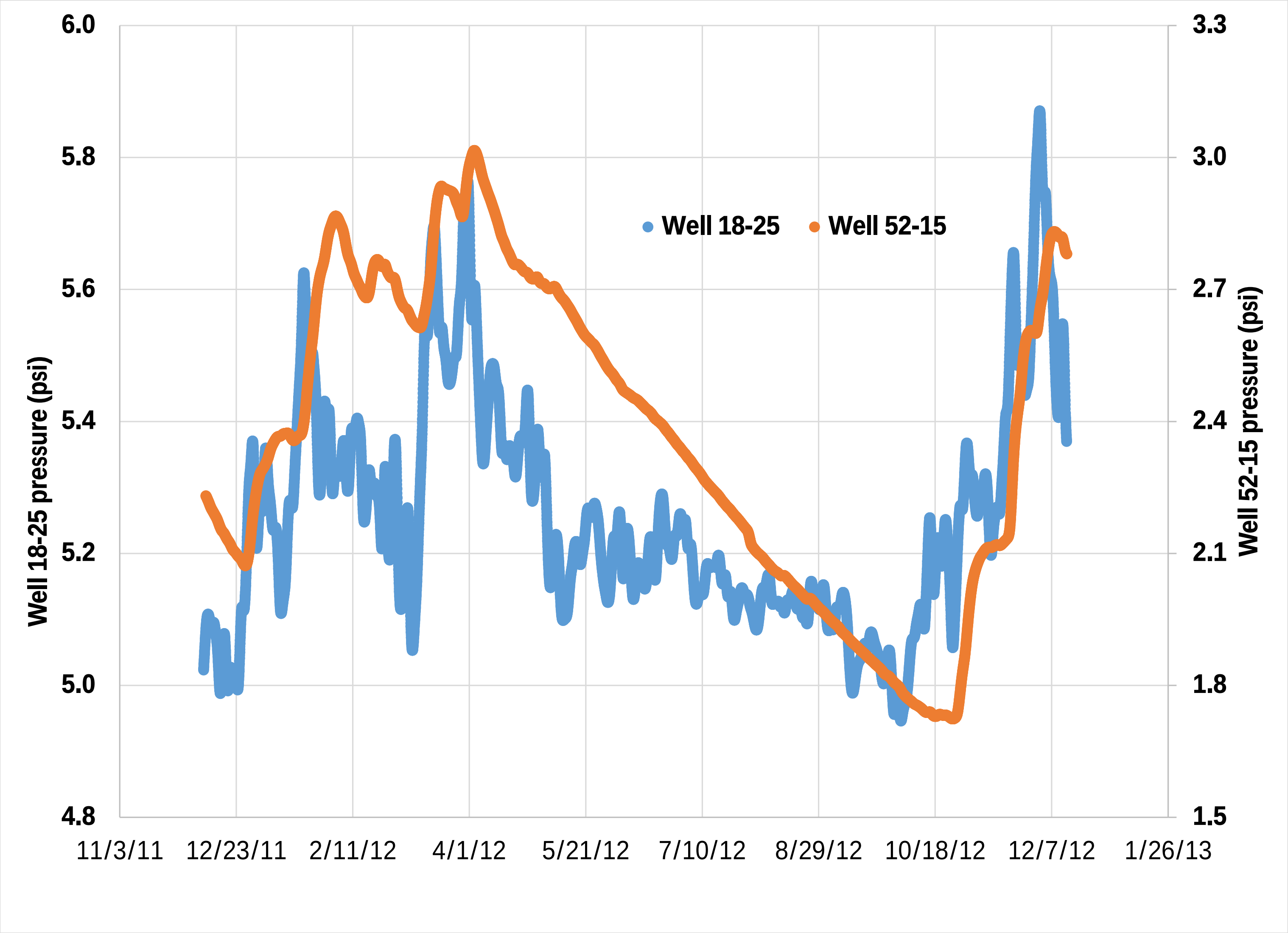

Figure 1. Representative results from continuous monitoring in shallow wells.

May 29, 2019

Monitoring Plan

Occidental Chemical Corporation
605 Alexander Avenue
Tacoma, Washington

Glenn Springs Holdings, Inc.

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Appendix Index

List of Acronyms

AOC Amendment	2005 Amendment to the Administrative Order on Consent
bgs	below ground surface
CB/NT site	Commencement Bay Nearshore/Tideflats Superfund site
cis-1,2-DCE	cis-1,2-dichloroethene
CRA	Conestoga-Rovers & Associates (now GHD)
Ecology	Washington State Department of Ecology
FS	approved as revised by Ecology Feasibility Study
FSP	Field Sampling Plan
ft	feet
HASP	Health and Safety Plan
Hylebos or Waterway	Hylebos Waterway
MP	Monitoring Plan
MTCA	Model Toxics Control Act
MVS/EVS	Mining Visualization System/Environmental Visualization System software package
OCC	Occidental Chemical Corporation
OSWER	USEPA Office of Solid Waste and Emergency Response
PCE	tetrachloroethene or perchloroethylene
POT	Port of Tacoma
QAPP	Quality Assurance Project Plan
ROD	Record of Decision
SCR	Site Characterization Report
SOW	Statement of Work for the Administrative Order on Consent
TCE	trichloroethene or trichloroethylene
TCVOC	total chlorinated volatile organic compound or total chlorinated volatile organic compounds
US Navy	United States Navy
USEPA	United States Environmental Protection Agency
VC	vinyl chloride
VI	vapor intrusion
WAC	Washington Administrative Code
ZGP	zone-grouping plane

1. Introduction

Occidental Chemical Corporation (OCC) has been working with the Washington State Department of Ecology (Ecology) and the United States Environmental Protection Agency (USEPA) (together referred to as the 'Agencies') to address remaining environmental issues at the 'Occidental' Site associated in part with the former OCC facility located in Tacoma, Washington (Site) under an Amendment to the Administrative Order on Consent (AOC Amendment or AOC) (USEPA, 2005). The work activities required under the AOC are outlined in the "Statement of Work for the Administrative Order on Consent" (SOW) (Conestoga-Rovers & Associates [CRA], 2005). Additional work not anticipated in the SOW has been conducted and scheduled consistent with the AOC.

The Site is located on the eastern-most peninsula of the area of ownership and operations of the Port of Tacoma (POT) that extends into Commencement Bay at the mouth of the Puyallup River Valley and is defined in the AOC. A general location map showing the Site, including the formerly OCC-owned properties and that portion of Segment 5 of the Hylebos Waterway (Waterway or Hylebos) contained within the Site, is presented on Figure 1.1.

A plan showing local property ownership is presented on Figure 1.2. The properties formerly owned and/or operated by OCC or its predecessors include:

- 605 Alexander Avenue (former OCC Facility currently owned by Mariana Properties, Inc.)
- 709 Alexander Avenue (currently owned by Mariana Properties, Inc.)

The properties are referred to as the '605 Alexander Ave.' and '709 Alexander Ave.' properties on Figure 1.2. The properties are bounded on the west, north, and south by former Todd Shipyards and/or United States Navy (US Navy) properties (now owned by the POT), and on the east by the Waterway.

The approximate extent of groundwater impacts (all depths) at the Site is shown on Figure 1.1. The Site is within the roughly 12-square-mile area Commencement Bay Nearshore/Tideflats Superfund site (CB/NT site) which includes several waterway problem areas and adjoining uplands as described by the CB/NT site Record of Decision (ROD) (USEPA, 1989).

The objective of this Monitoring Plan (MP) is to monitor groundwater quality and soil vapor at the Site to describe baseline conditions prior to future remedial measures at the Site and to provide information for remedy design.

This MP is organized as follows:

Section 2	Groundwater Quality
Section 3	Soil Vapor and Indoor Air
Section 4	Quality Assurance/Quality Control
Section 5	Reporting
Section 6	Schedule
Section 7	References

Per Washington Administrative Code (WAC) 173-340-350(7)(c)(iv) (Ecology, 2013), activities will be performed in accordance with the Field Sampling Plan (FSP) in Appendix A, the Quality Assurance Project Plan (QAPP) in Appendix B, and the Site-specific Health and Safety Plan (HASP).

2. Groundwater Quality

A single groundwater quality monitoring event will be performed during 2019 prior to implementation of the remedy. The objective of this event is to describe baseline conditions prior to proposed future remedial measures at the Site and to provide information for remedy design. The monitoring network will allow changes in overall groundwater quality trends and plume stability to be evaluated and assessed using data collected in future monitoring events.

The scope of groundwater quality monitoring was developed in consideration of the future total chlorinated volatile organic compound (TCVOC) mass removal and containment system and the TCVOC presence beneath the Hylebos and near Commencement Bay. It includes monitoring well locations proposed for water level monitoring at the limits of the hydraulic control boundaries, existing monitoring wells within the interior of the TCVOC plume that include wells recommended by the Agency team (or nearby well if the recommended well is no longer useable), and two proposed new standard monitoring well nest locations (one in Commencement Bay beyond the northern limit of the TCVOC plume and one on the east side of the Hylebos Waterway near the eastern limit of the TCVOC plume). These two new nest locations will consist of three proposed new standard monitoring wells per nest. Table 2.1 identifies the groundwater quality monitoring locations and rationale. The groundwater quality monitoring locations in each zone-grouping plane (ZGP) are depicted on Figures 2.1 to 2.6 showing the approximate extent of TCVOC groundwater plume at the Site within the ZGPs and summarized below in Table 2.2.

Table 2.2 Summary of Groundwater Quality Monitoring Locations

ZGP	Figure	# of Locations			
		Water Quality			
		Existing	Replacement	New	Total
25-ft	2.1	9	1	--	10
50-ft	2.2	13	1	1	15
75-ft	2.3	9	1	1	11
100-ft	2.4	14	1	2	17
130-ft	2.5	6	3	1	10
160-ft	2.6	9	--	1	10

The groundwater quality monitoring network consists of 73 wells, including 60 existing wells, 7 replacement standard wells, and 6 proposed new standard wells.

The 7 replacement (59-25, 20-50, 77C-75, 33-100, 21C-130, 74-130, 91C-130) and 6 proposed new (3 wells at Tribe finger pier and 3 wells at Army pier) standard monitoring wells will be installed as described in the FSP. Groundwater sampling will be conducted in accordance with the FSP.

Groundwater sample analyses will be conducted in accordance with the QAPP and will include field parameters (temperature, pH, conductivity, turbidity, oxidation-reduction potential, dissolved oxygen, and salinity) and laboratory parameters identified in Table 2.3. The collected analytical data will be tabulated. In addition, three-dimensional plumes will be developed for the following parameters: TCVOC, tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), vinyl chloride (VC), pH, and density using the three-dimensional kriging approach implemented in Environmental Visualization System (EVS) computer program (C Tech, 2007). These plumes will be compared to the three-dimensional plumes presented in the Site Characterization Report (SCR or RI Report) (CRA, 2014), which were used in the selection of the preferred remedy in the approved Feasibility Study (FS) Report (GHD, 2017). The representativeness the plumes derived from the monitoring network will be assessed through this comparison.

These baseline data that will be collected during the 2019 groundwater quality monitoring event will be used in conjunction with data from future monitoring events to track changes in groundwater quality over time after remedy implementation. The data will also be used in future plume stability analyses. If some of the new and replacement wells cannot be installed prior to the 2019 event because of scheduling limitations, the monitoring event will not be delayed and will include all available wells identified in Table 2.1.

3. Soil Vapor and Indoor Air

Ecology reviewed the soil vapor data and produced a memorandum (Ecology, 2017) that generally concurred with the findings of the approved vapor intrusion (VI) study report (GHD, 2016); however, Ecology identified a potential vapor footprint based on existing historical soil and groundwater data that may pose a future VI risk and therefore requires soil vapor to be monitored. Ecology recommended five monitoring locations to evaluate the inferred vapor footprint. In a subsequent memorandum titled "Response to Occidental Chemical (OCC) Source Removal Proposal" and dated February 19, 2019 (Ecology, 2019), Ecology added an additional 2 monitoring locations for a total of 7 monitoring locations. One of the locations has been adjusted to provide better spatial coverage over the inferred vapor footprint. An additional 3 locations associated with the shallow TCVOC Target Areas were added. The 10 monitoring locations are presented on Figure 3.1.

The scope of soil vapor monitoring considers the VI study (GHD, 2016), Ecology's recommendations, Ecology's Draft *Guidance for Evaluating Soil Vapor Intrusion in Washington State: Investigation and Remedial Action* (Draft VI Guidance) (Ecology, 2009) and final USEPA Office of Solid Waste and Emergency Response (OSWER) *Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air* (OSWER VI Guide) (USEPA, 2015). It includes 7 monitoring locations that are in close proximity to the buildings within and adjacent to the Ecology identified potential vapor footprint and provides spatial representation over the footprint. The buildings that are adjacent to the proposed monitoring locations include:

- OCC Office Building
- POT Building 326

- POT Building 532
- POT Building 595
- POT Building 596

Having the monitoring locations close to buildings is consistent with Ecology and USEPA guidance and eliminates potential ambiguity of what data are representative of the conditions near each building (i.e., a probe between buildings could misrepresent vapor concentrations near and beneath a building).

Soil vapor monitoring will be performed at the proposed locations shown on Figure 3.1. At each location, a proposed new vapor monitoring probe will be installed between 5 and 6 ft bgs and above the water table (approximately 10 ft bgs with fluctuation) consistent with the regulatory guidance from Ecology and USEPA. This will ensure that the possibility of diluting the collected soil vapor with atmospheric air is minimized and the samples are representative of shallow soil vapor concentrations that may migrate to indoor air.

Proposed new probes will be installed and sampled as described in the FSP. Soil vapor sample analyses will be conducted in accordance with the QAPP and will report Method TO-15 analytes including the main constituents of concern, PCE, TCE, and VC based on the findings of the previous VI study (GHD, 2016) and Ecology's recommendations (February, 2019).

In addition, as recommended in the approved VI study report (GHD, 2016), indoor air in POT Building 595 will also be monitored for PCE, TCE, and VC concentrations. The monitoring will include 3 indoor air locations previously sampled (IA-5, IA-26, and IA-36) as shown on Figure 3.1 and one outdoor air sample, upwind of the building at the time of sampling, to measure background concentrations. The sampling and analyses will be conducted in accordance with the FSP and QAPP, respectively, consistent with the methodologies used during the VI study.

These baseline data that will be collected during the 2019 soil vapor and indoor air monitoring event will be used in conjunction with data from future monitoring events to track changes over time after remedy implementation.

4. Quality Assurance/Quality Control

Per WAC 173-340-350(7)(c)(iv), activities will be performed in accordance with the FSP in Appendix A, the QAPP in Appendix B, and Site-specific HASP.

5. Reporting

In order to report the data as they become available and given that elements of the monitoring plan will be completed at different times, it is envisioned that reporting for the groundwater quality monitoring, soil vapor monitoring, and indoor air monitoring, will consist of separate reports, which will be developed and submitted following conclusion of each monitoring event. Each report will be submitted within 90 days following completion of all field activities and receipt of final laboratory data.

6. Schedule

The schedules for groundwater quality monitoring, soil vapor monitoring, and indoor air monitoring will depend on execution of the draft Agreed Order, approval of this Work Plan, and access agreements for new well clusters.

The single groundwater quality monitoring event will be performed during 2019 prior to implementation of the remedy. No other groundwater quality monitoring will be conducted prior to startup of the containment system.

The soil vapor monitoring event and the indoor air sampling event will be performed during 2019 following installation of the 7 new vapor monitoring probes. No other soil vapor or indoor air monitoring events will be conducted prior to startup of the targeted shallow source removal system.

7. References

CRA, 2014. Site Characterization Report, Groundwater and Sediment Remediation, Occidental Chemical Corporation, Tacoma, Washington, August. (Also known as the Remedial Investigation Report [RI Report]).

C Tech, 2007. Mining Visualization System/Environmental Visualization System (MVS/EVS) software package, developed by C Tech Development Corporation.

Ecology, 2019. Response to Occidental Chemical (OCC) Source Removal Proposal, February 19, 2019.

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Ecology, 2009. Guidance for Evaluating Soil Vapor Intrusion in Washington State: Investigation and Remedial Action, Toxics Cleanup Program, Publication No. 09 09 047, Review Draft, October.

GHD, 2017. Feasibility Study Report, Occidental Chemical Corporation, Tacoma, Washington, January.

GHD, 2016. Draft Vapor Intrusion Investigation Report, Occidental Chemical Corporation, Tacoma, Washington, March.

USEPA, 2015. Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air, Final, June 2015.

USEPA, 2005. Amendment, Administrative Order on Consent for Removal Activities Embankment and Area 5106, USEPA Docket No. 10 97 0011 CERCLA, as Amended February 1, 2005.

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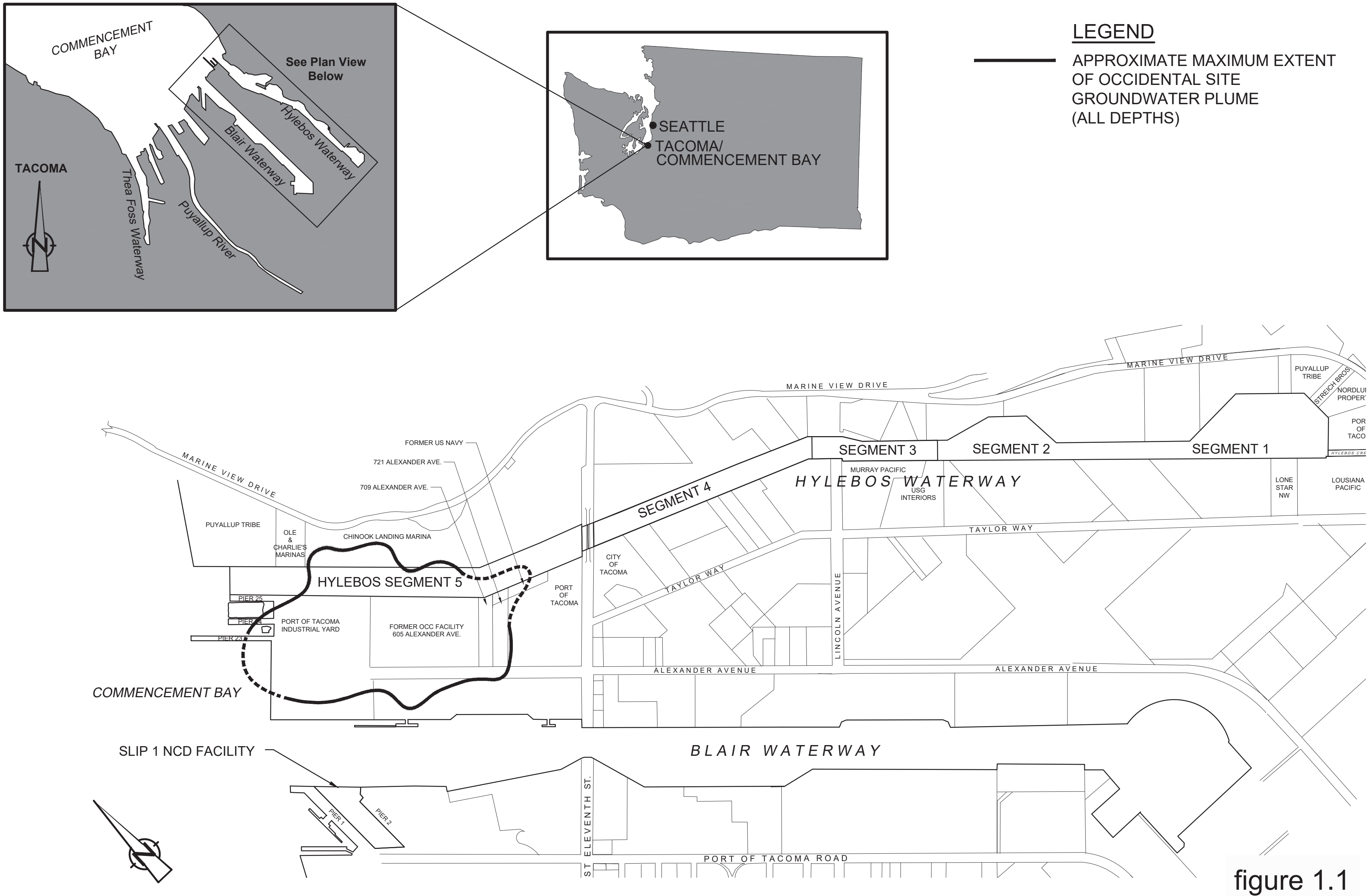

figure 1.1

VICINITY MAP

Occidental Chemical Corporation, Tacoma, Washington

SOURCE: ELECTRONIC FILE PROVIDED BY ANCHOR ENVIRONMENTAL LLC, JUNE 01, 2004.

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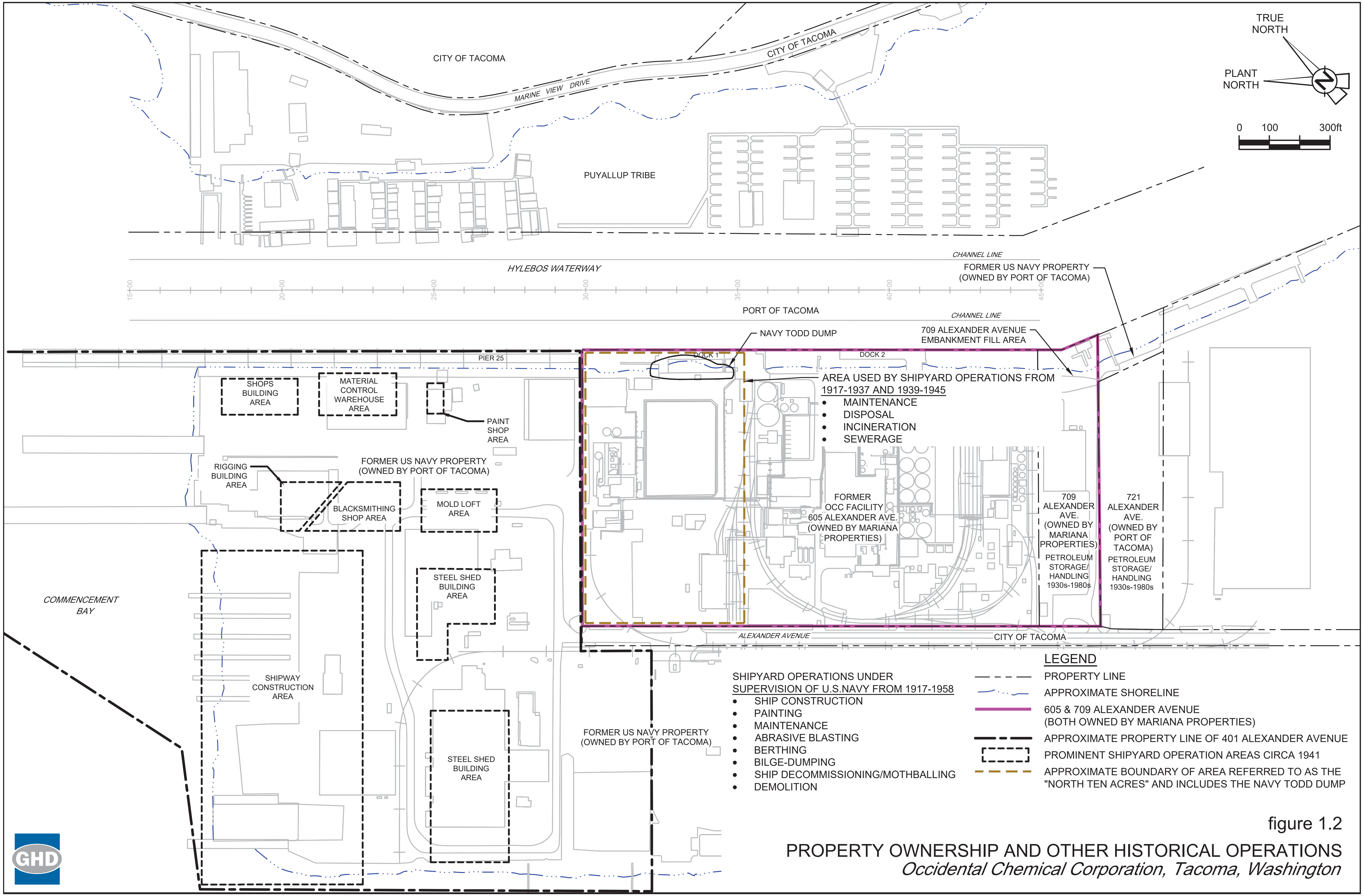

AREA USED BY SHIPYARD OPERATIONS FROM 1917-1937 AND 1939-1945
- MAINTENANCE
- DISPOSAL
- INCINERATION
- SEWERAGE

SHIPYARD OPERATIONS UNDER SUPERVISION OF U.S.NAVY FROM 1917-1958
- SHIP CONSTRUCTION
- PAINTING
- MAINTENANCE
- ABRASIVE BLASTING
- BERTHING
- BILGE-DUMPING
- SHIP DECOMMISSIONING/MOTHBALLING
- DEMOLITION

LEGEND

— — —	PROPERTY LINE
—·—·—	APPROXIMATE SHORELINE
▬	605 & 709 ALEXANDER AVENUE (BOTH OWNED BY MARIANA PROPERTIES)
▬ ·▬	APPROXIMATE PROPERTY LINE OF 401 ALEXANDER AVENUE
☐	PROMINENT SHIPYARD OPERATION AREAS CIRCA 1941
— — —	APPROXIMATE BOUNDARY OF AREA REFERRED TO AS THE "NORTH TEN ACRES" AND INCLUDES THE NAVY TODD DUMP

figure 1.2

PROPERTY OWNERSHIP AND OTHER HISTORICAL OPERATIONS

Occidental Chemical Corporation, Tacoma, Washington

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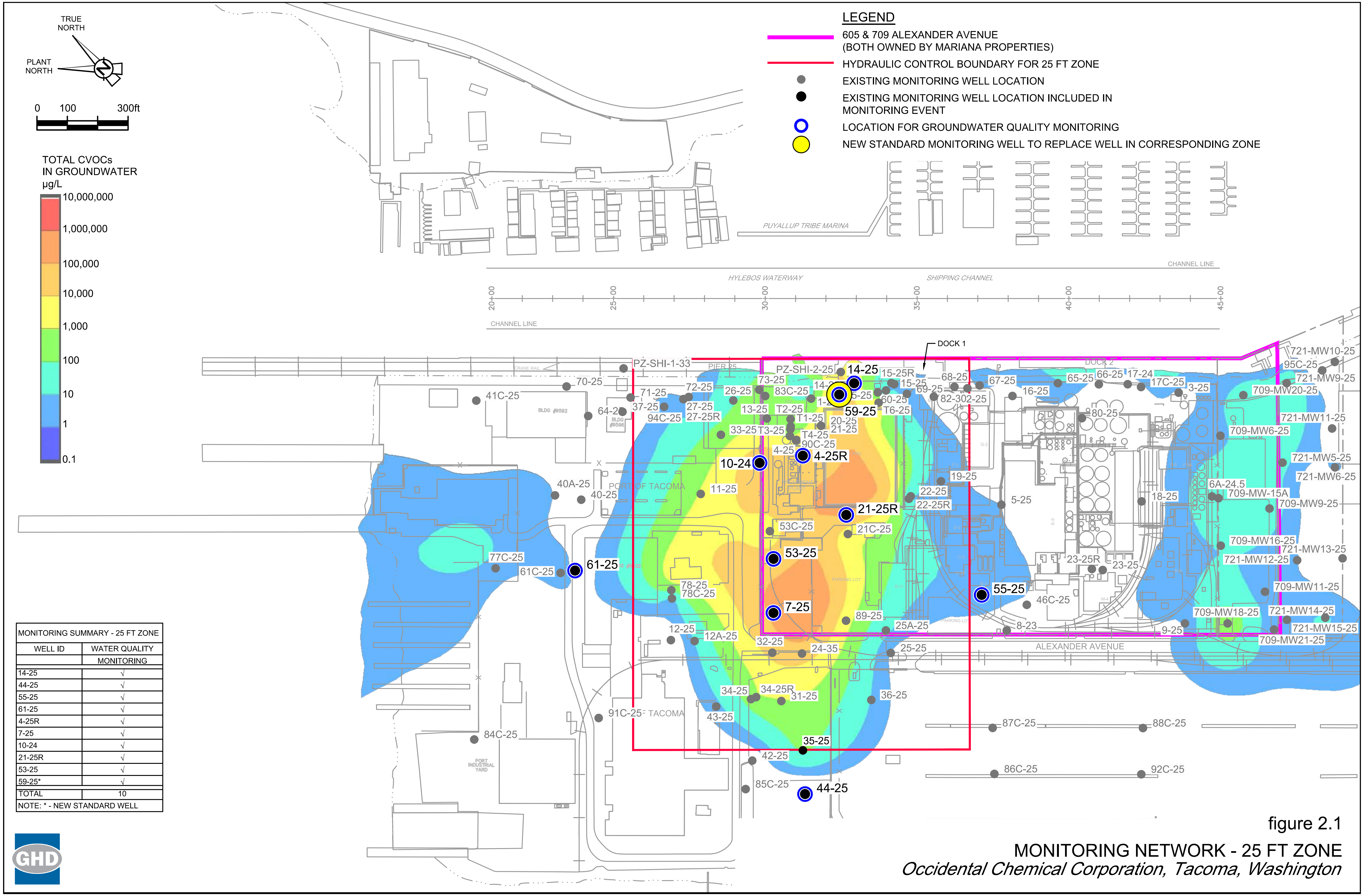

MONITORING SUMMARY - 25 FT ZONE	
WELL ID	WATER QUALITY MONITORING
14-25	√
44-25	√
55-25	√
61-25	√
4-25R	√
7-25	√
10-24	√
21-25R	√
53-25	√
59-25*	√
TOTAL	10
NOTE: * - NEW STANDARD WELL	

figure 2.1

MONITORING NETWORK - 25 FT ZONE

Occidental Chemical Corporation, Tacoma, Washington

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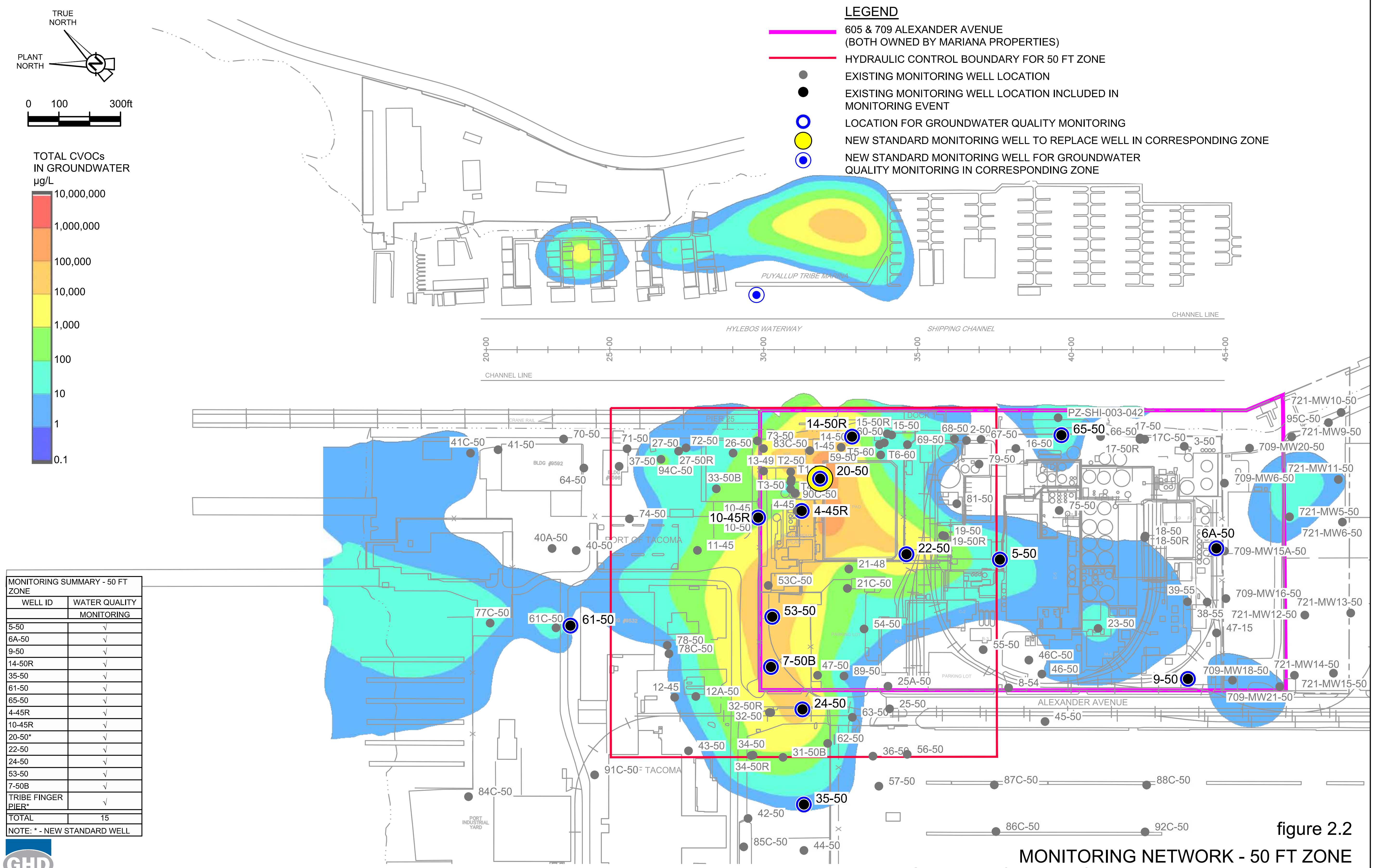

LEGEND

605 & 709 ALEXANDER AVENUE (BOTH OWNED BY MARIANA PROPERTIES)

HYDRAULIC CONTROL BOUNDARY FOR 50 FT ZONE

● EXISTING MONITORING WELL LOCATION

● EXISTING MONITORING WELL LOCATION INCLUDED IN MONITORING EVENT

○ LOCATION FOR GROUNDWATER QUALITY MONITORING

● NEW STANDARD MONITORING WELL TO REPLACE WELL IN CORRESPONDING ZONE

◉ NEW STANDARD MONITORING WELL FOR GROUNDWATER QUALITY MONITORING IN CORRESPONDING ZONE

MONITORING SUMMARY - 50 FT ZONE	
WELL ID	WATER QUALITY MONITORING
5-50	√
6A-50	√
9-50	√
14-50R	√
35-50	√
61-50	√
65-50	√
4-45R	√
10-45R	√
20-50*	√
22-50	√
24-50	√
53-50	√
7-50B	√
TRIBE FINGER PIER*	√
TOTAL	15
NOTE: * - NEW STANDARD WELL	

GHD

figure 2.2

MONITORING NETWORK - 50 FT ZONE

Occidental Chemical Corporation, Tacoma, Washington

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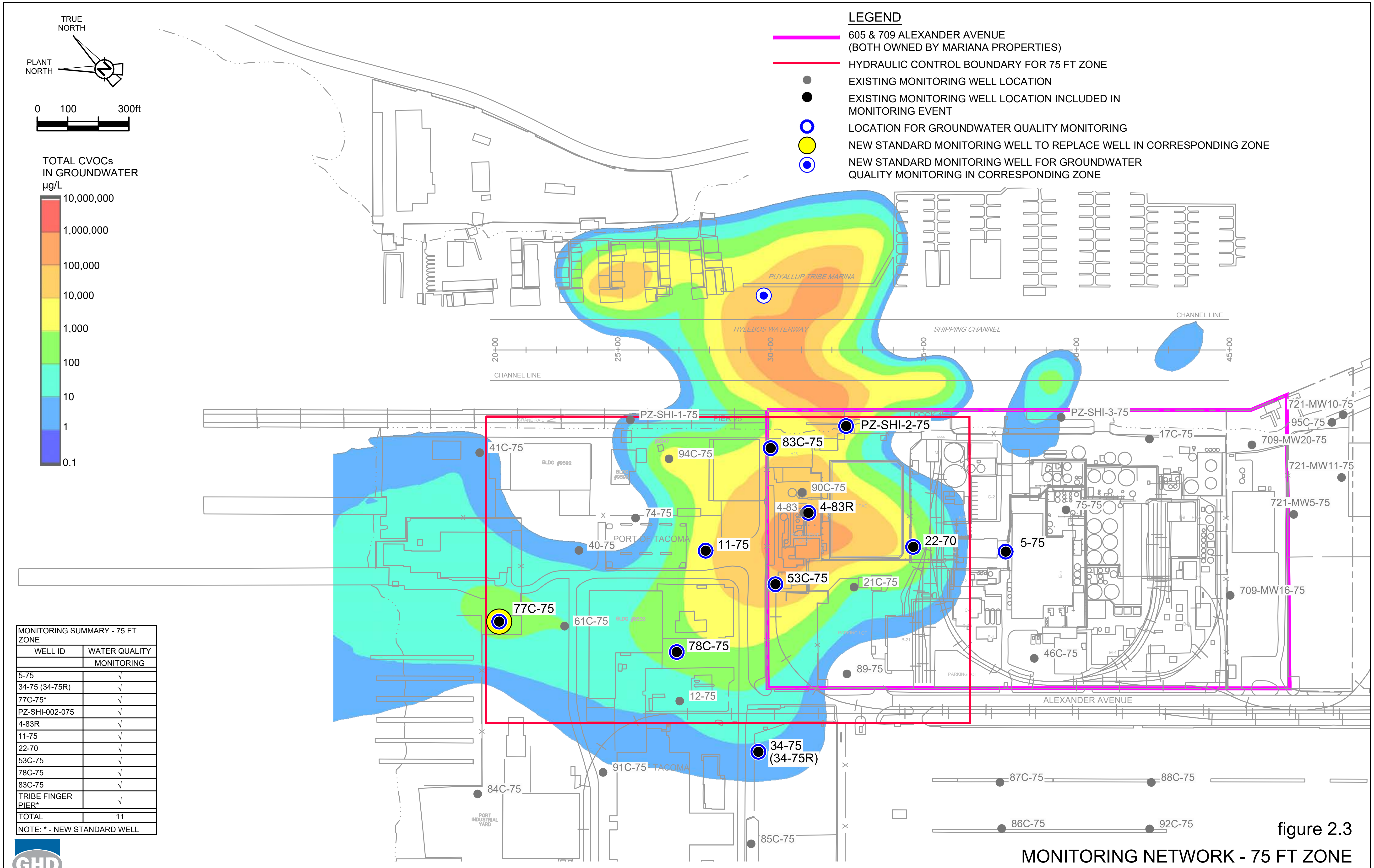

MONITORING SUMMARY - 75 FT ZONE	
WELL ID	WATER QUALITY MONITORING
5-75	√
34-75 (34-75R)	√
77C-75*	√
PZ-SHI-002-075	√
4-83R	√
11-75	√
22-70	√
53C-75	√
78C-75	√
83C-75	√
TRIBE FINGER PIER*	√
TOTAL	11
NOTE: * - NEW STANDARD WELL	

figure 2.3

MONITORING NETWORK - 75 FT ZONE

Occidental Chemical Corporation, Tacoma, Washington

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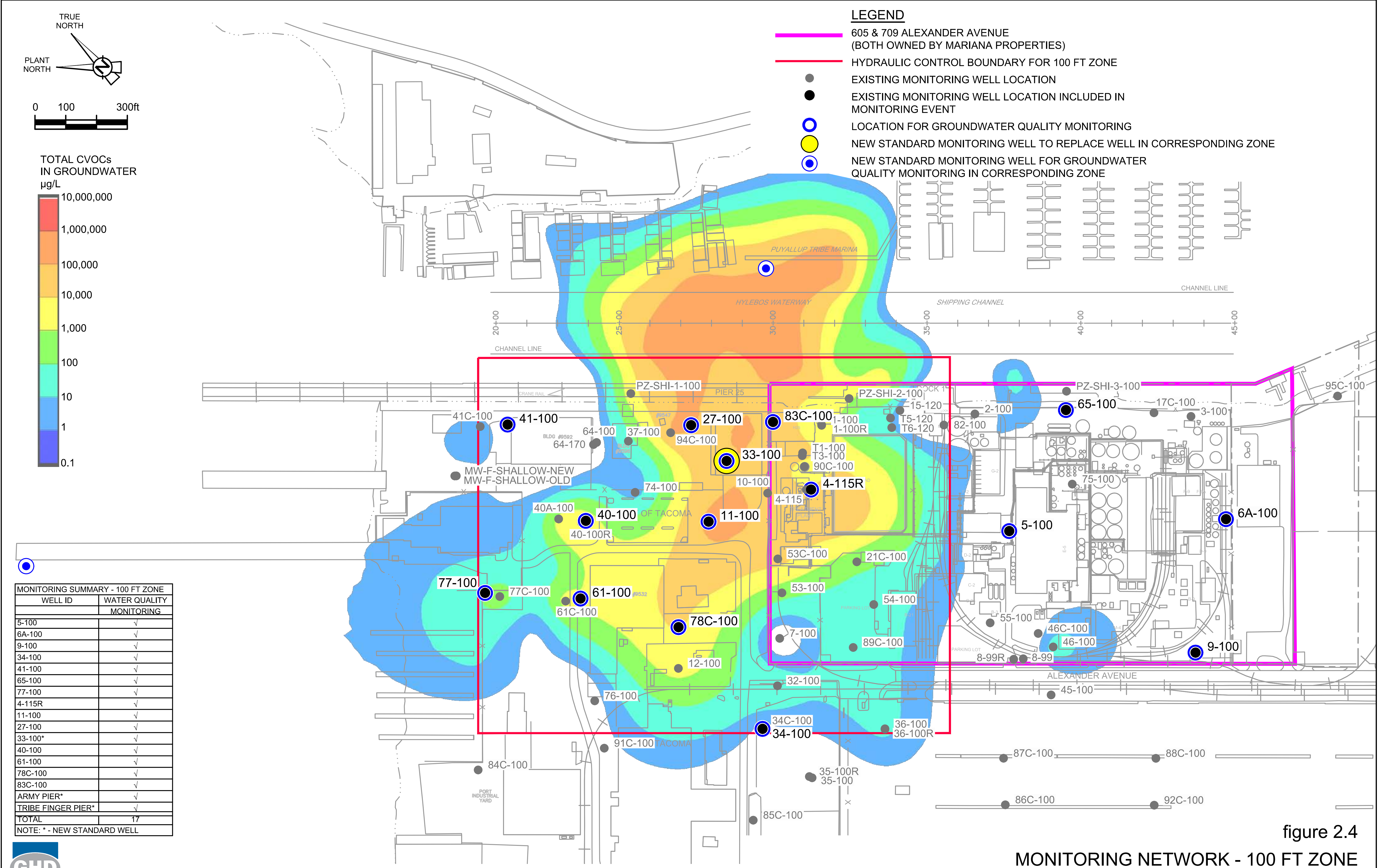

LEGEND

- 605 & 709 ALEXANDER AVENUE (BOTH OWNED BY MARIANA PROPERTIES)
- HYDRAULIC CONTROL BOUNDARY FOR 100 FT ZONE
- ● EXISTING MONITORING WELL LOCATION
- ● EXISTING MONITORING WELL LOCATION INCLUDED IN MONITORING EVENT
- ○ LOCATION FOR GROUNDWATER QUALITY MONITORING
- ● NEW STANDARD MONITORING WELL TO REPLACE WELL IN CORRESPONDING ZONE
- ◉ NEW STANDARD MONITORING WELL FOR GROUNDWATER QUALITY MONITORING IN CORRESPONDING ZONE

MONITORING SUMMARY - 100 FT ZONE	
WELL ID	WATER QUALITY MONITORING
5-100	√
6A-100	√
9-100	√
34-100	√
41-100	√
65-100	√
77-100	√
4-115R	√
11-100	√
27-100	√
33-100*	√
40-100	√
61-100	√
78C-100	√
83C-100	√
ARMY PIER*	√
TRIBE FINGER PIER*	√
TOTAL	17
NOTE: * - NEW STANDARD WELL	

figure 2.4

MONITORING NETWORK - 100 FT ZONE

Occidental Chemical Corporation, Tacoma, Washington

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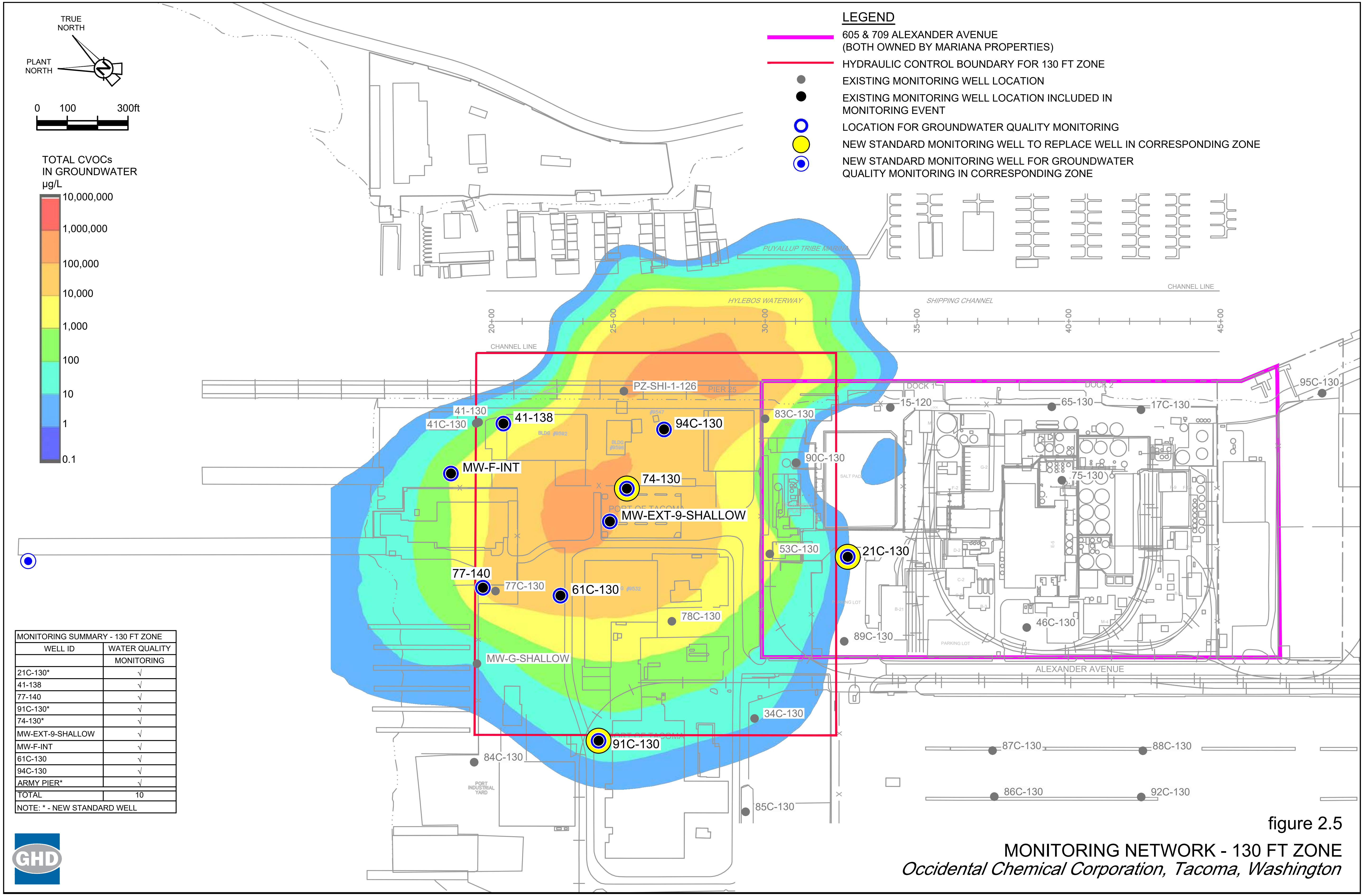

MONITORING SUMMARY - 130 FT ZONE	
WELL ID	WATER QUALITY MONITORING
21C-130*	√
41-138	√
77-140	√
91C-130*	√
74-130*	√
MW-EXT-9-SHALLOW	√
MW-F-INT	√
61C-130	√
94C-130	√
ARMY PIER*	√
TOTAL	10

NOTE: * - NEW STANDARD WELL

GHD

figure 2.5

MONITORING NETWORK - 130 FT ZONE
Occidental Chemical Corporation, Tacoma, Washington

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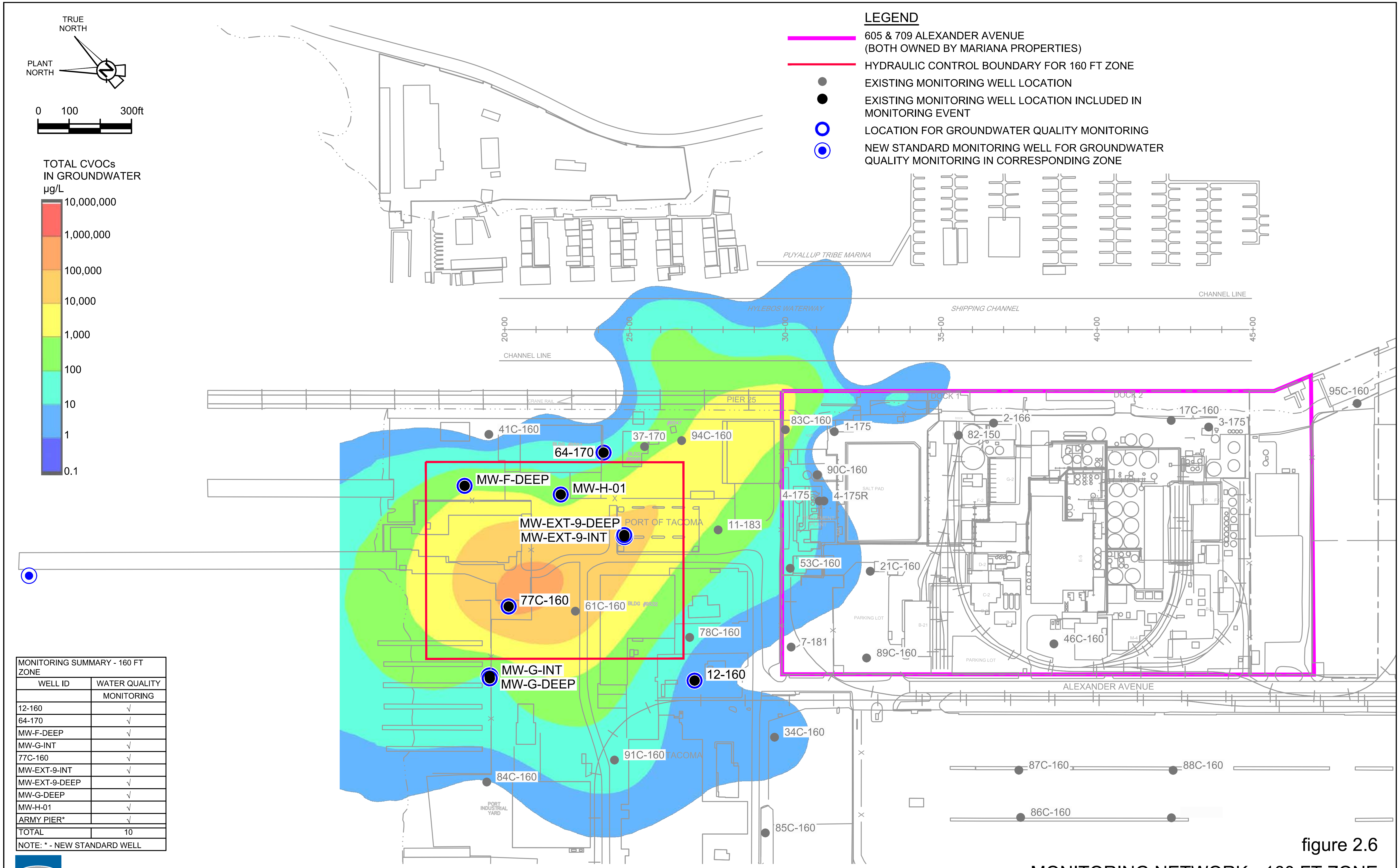

MONITORING SUMMARY - 160 FT ZONE	
WELL ID	WATER QUALITY
	MONITORING
12-160	√
64-170	√
MW-F-DEEP	√
MW-G-INT	√
77C-160	√
MW-EXT-9-INT	√
MW-EXT-9-DEEP	√
MW-G-DEEP	√
MW-H-01	√
ARMY PIER*	√
TOTAL	10
NOTE: * - NEW STANDARD WELL	

GHD

figure 2.6

MONITORING NETWORK - 160 FT ZONE

Occidental Chemical Corporation, Tacoma, Washington

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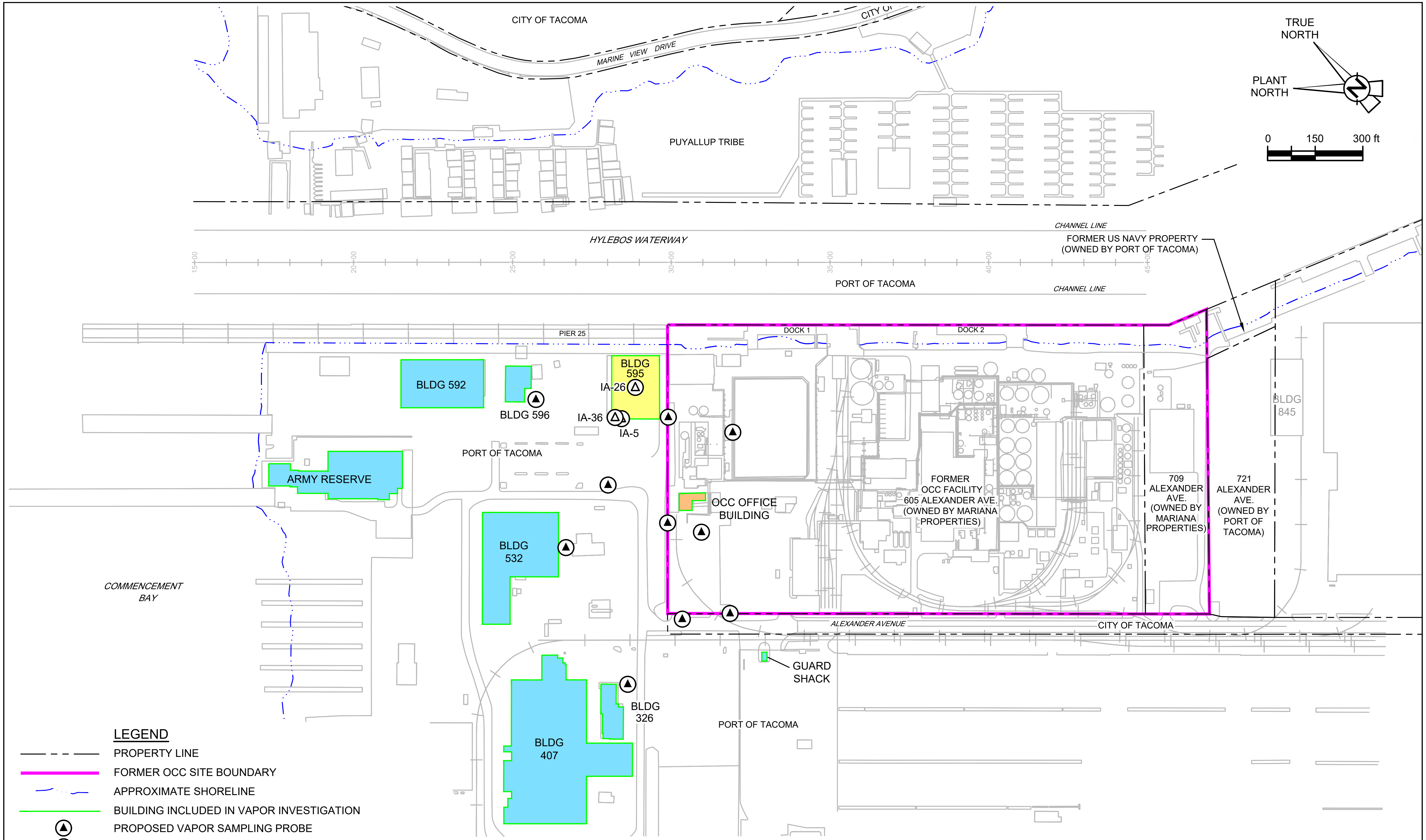

LEGEND

— — — PROPERTY LINE

━━ FORMER OCC SITE BOUNDARY

-·-·- APPROXIMATE SHORELINE

━━ BUILDING INCLUDED IN VAPOR INVESTIGATION

▲ PROPOSED VAPOR SAMPLING PROBE

△ PROPOSED INDOOR AIR SAMPLING LOCATION

RECOMMENDATIONS FOR ADDITIONAL WORK PER VAPOR INTRUSION INVESTIGATION REPORT

🟧 MANAGE OCCUPANCY BY GSH

🟨 CONTINUED MONITORING BY GSH

🟦 NO FURTHER ACTION BY GSH

figure 3.1

VAPOR INTRUSION MONITORING LOCATIONS

Occidental Chemical Corporation, Tacoma, Washington

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Table 2.1

Groundwater Quality Monitoring Locations and Rationale
Monitoring Plan
Occidental Chemical Corporation
Tacoma Washington

Location	Zone Grouping Plane	Ground Elevation (ft NGVD)	Reference Elevation (ft NGVD)	Well Diameter (in)	Screened Interval		Groundwater Quality Monitoring Rationale	Field Survey
					Bottom (ft BGS)	Top (ft BGS)		
Monitoring Wells								
4-25R	25 ft	12.15	11.88	2.0	25.25	20.25	Monitor water quality within plume	Useable
7-25	25 ft	12.95	13.88	2.0	24.95	19.95	Monitor water quality within plume	Useable
10-24	25 ft	9.90	8.36	2.0	24.00	19.00	Monitor water quality within plume	Useable
14-25	25 ft	11.29	10.98	2.0	24.50	19.50	Monitor water quality at east side of control boundary	Useable
21-25R	25 ft	13.03	12.40	2.0	25.03	20.03	Monitor water quality within plume	Useable
44-25	25 ft	11.76	10.54	2.0	23.46	18.46	Monitor water quality at west side of control boundary	Useable
53-25	25 ft	11.89	12.53	2.0	24.49	19.49	Monitor water quality within plume	Useable
55-25	25 ft	12.31	12.00	2.0	23.50	18.60	Monitor water quality at south side of control boundary	Useable
New 2-inch Replacement Well 59-25	25 ft	-	-	-	-	-	Monitor water quality within plume	NA
61-25	25 ft	11.33	11.02	2.0	23.50	18.50	Monitor water quality at north side of control boundary and north end of Site	Useable
4-45R	50 ft	12.07	11.21	2.0	45.17	40.17	Monitor water quality within plume	Useable
5-50	50 ft	11.66	11.42	2.0	49.96	44.96	Monitor water quality at south side of control boundary	Useable
6A-50	50 ft	12.22	12.87	2.0	50.32	45.32	Monitor water quality at south end of Site	Useable
7-50B	50 ft	12.98	14.97	2.0	50.20	35.20	Monitor water quality within plume	Useable
9-50	50 ft	12.15	13.85	2.0	50.35	45.35	Monitor water quality at southwest portion of Site	Useable
10-45R	50 ft	11.38	-	2.0	43.50	38.00	Monitor water quality within plume	Useable
14-50R	50 ft	11.43	10.56	2.0	51.53	46.53	Monitor water quality at east side of control boundary	Useable
New 2-inch Replacement Well 20-50	50 ft	-	-	-	-	-	Monitor water quality within plume	NA
22-50	50 ft	12.11	13.94	2.0	50.01	45.01	Monitor water quality within plume	Useable
24-50	50 ft	12.09	11.85	2.0	49.99	44.99	Monitor water quality within plume	Useable
35-50	50 ft	11.84	11.38	2.0	44.74	39.74	Monitor water quality at west side of control boundary	Useable
53-50	50 ft	11.96	11.24	2.0	49.56	44.56	Monitor water quality within plume	Useable
61-50	50 ft	11.29	10.96	2.0	48.00	43.00	Monitor water quality at north side of control boundary and north end of Site	Useable
65-50	50 ft	11.46	10.83	2.0	50.00	45.00	Monitor water quality at southeast portion of Site	Useable
New Standard Well (Tribe finger pier)	50 ft	-	-	-	-	-	Monitor water quality at east side of Hylebos Waterway	NA
4-83R	75 ft	12.05	11.28	2.0	81.85	76.85	Monitor water quality within plume	Useable
5-75	75 ft	11.71	11.48	2.0	74.20	69.20	Monitor water quality at south side of control boundary	Useable
11-75	75 ft	12.25	11.91	2.0	75.40	70.40	Monitor water quality within plume	Useable
22-70	75 ft	11.37	10.73	2.0	57.87	52.87	Monitor water quality within plume	Useable
34-75 (34-75R)	75 ft	11.87	14.73	2.0	74.30	69.30	Monitor water quality at west side of control boundary	Useable
53C-75	75 ft	12.16	15.25	0.4	74.23	69.23	Monitor water quality within plume	Useable
New Standard Well (77C-75)	75 ft	-	-	-	-	-	Monitor water quality at north side of control boundary and north end of Site	NA
78C-75	75 ft	11.48	10.92	0.43	74.01	69.01	Monitor water quality within plume	Useable
83C-75	75 ft	11.46	13.97	0.43	74.34	69.34	Monitor water quality within plume	Useable
PZ-SHI-002-075	75 ft	-4.18	10.91	2.0	59.50	54.50	Monitor water quality at east side of control boundary	Useable
New Standard Well (Tribe finger pier)	75 ft	-	-	-	-	-	Monitor water quality at east side of Hylebos Waterway	NA
4-115R	100 ft	12.05	11.42	2.0	115.65	110.65	Monitor water quality within plume	Useable
5-100	100 ft	11.69	11.45	2.0	99.99	94.99	Monitor water quality at south side of control boundary	Useable
6A-100	100 ft	12.11	13.38	2.0	99.91	94.91	Monitor water quality at south end of Site	Useable
9-100	100 ft	12.11	13.81	2.0	100.41	95.41	Monitor water quality at southwest portion of Site	Useable

Table 2.1

Groundwater Quality Monitoring Locations and Rationale
Monitoring Plan
Occidental Chemical Corporation
Tacoma Washington

Location	Zone Grouping Plane	Ground Elevation (ft NGVD)	Reference Elevation (ft NGVD)	Well Diameter (in)	Screened Interval		Groundwater Quality Monitoring Rationale	Field Survey
					Bottom (ft BGS)	Top (ft BGS)		
Monitoring Wells								
11-100	100 ft	12.32	11.77	2.0	98.32	93.32	Monitor water quality within plume	Useable
27-100	100 ft	11.60	11.10	2.0	100.50	95.50	Monitor water quality within plume	Useable
New 2-inch Replacement Well 33-100	100 ft	-	-	-	-	-	Monitor water quality within plume	NA
34-100	100 ft	12.00	11.30	2.0	100.00	95.00	Monitor water quality at west side of control boundary	Useable
40-100	100 ft	12.62	11.69	2.0	99.22	94.22	Monitor water quality within plume	Useable
61-100	100 ft	11.34	10.81	2.0	97.70	92.70	Monitor water quality within plume	Useable
65-100	100 ft	11.56	10.90	2.0	100.00	95.00	Monitor water quality at southeast portion of Site	Useable
77-100	100 ft	8.51	8.18	2.0	100.00	95.00	Monitor water quality at north side of control boundary and north end of Site	Useable
78C-100	100 ft	11.48	10.92	0.4	99.91	94.91	Monitor water quality within plume	Useable
83C-100	100 ft	11.46	13.97	0.4	99.30	94.30	Monitor water quality within plume	Useable
41-100	100 ft	10.84	10.31	2.0	99.14	94.14	Monitor water quality at east side of control boundary	Useable
New Standard Well (Tribe finger pier)	100 ft	-	-	-	-	-	Monitor water quality at east side of Hylebos Waterway	NA
New Standard Well (Army pier)	100 ft	-	-	-	-	-	Monitor water quality below Commencement Bay	NA
New Standard Well (21C-130)	130 ft	-	-	-	-	-	Monitor water quality at south side of control boundary	NA
41-138	130 ft	10.79	10.33	2.0	126.87	121.97	Monitor water quality at east side of control boundary	Useable
61C-130	130 ft	10.87	10.19	0.43	98.08	93.08	Monitor water quality within plume	Useable
New 2-inch Replacement Well 74-130	130 ft	-	-	-	-	-	Monitor water quality within plume	NA
77-140	130 ft	8.78	8.53	2.0	140.00	135.00	Monitor water quality at north side of control boundary and north end of Site	Useable
New Standard Well (91C-130)	130 ft	-	-	-	-	-	Monitor water quality at west side of control boundary	Useable
94C-130	130 ft	11.29	10.58	0.4	128.30	123.30	Monitor water quality within plume	Useable
MW-EXT-9-SHALLOW	130 ft	12.59	12.21	2.0	123.00	118.00	Monitor water quality within plume	Useable
MW-F-INT	130 ft	11.15	10.82	2.0	140.00	135.00	Monitor water quality within plume	Useable
New Standard Well (Army pier)	130 ft	-	-	-	-	-	Monitor water quality below Commencement Bay	NA
12-160	160 ft	10.64	9.24	4.0	159.66	149.66	Monitor water quality at south side of control boundary	Useable
64-170	160 ft	11.03	10.77	2.0	175.00	170.00	Monitor water quality at east side of control boundary	Useable
77C-160	160 ft	9.78	12.93	0.43	166.30	161.30	Monitor water quality within plume	Useable
MW-EXT-9-INT	160 ft	12.56	11.95	2.0	155.00	150.00	Monitor water quality within plume	Useable
MW-EXT-9-DEEP	160 ft	12.58	12.14	2.0	202.00	197.00	Monitor water quality at deep wells	Useable
MW-F-DEEP	160 ft	11.17	10.65	2.0	176.00	171.00	Monitor water quality at north side of control boundary and north end of Site	Useable
MW-G-INT	160 ft	10.39	10.05	2.0	171.00	166.00	Monitor water quality at west side of control boundary	Useable
MW-G-DEEP	160 ft	10.38	9.95	2.0	222.40	217.40	Monitor water quality at deep wells	Useable
MW-H-01	160 ft	11.41	10.93	2.0	167.25	162.25	Monitor water quality within plume	Useable
New Standard Well (Army pier)	160 ft	-	-	-	-	-	Monitor water quality below Commencement Bay	NA

Notes:

ft NGVD - feet National Geodetic Vertical Datum
ft BGS - feet below ground surface
in - inches

Table 2.3

Groundwater Parameter List
Monitoring Plan
Occidental Chemical Corporation
Tacoma Washington

Parameter	Comment
TCL VOCs	
TCL SVOCs	including 1,4-dioxane*
Dissolved gases	ethane/ethene
Specific Gravity	
Silica	
Field parameters	temperature, pH, specific conductance, turbidity, oxidation-reduction potential, dissolved oxygen, and salinity

Notes:

SVOCs - Semi-volatile Organic Compounds
TCL - Target Compound List
VOCs - Volatile Organic Compounds
* - standard reporting quantitation limit for 1,4-dioxane

Appendices

Appendix A
Field Sampling Plan

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List of Acronyms

ags	above ground surface
bgs	below ground surface
DNAPL	dense non-aqueous phase liquid
Ecology	Washington State Department of Ecology
FSP	Field Sampling Plan
ft	feet
HASP	Health and Safety Plan
Hylebos	Hylebos Waterway
mL/min	milliliters per minute
MP	Monitoring Plan
NGVD	National Geodetic Vertical Datum
OCC	Occidental Chemical Corporation
POT	Port of Tacoma
PVC	polyvinyl chloride
QAPP	Quality Assurance Project Plan
USCS	Unified Soil Classification System
USEPA	United States Environmental Protection Agency
VOC	volatile organic compound or volatile organic compounds

1. Introduction

Occidental Chemical Corporation (OCC) has been working with the Washington State Department of Ecology (Ecology) and the United States Environmental Protection Agency (USEPA) (together referred to as the 'Agencies') to address remaining environmental issues at the 'Occidental' Site associated in part with the former OCC facility located in Tacoma, Washington (Site).

This Field Sampling Plan (FSP) was prepared as part of the Monitoring Plan (MP) that was developed to monitor groundwater and surface water levels, groundwater quality, and soil vapor at the Site and indoor air in Port of Tacoma Building 595. The purpose of the FSP is to describe the field procedures required to implement the MP.

This FSP is organized as follows:

Section 2	Scope of Work
Section 3	Field Preparation
Section 4	Borehole Drilling Procedures
Section 5	Standard Monitoring Well Installation
Section 6	Vapor Probe Installation
Section 7	Monitoring Well Development / Redevelopment
Section 8	Groundwater Sampling from Monitoring Wells
Section 9	Vapor Sampling
Section 10	Indoor Air Sampling
Section 11	Field Log Book
Section 12	Labeling and Packaging
Section 13	Chain of Custody Procedure
Section 14	Equipment Cleaning
Section 15	Waste Material Handling
Section 16	References

2. Scope of Work

The scope of work for the FSP includes procedures for elements presented in the MP as follows:

- Groundwater quality monitoring
- Soil vapor monitoring
- Indoor air monitoring

The above proposed monitoring, as described in the MP, requires the installation of 13 standard 2-inch diameter monitoring wells and ten vapor probes at locations presented in the MP. The scope of work for the FSP includes the procedures for these installations.

Laboratory activities will be conducted in accordance with the Quality Assurance Project Plan (QAPP) presented in Appendix B of the MP.

All field activities will be conducted in accordance with the Site-specific Health and Safety Plan (HASP), including updates to cover the activities in the MP.

Modifications and/or amendments to the approved MP, FSP, and QAPP may be necessary during implementation of the scope of work due to unforeseen field conditions. Any proposed changes to the approved scope of work will be discussed with and approved by the Agencies at the time of occurrence.

3. Field Preparation

3.1 Borehole Clearance

The proposed drilling locations will be field verified to confirm that the locations are accessible and free of underground utilities or structures. The final locations of the boreholes may be adjusted to account for accessibility and avoid utilities.

3.2 Survey Monitoring Well and Vapor Probe Locations

The locations of all new monitoring wells and vapor probes will be surveyed by a qualified, licensed land surveyor. Ground surface or grade elevations will be surveyed at each location prior to installation to ensure accurate construction of the monitoring wells and vapor probes. Once the ground surface/grade survey is completed, the depth below ground surface (bgs) or grade for placement of each proposed well and probe screen will be determined.

The completed monitoring wells and vapor probes will be surveyed to determine the final constructed locations and elevations. Locations and elevations will be based upon the Washington State Plane Coordinate system and National Geodetic Vertical Datum (NGVD), respectively.

4. Borehole Drilling Procedures

The following methods and procedures apply to drilling boreholes.

Boreholes will be converted into standard 2-inch diameter groundwater monitoring wells as described in Section 5 or vapor probes as described in Section 6.

4.1 Soil Borings for Upland Monitoring Wells

Soil borings for upland standard monitoring wells will be completed using roto-sonic drilling methods. Continuous geologic soil samples will be retrieved from each borehole and logged by a licensed geologist in accordance with the Unified Soil Classification System (USCS). The soil borings will be installed by:

i. Drilling and collecting a soil core with a 4-inch diameter sonic core barrel advanced up to 20 feet (ft) at a time.

ii. Advancing a 6-inch diameter sonic casing over the 4-inch diameter core barrel, and then extracting the core barrel and soil core.

iii. Continuing to install the boring, advancing in up to 20-foot increments, following this procedure.

Sample disturbance will be minimized by adjusting the sonic frequencies during advancement of the core barrel. Monitoring wells will be installed in the boreholes as described in Section 5.1.

4.2 Soil Borings for Subtidal Monitoring Wells

Soil borings for subtidal monitoring wells will be completed using roto-sonic drilling methods described in Section 4.1 and the following additional procedures. The drilling rig will set up on an existing pier or barge, mounted over surface water in either the Hylebos Waterway (Hylebos) or Commencement Bay.

4.2.1 Drilling off a Fixed Pier

Prior to lowering the core barrel, the elevation of the end of the core barrel will be approximated from a pre-surveyed reference point (see Section 3.2) on the fixed pier in order that each interval (i.e., soil core) may be properly referenced to an elevation.

4.2.2 Drilling off a Barge or Floating Pier

Immediately before lowering the core barrel, the time and the surface water level elevation will be measured and recorded. Measurements of surface water level elevation will be made every 15 minutes during advancement of the core barrel in order that each interval may be properly referenced to an elevation (that accounts for tidal fluctuations in the surface water level elevation).

4.3 Temporary Isolation Casing Installation

In the event that pooled dense non-aqueous phase liquid (DNAPL) is observed in a boring, a temporary isolation casing will be installed to prevent downward migration of DNAPL. An 8-inch diameter overshot casing will be advanced over the 6-inch diameter roto-sonic drill pipe. The 8-inch diameter overshot casing will be advanced approximately 3 ft past the depth interval where DNAPL was observed in the 4-inch diameter core. Prior to advancing the borehole below the temporary isolation casing, approximately 3 ft of bentonite slurry will be poured in the annulus between the 6-inch diameter drill pipe and the 8-inch diameter overshot casing.

If a second interval of pooled DNAPL is encountered, the borehole will be terminated and the borehole will be backfilled with cement/bentonite grout.

4.4 Soil Borings for Upland Vapor Probes

The soil gas probes will be installed using direct-push drilling methods (i.e., a Geoprobe® drill-rig using a dual tube soil sampling system to permit the collection of continuous soil core samples). The Geoprobe® drill-rig will hydraulically push a series of drive rods to a target depth of approximately 5.5 ft below grade. The boreholes completed for each soil gas probe will be logged by a licensed geologist in accordance with the USCS.

The collection of overburden soil samples is proposed at each soil gas probe location for the analysis of the soil physical properties (grain size analysis, moisture content, dry bulk density, and porosity). The soil physical properties may be used in the future for modeling and/or calculating a site-specific soil gas to indoor air attenuation factor. Where more than one overburden soil type is observed at a specific location, a soil sample will be collected from each soil type.

5. Standard Monitoring Well Installation

5.1 Upland Monitoring Wells

Standard polyvinyl chloride (PVC) 2-inch diameter monitoring wells will be installed as follows:

i. Install a 2-inch diameter well consisting of a 5- to 10-foot long (depending on observed geological conditions), schedule 40 PVC (#10 slot) well screen set at the designated depth interval, and 2-inch diameter, schedule 40 PVC riser pipe of threaded construction with a lockable cap and lock.

ii. Backfill each well installation with a sandpack around the well screen (10 x 20 silica sand) placed to a measured minimum of 3 ft above the top of screen and a measured 2-foot bentonite gravel seal over the sandpack. If heaving sands are encountered that prevent the installation of an artificial sandpack, a natural sandpack may be substituted.

iii. Wait one hour after placing the bentonite seal and then grout the remaining annular space between the well pipe and borehole to ground surface by positive displacement using a tremie tube. The grout shall consist of Portland cement, bentonite, and clean water. The grout shall be mixed in a proportion of not less than five to nor more than six gallons of water to one bag (94 pounds) of cement. Bentonite powder shall be added at a ratio of approximately 3 percent by volume. The volume of grout needed to fill the annular space between the casing and borehole will be estimated for each well prior to installation. The actual amount of grout used during the well installation will be measured and recorded.

iv. Stick-up wells shall be enclosed in an approved 6-inch square protective steel shroud and set in 2 ft of concrete. The stick-up casings will be raised approximately 3 ft above ground surface (ags) or grade.

v. Wells installed on Port of Tacoma (POT) property will be finished with flush-mount casings (Figure 5.1). Flush-mount casings shall be set 3 inches bgs or grade and an approved 12-inch diameter protective, traffic-rated curb box casing will be grouted in place around the well for protection. The flush-mount casings will be raised slightly above ground surface to allow the sealing grout to be sloped away from the well to prevent surface water run-in.

vi. Identification labels will be clearly marked on the inside and outside of the well/well casing.

The standard 2-inch diameter monitoring well installation is shown on Figure 5.2.

Following well development (Section 7), each well will be allowed to stabilize for at least one week before conducting groundwater sampling.

5.2 Subtidal Monitoring Wells

Subtidal monitoring wells will be installed and grouted in a similar manner to the upland monitoring wells to the approximate base of the surface water bodies (i.e., Hylebos or Commencement Bay).

5.2.1 Fixed Pier

Above the base of the water body, the riser pipe will be extended to the top of the fixed pier and secured to the fixed pier. As noted above, a lockable cap and lock will be installed at the top of the riser pipe. A protective outer casing surrounding the riser pipe will be installed and secured to the fixed pier to help prevent damage to the riser pipe if struck by debris floating in the water, water craft docking at the fixed pier, etc.

5.2.2 Floating Pier

Above the base of the water body, the riser pipe will be extended to the top of the floating pier during near high tide. As noted above, a lockable cap and lock will be installed at the top of the riser pipe. A protective outer casing surrounding the riser pipe will be installed to help prevent damage to the riser pipe if struck by debris floating in the water, water craft docking at the floating pier, etc.

Following well development (Section 7), each well will be allowed to stabilize for at least one week before conducting groundwater sampling.

6. Vapor Probe Installation

Each soil gas probe will consist of a screen mid-point positioned within the unsaturated overburden at approximately 5.25 ft below grade. A 6-inch long pre-fabricated stainless steel screen implant or pre-packed vapor screen will be used for each probe and positioned at the bottom of the borehole. The screen mid-point depths may be adjusted depending on the current position of the groundwater table. The implant will be connected to 1/4-inch or 3/8-inch diameter nylon sampling tubing of sufficient length to extend to ground surface. Once the implant is set in position, the drive rods will be removed leaving the implant in the subsurface. While removing the drive rods, a sand pack of inert pea gravel or coarse silica sand will be placed around the implant to 3 inches above the screen. A 6-inch thick seal comprised of dry granular bentonite will be placed on top of the sand pack and manually hydrated in place. The remainder of the borehole will be filled with pre-hydrated granular bentonite to ground surface. Each soil gas probe will be completed at ground surface using a lockable flush-mount casing, approved by POT if on POT property (see Section 5.1), and the tubing at ground surface will be terminated with a valve connection. Figure 6.1 presents a typical soil gas probe construction detail.

7. Monitoring Well Development / Redevelopment

After installation, each standard monitoring well will be developed using a pump fitted with a surge block until the pumped water's turbidity is below 5 units or 20 well volumes have been removed for 2-inch diameter wells. A minimum of 48 hours will be allowed to elapse between well installation and well development to allow sufficient time for the grout to solidify.

Existing standard monitoring wells will be redeveloped using the same procedure if well sounding identifies solids have accumulated in the well covering more than 50 percent of the well screen as determined by well sounding. Well sounding involves measuring the depth to which solids have accumulated in the well. A well is sounded as follows:

i. Remove any sampling and water level equipment from the well

ii. Using a weighted, pre-cleaned measuring tape, measure the depth from the top of the well or the curb box to the interface between the water and any solids in the well

iii. Compare the depth to the solids interface with the depth of the well screen (as presented in Table 2.1 of the MP)

iv. If solids cover more than 50 percent of the screen, the well will be redeveloped

Water purged during development or redevelopment will be handled as described in Section 15.

8. Groundwater Sampling from Monitoring Wells

Groundwater quality samples will be collected using purging techniques described below and analyzed for field parameters, volatile organic compounds (VOC), dissolved gases ethene and ethane, and specific gravity. The groundwater samples will be collected using a bladder pump with dedicated air/water tubing and disposable bladder or similar variable flow DC submersible pump and flow-through cell connected to well-dedicated polyethylene tubing. Field parameters will be measured in the flow-through cell using a Horiba U-52XD water quality meter or equivalent that is calibrated per manufacturer's specifications. Groundwater samples will be collected using techniques as presented below:

i. Identify the well using the current Site map (update the map if needed) and inspect the well for damage. Note the condition of the surface protection, manhole or cover, and the well cap in the field book.

ii. Measure and record, in the field book, the water level in the well using an electric tape water level measuring device to the nearest 0.01 ft.

iii. Measure and record, in the field book, the total depth of the well to the nearest 0.1 ft to determine if there any accumulated sediments.

iv. Install the sample tubing in the well with the bottom of the tubing (intake) at the midpoint of the available well screen, and connect the pump.

v. With the pump controller set to its lowest setting, turn the pump on.

vi. Slowly increase the pump speed until discharge occurs.

vii. Once discharge occurs, record the visual observation of water quality and adjust the flow to a sustainable pumping rate.

viii. Record the groundwater pumping rate for subsequent sampling.

ix. Measure and record, in the field book, field parameters (pH, specific conductance, turbidity, temperature, dissolved oxygen, oxidation-reduction potential, salinity, and water level) and visual water quality every 5 minutes for the first well volume and then every 15 minutes for the remaining well volumes. Stabilization will be considered to be achieved and purging complete after three consecutive readings are within the following limits:

a)	pH	±0.1 unit
b)	Temperature	±3 percent
c)	Specific Conductance	±3 percent
d)	Dissolved Oxygen	±10 percent
e)	Oxidation-Reduction Potential	±10 percent
f)	Water level	±0.2 foot

If the well is purged dry, a sample will be collected and the field parameters will be recorded once the well recovers sufficiently to permit sample collection.

x. Prior to sample collection, the discharge tubing will be disconnected from the flow-through cell. Sample containers will then be filled per laboratory instructions. Samples for VOC and dissolved gases analyses will be filled directly from the tubing using zero headspace containers. VOC samples will be collected in unpreserved vials and analyzed within seven days to avoid the potential creation of air bubbles by an acid-base reaction between potentially high pH groundwater and the acid preservative. Samples for specific gravity will be unfiltered. If separate phases are observed in groundwater samples, specific gravity will be run on each phase, if possible. Field notes should indicate that the specific gravity results may reflect multiple phases of liquid in the sample(s).

xi. Record the conditions at the time of sampling in the field book, including a description of the sample, the date and time of sampling, the sample identification number, the sample location, and the weather conditions.

xii. The field parameters listed above will be measured and recorded. Sample containers will be labeled, wrapped in packing material, and immediately placed in a cooler with ice. Samples will be delivered to the analytical laboratory by courier under approved Chain of Custody procedures.

All laboratory analyses will be performed by a Washington State Department of Ecology accredited laboratory as described in the QAPP provided as Appendix B of the MP.

9. Vapor Sampling

Vapor samples will be collected for VOC analysis from installed soil gas probes using active soil gas sampling methods as follows:

i. Wait a minimum of 48 hours following the installation of the soil gas probes to allow installation disturbances in the unsaturated zone to dissipate and equilibrium conditions to re-establish.

ii. For probes not installed beneath asphalt or pavement cover, sampling will not be performed during or within 24 hours of a significant rain event (e.g., ≥0.5 inches during a 24-hour period after CAEPA [2015]).

iii. Evacuated canisters used for soil gas sample collection will be pre-fitted with a laboratory calibrated critical orifice flow regulating device sized to allow the collection of the soil gas sample at a maximum soil gas sample collection flow rate of approximately 100 milliliters per minute (mL/min).

iv. Conduct pre-purging and sampling leak test as described below:

    a) Vacuum test the sampling assembly to test the air-tightness of the assembly connections. If a leak in the sampling assembly is detected, the sampling assembly fittings will be tightened and/or replaced, and the vacuum testing will be repeated.

v. Calculate soil gas probe internal volume based on field measurements of probe construction (i.e., below ground tubing length, tubing inner diameter, and sand pack length and diameter indicated in the soil gas probe stratigraphic logs, assuming a sand pack porosity of 30 percent) and above ground sampling equipment.

vi. Conduct soil gas probe purging of a maximum of one to two soil gas probe internal volumes at a maximum flow rate of 200 mL/min and leak testing as described below:

    a) Release helium as a tracer compound under a shroud covering the soil gas probe.

    b) Monitor for helium within the sampling assembly using a helium meter during purging.

    c) If significant helium levels (defined as 5 percent of the helium concentration beneath the shroud consistent with CAEPA [2015]) are detected in the sampling assembly during purging, canister sampling will not be performed.

    d) Attempt to repair the soil gas probe by placing additional hydrated bentonite around the annulus of the soil gas probe at ground surface and allowing this to set.

    e) Repeat purging and leak testing. If soil gas probe leakage continues, the soil gas probe (or a portion of the probe) may require replacement.

vii. Connected laboratory certified sample container to soil gas probe and open laboratory calibrated critical orifice flow regulating device.

viii. Complete sample collection with a minimum residual negative pressure in the canisters of approximately 1 to 5 inches of Mercury.

ix. Conduct final leak test as described below:

   a) Release helium as a tracer compound under a shroud covering the soil gas probe

   b) Monitoring for helium within the sampling assembly using a helium meter

   c) If significant helium levels (defined as 5 percent of the helium concentration beneath the shroud consistent with CAEPA [2015]) are detected following sample collection, the canister will not be submitted for laboratory analysis

   d) Attempt to repair the soil gas probe by placing additional hydrated bentonite around the annulus of the soil gas probe at ground surface and allowing this to set

   e) Repeat purging and leak testing. If soil gas probe leakage continues, the soil gas probe (or a portion of the probe) may require replacement

x. Record all field activities, conditions, and sampling processes, including names of field personnel, dates, and times in the field book. Documentation includes weather conditions (temperature, barometric pressure, wind direction and speed, and humidity); surface conditions (presence of standing water and type of cover).

All laboratory analyses will be performed by a Washington State Department of Ecology accredited laboratory as described in the QAPP provided as Appendix B of the MP.

10. Indoor Air Sampling

A pre-sampling public outreach effort will be conducted to inform tenants of the sampling needs, what they will entail, where the sampling will occur, and when the results will be made available. This should occur at least one month in advance of any sampling. This lead time will also serve to evaluate tenant schedules for effective coordination.

Several days prior to commencement of sampling, the building indoor environments will be surveyed to identify and note potential VOC emitters (especially those that may emit the same VOCs potentially present in soil vapor). Where practical, the building tenants may be asked to remove, isolate, or control the potential emitters (e.g., cleaners, solvents, paints, adhesives, etc.) prior to and during the sampling. Potential VOC emitters present during sampling will be inventoried. If it is not feasible to remove or isolate potential general indoor air contaminant sources then additional indoor air monitoring locations may be added to account for the potential contribution from these background sources.

Sample collection may occur during weekdays or on weekend days depending on accessibility. If sample collection takes place on a weekend or during non-working hours, the heating and ventilation systems will be operated to be representative of typical working conditions.

The indoor and outdoor ambient air samples will be collected using 6-liter evacuated Summa canisters over a 24-hour period. Summa canisters will be received from the laboratory certified clean and equipped with laboratory-calibrated flow regulators set to fill the canisters over a 24-hour period but still leave a small amount of vacuum in the canister at completion of sampling. The canisters will be elevated such that the samples will be collected from a height of approximately

2 feet above the floor/ground. Canisters are approximately 1 foot high and with the intake near the top, and so the canisters will sit on top of an object approximately 1 foot tall. Any objects used to elevate the canisters should be selected so as to not affect the results (e.g., untreated wood would be acceptable).

The initial vacuum within each canister will be checked using a laboratory-supplied pressure gauge to ensure that each canister is evacuated prior to initiation of sample collection (initial vacuum should be approximately 30 inches Hg). The valve will then be opened to commence sample collection.

The time and weather conditions (temperature, wind direction, precipitation) at time of sampling commencement at each location will be recorded. Twice each day, the vacuum in each canister will be checked using the laboratory-supplied pressure gauge to ensure that each canister is filling at approximately the expected rate, and weather conditions will be recorded. The time and weather conditions at time of sampling completion will be recorded. The vacuum remaining in each canister will be recorded (a small residual vacuum should remain at time of sampling completion and confirmed by the laboratory prior to sample analysis).

The outdoor ambient air sample location will be selected based on predominant wind direction and entry points of air into the building and a sample will be collected concurrent with the indoor air samples. The outdoor sample location will be selected to represent background ambient air conditions for the building as a whole and will be placed to attempt to be upwind of the building.

QA/QC measures implemented during the program will include collecting a field duplicate sample and maintaining a minimum negative pressure in all the sample canisters following sample collection. All laboratory analyses will be performed by a Washington State Department of Ecology accredited laboratory as described in the QAPP provided as Appendix B of the MP.

11. Field Logbook

Field logbook procedures are presented in Section 7.1.1 of the QAPP.

12. Sample Numbering and Packaging

Sample numbering procedures are presented in Section 7.1.2 of the QAPP.

Sample containers for VOC, dissolved gases, and specific gravity will be individually wrapped and placed on ice or cooler packs in laboratory supplied coolers immediately after labeling. Sample containers for vapor and air samples do not require cooling. Packaging requirements are identified in Table 7.1 and in Section 7.1.3 of the QAPP.

13. Chain of Custody Procedure

Chain of Custody procedures are presented in Section 7.1.3 of the QAPP.

14. Equipment Cleaning

Prior to being placed into a well, all equipment will be cleaned according to the following protocol:

i. Disassemble equipment, if necessary

ii. Non phosphate detergent wash (e.g., Alconox®)

iii. Tap water rinse

iv. Distilled water rinse

v. Isopropanol rinse

vi. Air dry

vii. Distilled water rinse

When practicable, sampling equipment will be wrapped in aluminum foil to prevent it from becoming contaminated.

Prior to leaving the project, the drill rig and equipment shall be steam cleaned. The drilling contractor will remove soil material from the drill rig and equipment at the Site and OCC will provide a location where the drilling contractor shall steam clean the drill rig and equipment.

Between boreholes the casing and core barrel shall be cleaned with a wire brush to remove visible soils and subsequently shall be steam cleaned by the drilling contractor.

Wash waters shall be collected in a coverable container supplied by the drilling contractor for subsequent disposal in the on-Site groundwater treatment plant.

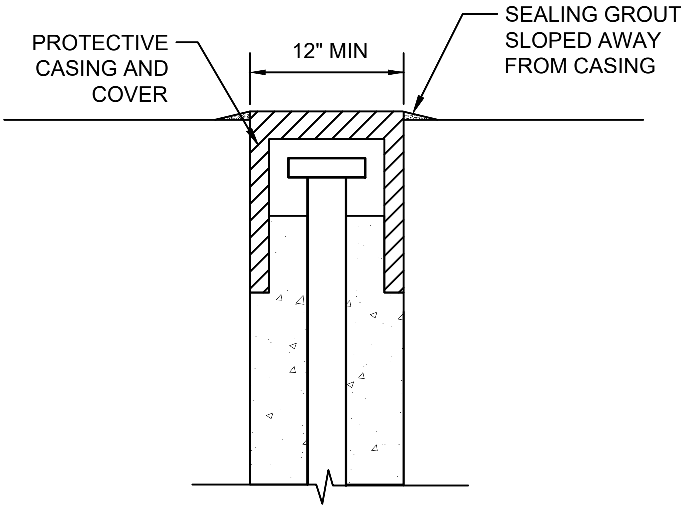
15. Waste Material Handling

Solid wastes (e.g., Tyvek® coveralls, gloves) will be containerized and disposed of in accordance with the appropriate regulations.

Borehole cuttings, wastewater, and decontamination solvents shall be placed in separate containers and covered. At the end of every day, all containers will be securely covered and full containers will be transferred to an on-Site staging area. All containers will be properly labeled as to contents in conformance with all federal and state regulations.

16. References

California Environmental Protection Agency (CAEPA), 2015. Advisory, Active Soil Gas Investigations, Prepared in cooperation with Department of Toxic Substances Control, Laos Angeles Regional Water Quality Control Board, and San Francisco Regional Water Quality Control Board, July



RAISED SLIGHTLY ABOVE GROUND
PROTECTIVE CASING INSTALLATION

figure 5.1

TYPICAL FLUSH-MOUNT PROTECTIVE CASING

Occidental Chemical Corporation, Tacoma, Washington

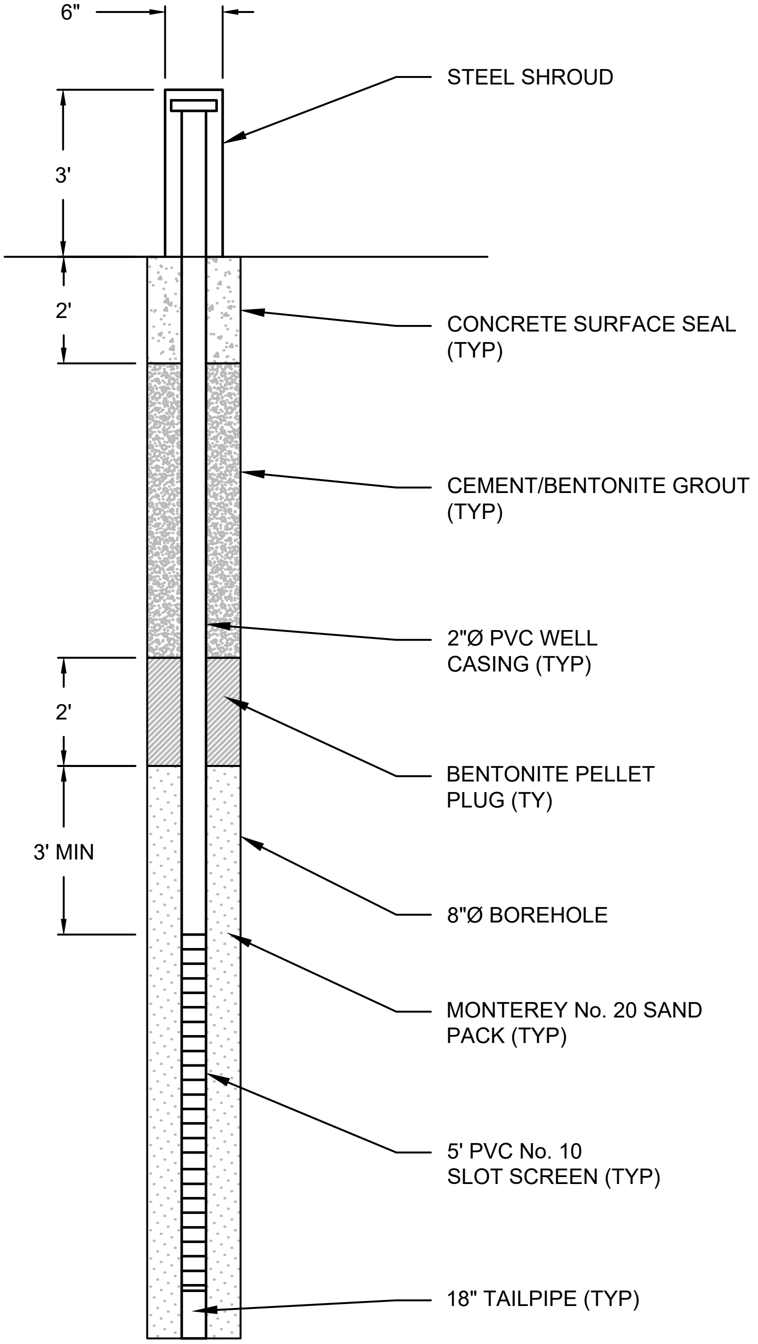


figure 5.2

TYPICAL STANDARD 2-INCH DIAMETER MONITORING WELL

Occidental Chemical Corporation, Tacoma, Washington

P:\drawings\07000s\07843\07843-REPORTS\07843-A8(146)\07843-A8(146)GN\07843-A8(146)GN-WA011.DWG Plot Date: MAR 25, 2019

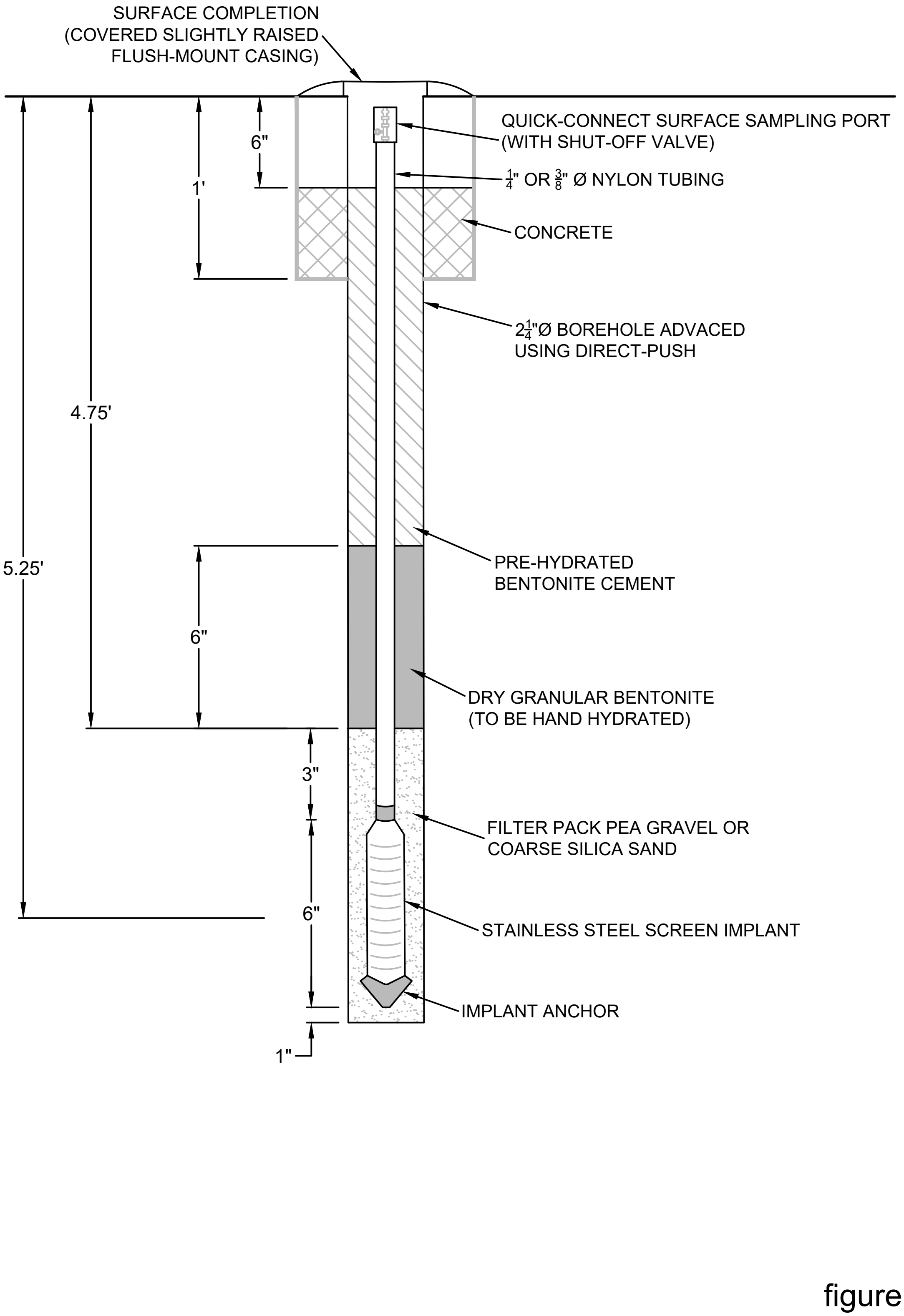


figure 6.1

TYPICAL SOIL GAS PROBE

Occidental Chemical Corporation, Tacoma, Washington

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Appendix B
Quality Assurance Project Plan

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QAPP Distribution List

Name/Organization	Number of Copies
_____________________ - GHD Project Manager	1
_____________________ - GHD Field Quality Assurance Officer	1
_____________________ - GHD Quality Assurance Officer	1
_____________________ - Laboratory Project Manager	1
_____________________ - Regulatory Agency	1

Quality Assurance Project Plan
Monitoring Plan
Occidental Chemical Corporation
Tacoma, Washington
Revision Number 1
June 2019

Prepared By: GHD Services Inc. (GHD)

Approved By: ______________________________ Date: ______________

GHD Project Manager

Approved By: ______________________________ Date: ______________

GHD Quality Assurance/Quality Control Officer

Approved By: ______________________________ Date: ______________

GHD Field Quality Assurance Officer

Approved By: ______________________________ Date: ______________

Laboratory Project Manager

Approved By: ______________________________ Date: ______________

Laboratory Quality Assurance Officer

1. Introduction

This Quality Assurance Project Plan (QAPP) presents the policies, organization, objectives, functional activities, and Quality Assurance/Quality Control (QA/QC) activities designed to achieve the specific data quality goals associated with the Monitoring Plan (MP). The MP addresses data collection at the Occidental Chemical Corporation (OCC) Site associated in part with the former OCC facility located in Tacoma, Washington (Site). The Site is located on the eastern-most peninsula of the area of ownership and operations of the Port of Tacoma (POT) that extends into Commencement Bay at the mouth of the Puyallup River Valley and is defined in a 2005 Amendment to the Administrative Order on Consent (AOC Amendment or AOC).

The objectives of this QAPP are to provide sufficiently thorough and concise descriptions of the measures to be applied during groundwater, indoor air, and soil vapor investigations such that the data generated will be of a known and acceptable level of precision and accuracy. This QAPP provides comprehensive information regarding the project personnel responsibilities, and sets forth specific procedures to be used during sampling of relevant environmental matrices and analyses of data.

A monitoring event will be performed prior to remedy implementation with the objective being to create a database for the evaluation of the post-construction remedies. Sampling of groundwater from existing wells, replacement standard wells, and proposed new standard wells will be performed. Soil vapor and indoor air monitoring will also be performed as part of an ongoing characterization of vapor intrusion at areas within the Site footprint.

The remaining sections of the QAPP outline the analytical activities and responsibilities for this investigation and are organized as follows:

Section 2 - Objective of Investigation: references the MP regarding the objective of the investigation.

Section 3 - Project Organization: describes the key project personnel and their duties.

Section 4 - Data Quality Objectives: summarizes the quality assurance objectives to achieve the required accuracy and precision.

Section 5 - Sampling Design: references the sampling design described in the MP.

Section 6 - Special Training/Certification: describes the field and laboratory training requirements.

Section 7 - Field Procedures: describes the documentation required for samples during collection, transport, and storage at the laboratory. Actual field procedures are described in the Field Sampling Plan (FSP) in Appendix A of the MP.

Section 8 - Laboratory Procedures: provides a description of the analytical methodologies to be used for the investigation. Summarizes instrument calibration and analyte identification and quantitation.

Section 9 - Quality Control: describes the different types of field and laboratory quality control required for the project.

Section 10 - Data Management Procedures: provides a summary of the laboratory's data flow from bench to final report, document control, and quality control check points.

Section 11 - Audits: describes the internal laboratory audits.

Section 12 - Data Review, Verifications, and Validation: provides a general overview of the validation of the laboratory data.

Section 13 - Data Quality Assessment: provides a summary of QA/QC topics to be included in the final report. Contains formulas for precision, accuracy, and completeness.

Section 14 - Preventive Maintenance: provides a brief description of maintenance on laboratory and field instrumentation and its documentation.

Section 15 - Corrective Action: provides a summary of the steps necessary for corrective actions.

2. Objective of Investigation

Section 1 of the MP describes the objective of the investigation.

3. Project Organization

A brief description of the duties of the key project personnel is presented below.

GHD Project Manager

- Provides day-to-day project management
- Provides managerial guidance to the GHD QA/QC Officer
- Prepares and reviews reports
- Conducts preliminary chemical data interpretation and assessment
- Responsible for overall project completion in accordance with the approved design

GHD Quality Assurance/Quality Control Officer

- Oversees and reviews laboratory activities
- Determines laboratory data corrective action
- Performs analytical data validation and assessment
- Reviews laboratory QA/QC
- Assists in preparation and review of final report
- Provides technical representation for analytical activities

- Provides managerial and technical guidance to the Field Sampling Supervisor
- Maintains officially approved QAPP document

Field Sampling Supervisor

- Provides immediate supervision of all on-Site activities
- Provides field management of sample collection and field QA/QC
- Provides technical representation for field activities
- Is responsible for maintenance of the field equipment
- Responsible that all field personnel are properly trained and certified

Laboratory - Project Manager, Analytical Contractor

- Ensures resources of laboratory are available on an as-required basis
- Coordinates laboratory analyses
- Supervises laboratory's in-house chain of custody
- Schedules analyses of samples
- Oversees review of data
- Oversees preparation of analytical reports
- Approves final analytical reports

Laboratory - Quality Assurance/Quality Control Officer, Analytical Contractor

- Overviews laboratory QA/QC
- Overviews QA/QC documentation
- Conducts detailed data review
- Decides laboratory corrective actions, if required
- Provides technical representation for laboratory QA/QC procedures
- Keeps up-to-date training records of analysts

Laboratory - Sample Custodian - Analytical Contractor

- Receives and inspects the sample containers
- Records the condition of the sample containers
- Signs appropriate documents
- Verifies chain of custody and their correctness
- Notifies laboratory Project Manager and laboratory QA/QC Officer of sample receipt and inspection
- Assigns a unique laboratory identification number correlated to the field sample identification number and enters each into the sample receiving log

- Initiates transfer of samples to the appropriate lab sections with assistance from the Laboratory Project Manager
- Controls and monitors access to and storage of samples and extracts

The analytical laboratory selected to perform the analyses will be ALS Environmental Laboratory (ALS). Soil vapor analyses, air analyses, and dissolved gases will be performed at the Simi Valley, California location, and the groundwater analyses will be performed at the Kelso, Washington location. ALS is accredited under the State of Washington Department of Ecology (WDOE) Environmental Laboratory Accreditation Program.

4. Data Quality Objectives (DQO)

4.1 Quality Assurance Objectives for Measurement Data

The overall quality assurance objective is to develop and implement procedures for sample collection and analyses, which will provide data with an acceptable level of accuracy and precision.

Quality assurance measures for this project will begin with sample containers. Groundwater sample containers will be purchased from a certified manufacturer and will be pre-cleaned (I-Chem Series 200 or equivalent). Vapor/air canisters will be rented from the laboratory. Rented canisters will be certified batched cleaned for soil vapors and individually cleaned for indoor/outdoor air according to United States Environmental Protection Agency (USEPA) Method TO-15.

4.2 Laboratory Quality Assurance

The following subsections define the quality assurance goals required to meet the DQOs of the project. A copy of the laboratory's Standard Operating Procedure (SOP) is presented in Attachment A.

4.2.1 Accuracy, Precision, and Sensitivity of Analyses

The fundamental quality assurance objective with respect to the accuracy, precision, and sensitivity of analytical data is to meet the quality control acceptance criteria of each analytical protocol. Summaries of the targeted quantitation limits are provided in Tables 4.1 (groundwater-organic analyses), 4.2 (groundwater-inorganic analyses) and 4.3 (vapor and air). It should be noted that these limits are targeted quantitation limits only; limits are highly matrix dependent and may not always be achieved.

The method accuracy (percent recovery) will be determined by spiking blank canisters and selected groundwater samples (matrix spikes) with the compounds of interest. Accuracy will be reported as the percent recovery of the spiking compounds and will compare with the criteria given in the appropriate methods, as identified in Section 8. The mathematical formula for accuracy is presented in Section 13.1.2.

The methods precision (reproducibility between duplicate analyses) will be determined based on the duplicate analysis of matrix spike samples of groundwater, a duplicate analysis of a vapor sample, and a duplicate analysis of an indoor air sample. Precision will be reported as Relative Percent

Differences (RPDs) between duplicate results. The mathematical formula for precision is presented in Section 13.1.1.

4.2.2 Completeness, Representativeness, and Comparability

A completeness requirement of 90 percent will be targeted for the program (see Section 13.1.3 for definition and mathematical formula of completeness).

The quantity of samples to be collected has been estimated in an effort to effectively represent the population being studied. Summaries of the sampling and analysis programs are presented in Table 4.4.

Analytical methods selected for this study are consistent with those used for previous studies (if applicable) to assure comparability of the data. All standards used by the laboratory will be traceable to reliable sources and will be checked with an independent standard.

4.3 Field Measurement Quality Assurance

Measurement data will be generated during field activities. These activities include, but are not limited to, the following:

i) Temperature

ii) pH

iii) Conductivity

iv) Turbidity

v) Oxidation-reduction potential

vi) Dissolved oxygen

vii) Salinity

viii) Documenting time and weather conditions

ix) Observation of sample location appearance and other conditions

The general quality assurance objective for measurement data is to obtain reproducible and comparable measurements to a degree of accuracy consistent with the use of standardized procedures.

5. Sampling (Experimental) Design

The sampling design is described in Sections 2 and 3 of the MP.

6. Special Training/Certification

GHD field personnel all hold current hazardous waste site operation (HAZWOPER) certification required by 29CFR 1910.120. GHD field personnel also undergo an extensive training program.

Field personnel must first read the SOPs and attend a series of live seminars and/or electronic courses on fieldwork topics that need to be monitored. A practical demonstration of skills learned must be provided in the field to senior staff three times, in order for field personnel to be able to work independently. These training requirements pertain to sampling procedures and the calibration/operation of field instrumentation. Field training records are stored electronically per the GHD Quality System.

7. Field Procedures

The field procedures are presented in the FSP in Appendix A of the MP.

The sample container, shipping, and packaging requirements are identified in Table 7.1 and in Section 7.1.3.

The following subsections define sample custody and document control.

7.1 Sample Custody and Document Control

The following documentation procedures will be used during sampling and analysis to provide chain of custody control during transfer of samples from collection through storage. Recordkeeping documentation will include use of the following:

i) Field logbooks (bound with numbered pages) to document sampling activities in the field

ii) Labels to identify individual samples

iii) Chain of custody record sheet to document analyses to be performed

iv) Laboratory sample custody logbook

7.1.1 Field Logbook

In the field, the sampler will record the following information in the field logbook (bound) for each sample collected:

i) Project number

ii) Sample matrix

iii) Name of sampler

iv) Sample source

v) Time and date

vi) Pertinent data (i.e., sampling duration)

vii) Analysis to be conducted

viii) Sampling method

ix) Appearance of each sample (e.g., color, particulates, effervescing)

x) Preservation added, if any

xi) Number of sample bottles collected

xii) Pertinent weather data

Each field logbook page will be signed by the sampler. Each logbook is stored in a filing cabinet located in GHD's Tacoma office per the GHD Quality System.

7.1.2 Sample Numbering

A unique sample numbering system will be used to identify each collected sample. This system will provide a tracking number to allow retrieval and cross-referencing of sample information. The sample numbering system to be used is described as follows:

Example:	WG-011618-AA-BBB-XXX
Where:	WG - Designates sample type (WG=Groundwater, SV=Soil Vapor, IA=Indoor Air, AA=Outdoor/Ambient Air, TB=Trip Blank, FD=Field Duplicate)
011618:	Date of collection (mm/dd/yy)
AA:	Sampler initials
BBB:	Location I.D.
XXX:	Unique sample number

All field samples will be numbered with a unique sample number.

Field duplicates will be submitted blind to the laboratory. The field duplicate location will be specified in the field notebook and on the field sample key submitted to data management.

7.1.3 Chain of Custody Records

Chain of custody forms will be completed for all samples collected during the program.

The chain of custody form will document the transfer of sample containers. Custody seals will be placed on each cooler (or box). The cooler (or box) will then be sealed with packing tape. Sample container labels will include sample number, place of collection, and date and time of collection. All samples should be delivered to the laboratory by same day or overnight delivery.

The chain of custody record, completed at the time of sampling, will contain, but not be limited to, the sample number, date and time of sampling, and the name of the sampler. The chain of custody document will be signed, timed, and dated by the sampler when transferring the samples.

Each sample cooler (or box) being shipped to the laboratory will contain a chain of custody form. The chain of custody form will consist of four copies which will be distributed as follows: The shipper will maintain a copy while the other three copies will be enclosed in a waterproof envelope within the cooler (or box) with the samples. The shipper's copy will be filed in the field project folder located in GHD's Tacoma office per the GHD Quality System. The cooler (or box) will then be sealed properly for shipment. The laboratory, upon receiving the samples, will complete the three remaining copies. The laboratory will retain one copy for their records. The laboratory will return one copy to the GHD QA/QC Officer upon receipt of the samples. One copy will be returned with the data deliverables package.

Upon receipt of the cooler (or box) at the laboratory, the Sample Custodian will inspect the shipping cooler (or box) and the custody seal. The Sample Custodian will note the condition of the cooler (or box) and the custody seal on the chain of custody record sheet. If the shipping cooler (or box) seal is intact, the sample containers will be accepted for analyses. The Sample Custodian will document the date and time of receipt of the container and sign the form.

If damage or discrepancies are noticed (including sample temperature exceedances), they will be recorded in the remarks column of the record sheet, dated, and signed. Any damage or discrepancies will be reported to the Laboratory Project Manager and Laboratory QA/QC Officer before samples are processed.

7.1.4 Sample Documentation in the Laboratory

Each sample or group of samples shipped to the laboratory for analysis will be given a unique identification number. The Sample Custodian will record the client name, number of samples, and date of receipt of samples in the Sample Control Logbook. Samples removed from storage for analyses will be documented in the Sample Control Logbook.

The laboratory will be responsible for maintaining analytical logbooks and laboratory data as well as a sample (on hand) inventory for submittal to the GHD QA/QC Officer on an 'as required' basis. Raw laboratory data produced from the analysis of samples submitted for this program will be inventoried and maintained by the laboratory for a period of 5 years at which time the GHD QA/QC Officer will advise the laboratory regarding the need for additional storage.

7.1.5 Storage of Samples

After the Sample Custodian has completed the chain of custody forms and the incoming sample log, the chain of custody will be checked to ensure that all samples are stored in the appropriate locations. All samples will be stored within an access controlled custody room.

7.1.6 Sample Documentation

Evidentiary files for the entire project shall be inventoried and maintained by the GHD QA/QC Officer and shall consist of the following:

i) Project related plans

ii) Project logbooks

iii) Field data records

iv) Sample identification documents

v) Chain of custody records

vi) Report notes, calculations, etc.

vii) Lab data, etc.

viii) References, copies of pertinent literature

ix) Miscellaneous - photos, maps, drawings, etc.

x) A copy of all final reports pertaining to the project

7.1.7 Field Instrumentation

Field equipment used during this investigation will be calibrated both prior to and following the day's surveys in accordance with the manufacturer's instructions. The equipment will also be operated in accordance with the manufacturer's instructions. Records of calibrations of field equipment will be recorded in a bound field notebook.

8. Laboratory Procedures

8.1 Analytical Methods

Investigative samples will be analyzed for the parameters listed in Tables 4.1, 4.2, and 4.3 using the methods cited in Table 4.4. These methods have been selected to meet the DQOs for each sampling activity.

Data deliverables for this program will include final results for the investigative samples and corresponding quality control parameters as specified in Section 10.2.

8.2 Calibration Procedures and Frequency

8.2.1 Instrument Calibration

Calibration of instrumentation is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet established reporting limits. Each instrument is calibrated with standard solutions appropriate to the type of instrument and the linear range established for the analytical method. The frequency of calibration and the concentration of calibration standards are determined by the manufacturer guidelines, the analytical method, or the requirements of special contracts.

A bound notebook will be kept with each instrument requiring calibration in which will be recorded activities associated with quality assurance monitoring and repairs program. These records will be checked during periodic equipment review and internal and external QA/QC audits.

8.2.2 Gas Chromatography/Mass Spectrometry (GC/MS)

It is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria prior to initiating any ongoing data collection. This is accomplished through the analyses of tuning compounds as specified in the analytical methods.

Calibration of the GC/MS system will consist of an initial calibration curve utilizing at least 5 points. The initial calibration curve for each compound of interest will be verified at the beginning of the day or with each 12 hours (24 hours for method TO-15) of instrument operating time.

All method-specified calibration criteria must be met prior to sample analyses. All calibrations must be performed using either average response factors or first-order linear regression (with a correlation coefficient requirement of 0.99). Higher order fits will not be allowed unless the laboratory can demonstrate that the instrument is working properly and that the instrument response over the concentration range of interest is second-order.

Quantification of samples that are analyzed by GC/MS will be performed by internal standard calibration. For quantitation, the nearest internal standard free of interferences must be used.

8.2.3 Gas Chromatography (GC)

Quantification for samples that are analyzed by GC with element selective detectors will be performed by external standard calibration. Standards containing the compounds of interest will be analyzed at a minimum of five concentrations to establish the linear range of the detector. Single point calibration will be performed at the beginning of each day and at every tenth injection. The response factors from the single point calibration will be checked against the average response factors from multi-level calibration. If deviations in response factors are greater than those allowed by the analytical method protocols, then system recalibration will be performed. Alternatively, fresh calibration standards will be prepared and analyzed to verify instrument calibration.

All method-specified calibration criteria will be met prior to sample analyses. All calibrations will be performed using either average response factors or first-order linear regression (with a correlation coefficient requirement of 0.995). Higher order fits will not be allowed.

8.2.4 Instrumentation for Inorganic Analyses

All method-specified calibration procedures will be performed and acceptance criteria will be met prior to sample analyses. Standard curves derived from data consisting of one reagent blank and a minimum of three concentrations (one reagent blank and one concentration for ion coupled plasma [ICP]) will be prepared for each inorganic analyte. Calibrations will be performed using either average response factors, or first-order linear regression (with a correlation coefficient requirement of 0.995). Higher order fits will not be allowed unless the laboratory can demonstrate that the instrument is working properly, and that the instrument response over the concentration range of interest is second-order.

The standard curve will be used with each subsequent analysis provided the standard curve is verified by using at least one reagent blank and one standard at a level normally encountered or expected in such samples. If the results of the verification are not within ±10 percent of the original curve, a new standard will be prepared and analyzed. If the results of the second verification are not within ±10 percent of the original standard curve, a reference standard will be used to determine if the discrepancy is with the standard or with the instrument.

New standards will also be prepared on a quarterly basis at a minimum. All data used in drawing or describing the curve will be so indicated on the curve or its description. A record will be made of the verification.

8.3 Compound Identification

Compounds, which will be analyzed by GC/MS, will be identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard references should be obtained on the user's GC/MS within the same 12 hours (24 hours for method TO-15) as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. The following criteria must be satisfied to verify identification:

i) The relative retention time (RRT) of the sample component is within ±0.06 RRT units of the RRT of the standard component.

ii) Correspondence of the sample component and the standard component mass spectrum.

8.4 Quantitation

The procedures for quantitation of analytes are discussed in the appropriate analytical methods. Sample results are calculated using either an external standard or an internal standard technique. External standard techniques directly compare the response from the sample to the response of the target analyte in the calibration standards. Internal standard technique utilizes the addition of a compound that resembles the target compound but is not commonly found in nature. This compound is added to all standards, samples, and quality control samples. Quantitation is based on the ratio of the target compound in the sample to the response of the internal standard in the sample compared to a similar ratio derived for each calibration standard.

8.5 Quantitation Limit Requirements

Targeted method reporting limits (MRLs) will be consistent with those presented in Tables 4.1, 4.2, and 4.3. When matrix interferences are noted during sample analysis, actions will be taken by the laboratory to achieve the specified quantitation limits. Samples will not be diluted by more than a factor of five to reduce matrix effects.

Samples may be diluted to a greater extent if the concentrations of analytes of concern exceed the calibration range of the instrument. In such cases, the laboratory QA/QC Officer will assure that the laboratory demonstrates good analytical practices and such practices are documented in order to achieve the specified quantitation limits.

9. Quality Control

9.1 Quality Control for Laboratory Analyses

Specific procedures related to internal laboratory quality control samples are described in the following subsections. The types and frequency of quality control samples is presented in Table 4.4. The laboratory is not limited to what is specified on the table, but must include it.

9.1.1 Method Blanks

A method blank will be analyzed by the laboratory at a frequency of one blank per each group of up to 20 samples analyzed or prepared at the same time. The method blank will be carried through the entire analytical procedure. No compound of interest should be detected above the quantitation limit. If a positive result is calculated, the laboratory will contact the GHD QA/QC Officer for further instructions.

9.1.2 Laboratory Control Sample/Duplicate Analyses

A laboratory control sample will be analyzed for all compounds of interest. A laboratory duplicate will be analyzed at a minimum frequency of one per analytical batch. Where method specified limits were not available, general control limits will be used. Percent recoveries will be used to evaluate analytical accuracy while the RPD between duplicate analyses will be used to assess analytical precision.

9.1.3 Matrix Spike/Matrix Spike Duplicate Analyses

An MS/MSD sample will be analyzed for all parameters, where applicable. MS/MSD or laboratory duplicate will be analyzed at a minimum frequency of one per analytical batch. Acceptable criteria and analytes that will be used for matrix spikes are identified in the methods (see Table 4.4 for methods). Where method specified limits were not available, general control limits will be used. Percent spike recoveries will be used to evaluate analytical accuracy, while the RPD between duplicate analyses will be used to assess analytical precision.

9.1.4 Surrogate Analyses

Surrogates are organic compounds which are similar to the analytes of interest, but which are not normally found in environmental samples. Surrogates are added to samples to monitor the effect of the matrix on the accuracy of the analysis. Every blank, standard, and environmental sample analyzed by GC or GC/MS, including MS/MSD samples, will be spiked with surrogate compounds prior to sample preparation.

The compounds that will be used as surrogates and the levels of recommended spiking are specified in the methods. Surrogate spike recoveries must fall within the control limits specified in the methods (see Table 4.4 for methods). If any recoveries are excessively low (<10 percent), or if all recoveries in a sample are low, the laboratory will reanalyze the sample.

9.2 Quality Control for Field Sampling

To assess the quality of data resulting from the field sampling program, field duplicate and trip blanks samples will be collected and submitted to the analytical laboratory as blind samples.

9.2.1 Field Duplicate Samples

Field duplicate samples will be collected and used to assess the aggregate precision of sampling techniques and laboratory analysis. For every 20 investigative samples, a field duplicate sample will be collected and submitted blind to the laboratory. Field duplicates will be assessed using an RPD of ±30 percent for groundwater and ±20 for vapor/air.

9.2.2 Trip Blank Sample Analysis

Trip blank samples will be collected with the groundwater samples to evaluate contamination from sample collection, transportation, storage, and analytical activities. One trip blank will be submitted per sample cooler.

9.3 Quality Control Documentation

All quality control results will be reported as part of the data package. All results will be tabulated and reported using Contract Laboratory Program (CLP)-like forms where applicable. Section 10.2 describes the requirements of the data package.

9.4 Inspection/Acceptance of Supplies and Consumables

Critical supplies and consumables for this project include field equipment, such as meters and pumps, decontamination reagents, sample bottles, and laboratory standards. The laboratory follows strict SOPs that define log in, preparation, and tracking of standards. Field equipment that is supplied by pre-approved vendors is maintained and calibrated by the vendor. All GHD-owned field equipment and reagents used in the field are ordered through the equipment manager per the GHD Quality System. The equipment manager is responsible for maintaining and calibrating all GHD-owned field instruments. All maintenance and calibrations are documented and filed. All field reagents are maintained by the equipment manager and tracked per the GHD Quality System. All field instrumentation is calibrated again in the field prior to use. This calibration is documented in the logbook and on the proper Quality System form, which is kept in the main project file.

10. Data Management Procedures

10.1 General

The contract laboratory will perform internal data verification and data review under the direction of the Laboratory QA/QC Officer. The Laboratory QA/QC Officer will be responsible for assessing data quality and advising of any data which were rated 'preliminary' or 'unacceptable' or other qualifications based on the quality control criteria outlined in the relevant methods, which would caution the data user of possible unreliability. Data reduction, verification, and reporting by the laboratory will be conducted as detailed in the following:

i) Raw data produced and checked by the responsible analysts is turned over for independent review by another analyst.

ii) The area supervisor reviews the data for attainment of quality control criteria presented in the referenced analytical methods.

iii) Upon completion of all reviews and acceptance of the raw data by the laboratory operations manager, a computerized report will be generated and sent to the Laboratory QA/QC Officer.

iv) The Laboratory QA/QC Officer will complete a thorough inspection of all reports.

v) The Laboratory QA/QC Officer and area supervisor will decide whether any sample reanalysis is required.

vi) Upon acceptance of the preliminary reports by the Laboratory QA/QC Officer, final reports will be generated and signed by the Laboratory Project Manager.

10.2 Laboratory Reporting, Data, Presentation, and Final Report

Reporting and deliverables shall include, but not be limited to, all items listed in Table 10.1.

All sample data and corresponding QA/QC data as specified in the analytical methods, shall be maintained accessible either in hard copy and/or computer data files.

The laboratory will submit one copy of the final analytical report and an electronic submission of the data within 15 business days of receipt of the final sample included in the sample delivery group (SDG). An SDG will consist of 20 field samples or all samples collected over a period of a week, whichever occurs first. All due dates will be calculated from the Friday of every sampling event. An electronic copy of the results and quality control will be in EQuIS format.

10.3 Document Control System

A document control system ensures that all documents are accounted for when the project is complete.

A project number will be assigned to the project. This number will appear on sample identification tags, logbooks, data sheets, control charts, project memos, analytical reports, document control logs, corrective action forms and logs, quality assurance plans, and other project analytical records. With the exception of field related documents, all documents are stored in a central filing area in a labeled project folder per the GHD Quality System. Field related documents are stored at GHD's Tacoma office. An electronic copy of the report is archived on the GHD network.

Electronic deliverables are maintained on a secured drive of the GHD network and are only accessible to approved GHD personnel. Electronic data deliverables are uploaded into a main project database. The database is only accessible to approved database personnel.

10.4 Quality Control Check Points and Data Flow

The following specific quality control checkpoints will be common to all analyses. They are presented with the decision points.

Chemist - Bench Level Checks

- Systems Check: sensitivity, linearity, and reproducibility within specified limits
- Duplicate analyses within control limits
- Blank spike results within control limits
- Calculation/data reduction checks: calculations cross-checked, any discrepancies between forms and results evident, results tabulated sequentially on the correct forms

Laboratory Project Manager

- Systems operating within limits
- Data transcription correct
- Data complete
- Data acceptable

Sample Control

- Samples returned to sample control following analysis

Laboratory Quality Assurance/Quality Control Officer

- Quality assurance objectives met
- Quality control checks are completed
- Final data and report package is complete

11. Audits

For the purpose of external evaluation, performance evaluation check samples are analyzed periodically by the laboratory. Internally, the evaluation of data from these samples is done on a continuing basis over the duration of a given project.

The GHD QA/QC Officer may carry out performance and/or systems audits to insure that data of known and defensible quality are consistently produced during this program.

Systems audits are qualitative evaluations of all components of field and laboratory quality control measurement systems. They determine if the measurement systems are being used appropriately. The audits may be carried out before all systems are operational during the program or after completion of the program. Such audits typically involve a comparison of the activities given in the QA/QC Plan described herein, with activities actually scheduled or performed. A special type of systems audit is the data management audit. This audit addresses only data collection and management activities.

The performance audit is a quantitative evaluation of the measurement systems used for a monitoring program. It requires testing the measurement systems with samples of known composition or behavior to quantitatively evaluate precision and accuracy. A performance audit may be carried out by or under the auspices of the GHD QA/QC Officer without the knowledge of the analyst during each sampling event for this program.

It should be noted, however, that any additional external quality assurance audits will only be performed if deemed necessary.

12. Data Review, Verification, and Validation

12.1 General

Validation of the analytical data will be performed by the GHD QA/QC Officer. The data validation will be performed in accordance with the methods and guidance from the document, "USEPA National Functional Guidelines for Superfund Organic Methods Data Review", EPA 540-R-2016-002, September 2016.

Data associated with the MP will receive a Level IV validation that includes checking all raw data and recalculations of results. Assessment of analytical and in-house data will include checks on data consistency by looking for comparability of duplicate analyses, comparability to previous data from the same sampling location (if available), adherence to accuracy and precision control criteria detailed in this QAPP and anomalously high or low parameter values. The results of these data validations will be reported to the Project Manager and the contract laboratory, noting any discrepancies and their effect upon acceptability of the data.

Raw data from field measurements and sample collection activities that are used in project reports will be appropriately identified and appended to the report. Where data have been reduced or summarized, the method of reduction will be documented in the report. Field data will be audited for anomalously high or low values that may appear to be inconsistent with other data.

13. Data Quality Assessment

Final reports will contain a discussion on QA/QC summarizing the quality of the data collected and/or used as appropriate for each phase of the project. The Project Manager who has responsibility for these summaries will rely on written reports/memoranda documenting the data assessment activities, performance and systems audits, and footnotes identifying qualifications to the data, if any.

Each summary of sampling activities will include a tabulation of the data including:

i) Field duplicate sample results

ii) Maps showing sample locations

iii) An explanation of any sampling conditions or quality assurance problems and their effect on data quality

The GHD QA/QC Officer will prepare quality assurance reports following receipt of all analytical data. These reports will include discussions of the following and their effects on the quality of the data reported:

i) Sample holding times

ii) Laboratory/method blank data

iii) Laboratory control sample recoveries

iv) Internal standard recoveries

v) Field QA/QC data

vi) Pertinent instrument performance per method protocols

vii) Audit results (if performed)

In addition, the quality assurance reports will summarize all quality assurance problems, and give a general assessment of quality assurance results versus control criteria for such parameters as accuracy, precision, etc. The quality assurance reports will be forwarded to the Project Manager.

13.1 Specific Routine Procedures Uses to Assess Data Precision, Accuracy, and Completeness

13.1.1 Precision

Precision will be assessed by comparing the analytical results between duplicate analyses. Precision as percent relative difference will be calculated as follows for values significantly greater than the associated detection limit:

$$\text{Precision} = \left| \frac{(D_2 - D_1)}{(D_1 + D_2)/2} \right| \times 100$$

- D_1 = sample result
- D_2 = duplicate sample result

For results near the associated detection limits, precision will be assessed based on the following criteria:

$$\text{Precision} = \left| \text{Original result} - \text{duplicate result} \right| < \text{CRDL}^{1}$$

13.1.2 Accuracy

Accuracy will be assessed by comparing a set of analytical results to the accepted or 'true' values that would be expected. In general, laboratory control sample recoveries will be used to assess accuracy. Accuracy as percent recovery will be calculated as follows:

$$\text{Accuracy} = \frac{A - B}{C} \times 100$$

- A = The analyte determined experimentally from the spike sample
- B = The background level determined by a separate analysis of the unspiked sample
- C = The amount of spike added

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[1] CRDL - Contract Required Detection Limit.

13.1.3 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared with the amount that was expected to be obtained under normal conditions.

To be considered complete, the data set must contain all quality control check analyses verifying precision and accuracy for the analytical protocol. In addition, all data are reviewed in terms of stated goals in order to determine if the database is sufficient.

When possible, the percent completeness for each set of samples will be calculated as follows:

$$\text{Completeness} = \frac{\text{usable data obtained}}{\text{total data planned}} \times 100 \text{ percent}$$

13.1.4 QC Exceedances

Procedures discussed previously will be followed for documenting deviations. In the event that a result deviates significantly from method established control limits, this deviation will be noted and its effect on the quality of the remaining data assessed and documented.

14. Preventative Maintenance

This section applies to both field and laboratory equipment. Specific preventive maintenance procedures for field equipment will be consistent with the manufacturer's guidelines. Specific preventive maintenance protocols for laboratory equipment will be consistent with the contract laboratory's SOPs.

All analytical instruments to be used in this project will be serviced by laboratory personnel at regularly scheduled intervals in accordance with the manufacturers' recommendations. Instruments may also be serviced at other times due to failure. Requisite servicing beyond the abilities of laboratory personnel will be performed by the equipment manufacturer or their designated representative.

Routine maintenance of the instruments will be performed as per manufacturers' recommendations. The Laboratory Project Manager is responsible for the preventive maintenance of the instruments.

15. Corrective Action

The need for corrective action may be identified by system or performance audits or by standard quality control procedures. The essential steps in the corrective action system will be:

i) Checking the predetermined limits for data acceptability beyond which corrective action is required

ii) Identifying and defining problems

iii) Assigning responsibility for investigating the problem

iv) Investigating and determining the cause of the problem

v) Determination of a corrective action to eliminate the problem (this may include reanalysis or resampling and analyses)

vi) Assigning and accepting responsibility for implementing the corrective action

vii) Implementing the corrective action and evaluating the effectiveness

viii) Verifying that the corrective action has eliminated the problem

ix) Documenting the corrective action taken

x) Follow-up audits will be performed to verify deficiencies have been corrected

For each measurement system, the laboratory QA/QC Officer will be responsible for initiating the corrective action, and the Laboratory Project Manager will be responsible for implementing the corrective action.

Table 4.1

Analytical Parameters - Groundwater (Organics)
Monitoring Plan
Tacoma, Washington

	Targeted Quantitation Limit (µg/L)
Volatile Organic Compounds (VOCs)	
1,1,1,2-Tetrachloroethane	0.5
1,1,1-Trichloroethane (TCA)	0.5
1,1,2,2-Tetrachloroethane	0.5
1,1,2-Trichloroethane	0.5
1,1-Dichloroethane	0.5
1,1-Dichloroethene	0.5
1,1-Dichloropropene	0.5
1,2,3-Trichlorobenzene	2
1,2,3-Trichloropropane	0.5
1,2,4-Trichlorobenzene	2
1,2,4-Trimethylbenzene	2
1,2-Dibromo-3-chloropropane	2
1,2-Dibromoethane (EDB)	2
1,2-Dichlorobenzene	0.5
1,2-Dichloroethane (EDC)	0.5
1,2-Dichloropropane	0.5
1,3,5-Trimethylbenzene	2
1,3-Dichlorobenzene	0.5
1,3-Dichloropropane	0.5
1,4-Dichlorobenzene	0.5
2,2-Dichloropropane	0.5
2-Butanone (MEK)	20
2-Chlorotoluene	2
2-Hexanone	20
4-Chlorotoluene	2
4-Isopropyltoluene	2
4-Methyl-2-pentanone (MIBK)	20
Acetone	20
Benzene	0.5
Bromobenzene	2
Bromochloromethane	0.5
Bromodichloromethane	0.5
Bromoform	0.5
Bromomethane	0.5
Carbon Disulfide	0.5

Table 4.1

Analytical Parameters - Groundwater (Organics)
Monitoring Plan
Tacoma, Washington

	Targeted Quantitation Limit (µg/L)
VOCs-Continued	
Carbon Tetrachloride	0.5
Chlorobenzene	0.5
Chloroethane	0.5
Chloroform	0.5
Chloromethane	0.5
cis-1,2-Dichloroethene	0.5
cis-1,3-Dichloropropene	0.5
Dibromochloromethane	0.5
Dibromomethane	0.5
Dichlorodifluoromethane	0.5
Ethylbenzene	0.5
Hexachlorobutadiene	2
Isopropylbenzene	2
m,p-Xylenes	0.5
Methylene Chloride	2
Naphthalene	2
n-Butylbenzene	2
n-Propylbenzene	2
o-Xylene	0.5
sec-Butylbenzene	2
Styrene	0.5
tert-Butylbenzene	2
Tetrachloroethene (PCE)	0.5
Toluene	0.5
trans-1,2-Dichloroethene	0.5
trans-1,3-Dichloropropene	0.5
Trichloroethene (TCE)	0.5
Trichlorofluoromethane	0.5
Vinyl Chloride	0.5
1,4-Dioxane	100
Dissolved Gases	
Ethene	1.0
Ethane	1.0

Table 4.1

Analytical Parameters - Groundwater (Organics)
Monitoring Plan
Tacoma, Washington

	Targeted Quantitation Limit (µg/L)
TCL SVOC	
1,2,4-Trichlorobenzene	10
1,2-Dichlorobenzene	10
1,2-Diphenylhydrazine	10
1,3-Dichlorobenzene	10
1,4-Dichlorobenzene	10
2,4,5-Trichlorophenol	10
2,4,6-Trichlorophenol	10
2,4-Dichlorophenol	10
2,4-Dimethylphenol	10
2,4-Dinitrophenol	25
2,4-Dinitrotoluene	10
2,6-Dinitrotoluene	10
2-Chloronaphthalene	10
2-Chlorophenol	10
2-Methyl-4,6-dinitrophenol	25
2-Methylnaphthalene	10
2-Methylphenol	10
2-Nitroaniline	25
2-Nitrophenol	10
3,3'-Dichlorobenzidine	25
3-Nitroaniline	25
4-Bromophenyl Phenyl Ether	10
4-Chloro-3-methylphenol	10
4-Chloroaniline	10
4-Chlorophenyl Phenyl Ether	10
4-Methylphenol	10
4-Nitroaniline	25
4-Nitrophenol	25
Acenaphthene	10
Acenaphthylene	10
Aniline	25
Anthracene	10
Azobenzene	10
Benz(a)anthracene	10
Benzo(a)pyrene	10

Table 4.1

Analytical Parameters - Groundwater (Organics)
Monitoring Plan
Tacoma, Washington

	Targeted Quantitation Limit (µg/L)
SVOCs-Continued	
Benzo(b)fluoranthene	10
Benzo(g,h,i)perylene	10
Benzo(k)fluoranthene	10
Benzoic acid	25
Benzyl alcohol	10
Bis(2-chloroethoxy)methane	10
Bis(2-chloroethyl) Ether	10
2,2'-Oxybis(1-chloropropane)	10
Bis(2-ethylhexyl) Phthalate	10
Butyl Benzyl Phthalate	10
Chrysene	10
Dibenz(a,h)anthracene	10
Dibenzofuran	10
Diethyl Phthalate	10
Dimethyl Phthalate	10
Di-n-butyl Phthalate	10
Di-n-octyl Phthalate	10
Fluoranthene	10
Fluorene	10
Hexachlorobenzene	10
Hexachlorobutadiene	10
Hexachlorocyclopentadiene	10
Hexachloroethane	10
Indeno(1,2,3-cd)pyrene	10
Isophorone	10
Naphthalene	10
Nitrobenzene	10
N-Nitrosodimethylamine	25
N-Nitrosodi-n-propylamine	10
N-Nitrosodiphenylamine	10
Pentachlorophenol	25
Phenanthrene	10
Phenol	10
Pyrene	10

Notes:

TCL	- Target Compound List
VOCs	- Volatile Organic Compounds
SVOCs	- Semi-Volatile Organic Compounds

Table 4.2

Analytical Parameters - Groundwater (Inorganics)
Monitoring Plan
Tacoma, Washington

	Targeted Quantitation Limit (µg/L)
Metals	
Silica (Silicon, as SiO2)	430
General Chemistry	
Specific Gravity	-

Table 4.3

Analytical Parameters - Vapor and Air Monitoring Plan
Tacoma, Washington

	Targeted Quantitation Limit ($\mu g/m^3$)
Volatile Organic Compounds (VOCs)	
Tetrachloroethene	0.53
Trichloroethene	0.53
Vinyl Chloride	0.53
Propene	0.52
Dichlorodifluoromethane (CFC 12)	0.52
Chloromethane	0.5
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	0.51
1,3-Butadiene	0.52
Bromomethane	0.5
Chloroethane	0.51
Ethanol	5.1
Acetonitrile	0.52
Acrolein	1.0
Acetone	5.4
Trichlorofluoromethane	0.53
2-Propanol (Isopropyl Alcohol)	2.1
Acrylonitrile	0.52
1,1-Dichloroethene	0.54
Methylene Chloride	0.54
3-Chloro-1-propene (Allyl Chloride)	0.53
Trichlorotrifluoroethane	0.53
Carbon Disulfide	1.1
trans-1,2-Dichloroethene	0.53
1,1-Dichloroethane	0.52
Methyl tert-Butyl Ether	0.54
Vinyl Acetate	5.3
2-Butanone (MEK)	1.0
cis-1,2-Dichloroethene	0.53
Ethyl Acetate	1.1
n-Hexane	0.54
Chloroform	0.54
Tetrahydrofuran (THF)	0.53
1,2-Dichloroethane	0.53
1,1,1-Trichloroethane	0.54
Benzene	0.52
Carbon Tetrachloride	0.52
Cyclohexane	1.0
1,2-Dichloropropane	0.54
Bromodichloromethane	0.53
1,4-Dioxane	0.53
Methyl Methacrylate	1.1
n-Heptane	0.54
cis-1,3-Dichloropropene	0.56
4-Methyl-2-pentanone	0.53
trans-1,3-Dichloropropene	0.53
1,1,2-Trichloroethane	0.54
Toluene	0.53
2-Hexanone	0.54

Table 4.3

Analytical Parameters - Vapor and Air Monitoring Plan
Tacoma, Washington

	Targeted Quantitation Limit ($\mu g/m^3$)
Volatile Organic Compounds (VOCs)	
Dibromochloromethane	0.54
1,2-Dibromoethane	0.54
n-Butyl Acetate	0.54
n-Octane	0.54
Chlorobenzene	0.53
Ethylbenzene	0.52
m,p-Xylenes	1.1
Bromoform	0.53
Styrene	0.53
o-Xylene	0.53
n-Nonane	0.54
1,1,2,2-Tetrachloroethane	0.53
Cumene	0.53
alpha-Pinene	0.52
n-Propylbenzene	0.54
4-Ethyltoluene	0.53
1,3,5-Trimethylbenzene	0.53
1,2,4-Trimethylbenzene	0.53
Benzyl Chloride	1.1
1,3-Dichlorobenzene	0.54
1,4-Dichlorobenzene	0.54
1,2-Dichlorobenzene	0.54
d-Limonene	0.51
1,2-Dibromo-3-chloropropane	0.52
1,2,4-Trichlorobenzene	0.53
Naphthalene	0.51
Hexachlorobutadiene	0.53

Table 4.4

Sampling and Analysis Summary
Monitoring Plan
Tacoma, Washington

Matrix	Analytical Parameter	Analytical Method	Estimated Number of Samples	Field Duplicates	Trip Blanks	MS/MSD/Dup
Groundwater						
	TCL VOCs	SW-846-8260C	73	4	1 / day	4/4/0
	TCL SVOCs	SW 846 8270D	73	4	-	4/4/0
	Specific Gravity	ASTM D1429-03	73	4	-	0/0/4
	Dissolved Gases	RSK 175	73	4	-	4/4/0
	Silica	SW 846 6010	73	4	-	4/4/0
Soil Vapor						
	VOCs	TO-15	10	1	-	1/0/1
Indoor/Outdoor Air						
	VOCs	TO-15	4	1	-	1/0/1

Notes:

Dup	- Duplicate
MS	- Matrix Spike
MSD	- Matrix Spike Duplicate
TCL	- Target Compound List
VOCs	- Volatile Organic Compounds
SVOCs	- Semi-Volatile Organic Compounds

Table 7.1

Sample Container, Preservation, and Holding Time Periods
Monitoring Plan
Tacoma, Washington

Analyses	Sample Containers	Preservation	Maximum Holding Time	Notes
Groundwater				
TCL VOCs	Three 40 mL glass vials Teflon-lined septum	pH <2, HCl Cool <6°C	14 days from collection to analysis	Fill completely with no head space
TCL SVOCs	Two 1L glass	Cool <6°C	7 days from collection to extraction 40 days from extraction to analysis	Fill completely to neck
Specific Gravity	1L plastic	Cool <6°C	7 days	Fill completely
Dissolved Gases	Three 40 mL glass vials Teflon-lined septum	Cool <6°C	14 days from collection to analysis	Fill completely with no head space
Silica	One 1L plastic	HNO3 to pH<2 Cool <6°C	6 months from collection to analysis	Fill completely to neck
Vapor and Air				
VOCs	6L stainless steel canister	none	30 days	Fill to a residual vacuum of 2-10" Hg

Notes:

HCl	- Hydrochloric Acid
HDPE	- High Density Polyethylene
VOCs	- Volatile Organic Compounds
SVOCs	- Semi-Volatile Organic Compounds

Table 10.1

Laboratory Reporting Deliverables
Monitoring Plan
Tacoma, Washington

A detailed report narrative should accompany each submission, summarizing the contents and results.

A. Chain of Custody Documentation and Detailed Narrative (1)

B. Sample Information
   1. date collected
   2. date extracted or digested
   3. date analyzed
   4. analytical method and reference

C. Data (including all raw data and CLP-like summary forms)
   1. samples
   2. laboratory duplicates (2)
   3. method blanks
   4. spikes, spike duplicates (2) (3)
   5. surrogate recoveries (2)
   6. internal standard recoveries
   7. calibration
   8. any other applicable quality control (QC) data (e.g., serial dilution)
   9. tentatively identified compounds (TICs) (if applicable)

D. Miscellaneous
   1. method detection limits and/or instrument detection limits
   2. percent solids (where applicable)
   3. metals run logs
   4. standard preparation logs
   5. sample preparation logs

All sample data and its corresponding quality assurance/quality control (QA/QC) data shall be maintained accessible to GHD in electronic format.

Notes:

(1) - Any QC outliers must be addressed and corrective action taken must be specified
(2) - Laboratory must specify applicable control limits for all QC sample results
(3) - A blank spike must be prepared and analyzed with each sample batch

Attachment A

SOPs (Standard Operation Procedures)

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AIR SAMPLES COLLECTED IN SPECIALLY PREPARED CANISTERS AND GAS COLLECTION BAGS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

DOCUMENT I.D. VOA-TO15

Approved By: Kate Kaneko Date: 8/6/18
Interim Laboratory Manager – Kate Kaneko

Prepared By: Chaney Arend Date: 8/3/18
Quality Assurance Manager – Chaney Arend

Prepared By: Chris Parnell Date: 8/3/18
Technical Services Manager – Chris Parnell

Prepared By: Wida Ang Date: 8/3/18
Team Leader (VOA GC/MS) – Wida Ang

Doc Control ID:	Uncontrolled	Archived Date:	

SOP CHANGE FORM

SOP Title: Determination of Volatile Organic Compounds in Air Samples Collected in Specially Prepared Canisters and Gas Collection Bags by Gas Chromatography/Mass Spectrometry (GC/MS)
SOP Code: VOA-TO15
SOP Revision No.: 25
SOP Date: 08/18/18
SOP Section(s) Affected by Change: 7.3 & Attachment 4

Description of Change: Remove 14 day hold time requirement for Region 9 samples collected in canisters.

Reason(s) for Change(s): Determined there is no documentation requiring a 14 day hold time for Region 9 samples collected in canisters.

Change(s) Submitted by: Chaney Arend	Date: 02/08/19

Approvals:

QA Manager Signature: Chaney Arend By Chaney Arend at 5:38 pm, Feb 08, 2019	Date:
Supervisor/Manager Signature: NA	Date: NA

Change(s) Effective Date: 02/08/19

Distribution: Original filed with original SOP
Copy attached to each controlled copy

Complete on hardcopy filed with original SOP
Verified electronic copy attached: ☐

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1) Scope and Applicability

1.1 This procedure is based on and incorporates the requirements detailed in EPA Compendium Methods TO-15 and TO-14A and is used to quantify a wide range of volatile organic compounds (VOCs) in gaseous matrices collected in gas collection bags (method modification) and specially prepared stainless steel canisters or glass bottles. This method typically applies to ambient concentrations of VOCs 0.50ug/m3 (down to 0.10ug/m3 for low level ambient analyses) and above for the SCAN mode and 0.010ug/m3 and above for the SIM mode; however, refer to Tables 3 and 3A for the specific laboratory initial calibration ranges for each target compound. The method requires VOC enrichment by concentrating up to one liter of a sample volume, with a virtually unlimited upper concentration range using dilutions from source level samples.

In this document, Tables 2 and 2A (see Note 1 below) list compounds that can be determined by this procedure along with their corresponding laboratory method reporting limits (MRLs) and method detection limits (MDLs). The reported MRL may be adjusted higher; however, the capability of achieving lower MRLs for specific project requirements must be thoroughly demonstrated (by an acceptable initial calibration and method reporting limit check standard) and documented as long as the MRL is higher than the current method detection limit for each compound. Additional compounds may be analyzed according to this procedure as described in the referenced methods as long as the requirements of this document are adhered to. The number of samples that may be analyzed in a 24-hour period is about twenty. The number of sample results that may be reduced in an eight-hour day is approximately twenty.

2) Summary of Procedure

2.1 The analytical method involves using a high-resolution gas chromatograph (GC) coupled to a mass spectrometer (MS). The GC/MS utilizes a linear quadrupole system, which allows for it to be operated by either continuously scanning a wide range of mass to charge ratios (SCAN mode) or by Select Ion Monitoring mode (SIM), which consists of monitoring a small number of ions from a specified compound list.

An aliquot of an air sample is concentrated on a solid adsorbent trap (either cryogenically or fan cooled glass beads or stronger adsorbents at higher temperatures) to collect the analytes of interest. To remove co-collected water vapor, the concentrated sample then goes through a water removal (dry purge) step. After the sample is pre-concentrated on a trap, the trap is heated and the VOCs are thermally desorbed onto a refocusing cold trap. The VOCs are then thermally desorbed onto the head of a capillary column once the cold trap is heated. The oven temperature (programmed) increases and the VOCs elute and are detected by the mass spectrometer.

Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This method utilizes the internal standard calibration technique; refer to Section 3.16 for a complete definition.

3) Definitions

3.1 Cryogen A refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Liquid nitrogen (cryogen) is used for this purpose and it has a boiling point of -195.8°C.

3.2 Gauge Pressure Pressure measure with reference to the surrounding atmospheric (barometric) pressure, usually expressed in units of psig. Zero gauge pressure is equal to atmospheric pressure.

3.3 MS-SCAN Mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

3.4 MS-SIM Mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

3.5 Analytical Sequence The analytical sequence describes exactly how the field and QC samples in an analytical batch are to be analyzed.

3.6 Neat Stock Standard A purchased, single component assayed reference material having a stated purity used to prepare working calibration standards.

3.7 Stock Standards Solution A concentrated solution of one or more target analytes at a known concentration purchased from a reputable commercial vendor. Stock standard solutions are used to prepare working calibration standards.

3.8 Intermediate Calibration Standard A solution of one or more target analytes at a known concentration prepared either from one or more neat stock standards or from one or more stock standards solutions.

3.9 Working Calibration Standard A solution of all the target analytes at a known concentration prepared either from one or more intermediate calibration standards and/or from one or more stock standard solutions.

3.10 Calibration or Standard Curve A calibration or standard curve is a graph which plots the concentration of a compound (or an analyte) versus the instrument response to the compound.

3.11 Initial Calibration Verification (ICV) Standard A solution prepared in the laboratory containing known concentration(s) of analytes of interest. The solution is prepared from neat stock standards and/or stock standards solutions which are from a different source than the standards used to prepare the working calibration standards.

3.12 Continuing Calibration Verification (CCV) Standard A working calibration standard which is analyzed at specific intervals in order to verify that the instrument continues to meet the calibration criteria.

3.13 Field Sample A sample collected and delivered to the laboratory for analysis.

3.14 Manual Integration This term applies to a data file in which setpoints have been changed and reintegration has occurred under the changed setpoints; baselines have been adjusted; peak integration start and stop “ticks” have been changed; peak area, or peak height, are changed after the time of data collection and data file generation.

3.15 Batch Quality Control (QC) Batch QC refers to the QC samples that are analyzed in an analytical batch of field samples and includes the Method Blank (MB), Laboratory Control Sample (LCS) and Laboratory Duplicate (LD).

3.16 Internal Standard Calibration Compares the instrument responses from the target compound in the sample to the responses of specific standards (called internal standards), which are added to the sample or sample preparation prior to analysis. The ratio of the peak area (or height) of the target compound in the sample or sample preparation is compared to a similar ratio derived for each calibration standard.

3.17 May This action, activity, or procedural step is neither required nor prohibited.

3.18 Must This action, activity, or procedural step is required.

3.19 Shall This action, activity, or procedural step is required.

3.20 Should This action, activity, or procedural step is suggested, but not required.

3.21 SOP Standard Operating Procedure

3.22 Service Request A form generated, at the time of sample receipt, which details pertinent information such as client name, address, contact, client and laboratory sample identifications, sampling and receipt dates and times, requested analyses, sample type, canister pressures (initial and final), and the service request number (unique number for each submitted job) and serves as an inter-laboratory "custody" form which accompanies all samples throughout the laboratory.

3.23 Selectivity Selectivity of a method refers to the extent to which it can determine particular analyte(s) in a complex mixture without interference from other components in a mixture. Another definition is the extent to which a particular method can be used to determine analytes under given conditions in the presence of other components of similar behavior.

3.24 Limit of Detection (LOD) The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%. (DoD Clarification). For consistency purposes, the LOD may be referred to as the MDL once it is reported; however, full verification will be on file in the laboratory per the procedures detailed in this document.

3.25 Limit of Quantitation (LOQ) The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. (DoD Clarification). For consistency purposes and since the LOQ and MRL are equivalent with regards to laboratory procedure, the LOQ will be referred to as the MRL in this document and once it is reported. Full verification will be on file in the laboratory per the procedures detailed in the document.

3.26 Detection Limit (DL) / Method Detection Limit (MDL) The smallest analyte concentration that can be demonstrated to be different from zero or a blank concentration at the 99% level of confidence. At the DL, the false positive rate (Type 1 error) is 1%. (DoD Clarification). For consistency purposes, the DL may be referred to as MDL. Also, as far as reporting is concerned the MDL will be raised up (where necessary) to the verified LOD per the procedures defined in this document and reported accordingly.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP may perform analysis, interpretation and peer review of the results. Data reduction and/or peer review may be performed by another qualified employee. This employee must be familiar with the analytical technique and have completed a data review training plan to ensure familiarity with specific analysis and requirements.

4.2 The supervisor/manager must ensure that method proficiency is documented initially and whenever significant changes in the instrument type, personnel, and matrix or test method are made.

4.3 The department supervisor/manager or designee shall perform final review and sign-off of the data.

5) Interferences

5.1 Canisters

Canisters shall be stored in a contaminant free location and shall be capped tightly during shipment to prevent leakage and minimize any compromise of the sample. The pressure/vacuum is checked prior to shipment and upon receipt from the field. Any problems with the sample from the field are noted and the Project Manager contacted.

Also, canisters must be cleaned and certified to be free from target analytes before being shipped to the field for sample collection. The procedure is described in detail in the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters* (refer to this procedure as well as Section 12.7 for the acceptance criteria).

Current laboratory practice entails the segregation of 6L canisters into ambient (low) level and source levels. All the ambient canisters are used for low level (indoor air, ambient air) projects and not intentionally for soil gas, SVE monitoring, or other higher level applications. It may be necessary to “retire” an ambient canister and re-assign for source level use if high concentrations are encountered. This decision will be made by management based on analytical concentrations and what compounds were encountered at these levels. If the level of any analyte is detected above 5,000ug/m*3* in the ambient can, then the supervisor/team leader must be contacted to determine if the canister(s) is to be retired. If retirement is decided upon, make a notation on the sample tag (or other color coded tag) of each canister in question. The notation must contain the analyte, threshold levels and retirement from ambient use (initial and date notation) so that the canister conditioning/management department may properly execute the retirement.

5.2 Analytical System

The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with buna-N rubber components must be avoided.

5.3 Carbon Dioxide

Excessive levels of carbon dioxide present in a sample may interfere with analysis by freezing up the cryogenic trap. A smaller aliquot must be analyzed to eliminate this problem, or the sample should be analyzed using the higher temperature multi-adsorbent trapping technique which allows carbon dioxide to pass.

5.4 Gas Collection Bags

This procedure covers the use of gas collection vessels such as Tedlar® or Mylar® bags. However, due to the nature of these types of bags it is not recommended that clients use this option for ambient air samples. Sample collection bags made out of Tedlar®

have contaminants that are inherent to the manufacturing process. The two main contaminants are phenol and N,N-Dimethylacetamide. However, this only becomes a problem when the concentration levels in the sample are low ppbv such as ambient air monitoring samples where more of the sample usually has to be concentrated and analyzed. To minimize the loss of sample integrity, a 72-hour hold time has been incorporated into the procedure.

5.5 Glassware

Interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware results in discrete artifacts and/or elevated baselines in the detector profiles should be minimized. All glassware associated with this method must be scrupulously cleaned to avoid possible contamination. The cleaning shall be performed in accordance with the procedure outlined in the *SOP for Glassware Cleaning*. The use of high purity water, reagents, and solvents helps to minimize these problems.

6) Safety

6.1 Each compound, mixture of compounds, standards, and surrogates, as well as samples, should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest level possible through the use of gloves (to minimize absorption through the skin) and hoods (to minimize inhalation). Refer to the laboratory waste management plan for the safe disposal of chemicals and samples.

6.2 Safety Data Sheets (SDS)

The analyst should consult SDS for compounds being handled in the course of this procedure, and be familiar with proper safety precautions to be followed when handling hazardous chemicals. Care should be taken when handling standard material in a neat or highly concentrated form.

6.3 Liquid Nitrogen

Liquid nitrogen can cause serious tissue damage (frostbite) with only a few seconds of contact. The valves on the cryogen dewars should be opened slowly so leaky fittings can be identified. Neoprene or leather gloves should be worn when turning valves and handling tubing and fittings that have been in contact with the cryogen.

6.4 Protective Clothing

Personal protective clothing (safety glasses, gloves and lab coat) are required when preparing standards and handling standard material in neat form.

6.5 Pressurized Gases

The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp when not in use. The regulator should never remain on small “D” size cylinders following use. Sources of flammable gases (i.e. pressurized hydrogen) should be clearly labeled.

6.6 Syringes

The proper use of syringes should be part of employee training for this SOP. Care should be taken to avoid personal injury as a result or improper handling techniques.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Air samples are collected in the field and delivered to the laboratory and shall be collected in either a specially prepared, leak-free, passivated stainless steel canister (with valve) of desired volume (e.g., 6L), a glass sampling bottle (Bottle Vac, Entech Inntruments) or a sample collection bag (Tedlar). Canister samples may either be grab or time integrated (using a variable flow controller, refer to the *SOP for Flow Controllers and Critical Orifices*) utilizing the canister vacuum to draw the sample. Bags require the use of an upstream pump or a “lung machine.”

7.2 There are no special preservation requirements for either canisters, Bottle Vacs or bags. However, bags should be stored in an environment free from puncture or deterioration sources (by hanging them from clips), labeled with the specific service request number, in accordance with the *SOP for Laboratory Storage, Analysis and Tracking*. Canisters and bottles should be stored on the appropriate shelves until they are to be analyzed.

7.3 Sample collection bags must be analyzed within 72 hours from the confirmed time of sampling. Samples received by the laboratory shall be analyzed within 30 days of sampling or sooner if project specific requirements dictate. Programs, which have shorter recommended or required hold times, include the Department of Toxic Substances Control (DTSC), which advises a 72 hour hold time. The Minnesota Pollutions Control Agency (MPCA) and EPA Region 9 both require a 14 days hold time. Additionally, the MPCA does not allow the use of Tedlar bags for sampling or sample dilution. The DTSC requirement is an advisory notice, but the laboratory shall make every effort to comply. However, the following statement shall be added to each report where sample analyses do not meet the 72 hour hold time and the client project is intended to comply with DTSC requirements. “The recommended 72-hour hold time for the analysis of TO-15 was exceeded per the DTSC and LARWQCB Advisory – Active Soil Gas Investigations document dated January 28, 2003; however, this specific hold time statement is advisory and not considered as regulation. In addition, the samples were analyzed within the EPA Method TO-15 stated requirement of 30 days.”

8) Apparatus and Equipment

8.1 Additional instruments and/or differing models may be utilized as long as they are equivalent and meet the minimum requirements of this document.

8.2 Gas Chromatograph (GC)

An instrument capable of temperature programming, with a column oven that may be cooled to sub-ambient temperature at the start of the gas chromatographic run to result in the resolution of the VOCs.

Hewlett Packard 5890 Series II Plus
Hewlett Packard 6890 Series
Hewlett Packard 6890A Series
Agilent 6890N Series
Agilent 7890A Series
Agilent 7890B Series

8.3 Autosampler

Tekmar-Dohrmann AUTOCan Autosampler: 14-ACAN-074

Markes Autosampler:	UNITY 2/CIA Advantage
Concentrating Trap (cryogenic trap, built-in):	14-6938-020
Cryofocusing Module w/split valve:	14-6520-A00
GAST Vacuum Pump:	DOA-P104-AA or equivalent

8.4 Mass Spectrometer (MS)

A MS capable of scanning from 34 to 350 amu every second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Bromofluorobenzene (BFB) which meets all of the criteria when 50ng or less of BFB is injected onto the GC/MS system.

Hewlett Packard 5972 Series
Hewlett Packard 5973 Series
Agilent 5973N
Agilent 5973 *inert*
Agilent 5975B *inert*
Agilent 5975C *inert*
Agilent 5977A

8.4.1 Ionization Gauge Controller

- Agilent: 59864B
- Granville-Phillips 330 Ionization Gauge Controller: 330001/2/3
- Hewlett Packard Ionization Gauge Controller: 59864B

8.5 Analytical Column

Any analytical column capable of separating the compounds of interest may be used. The capillary column should be directly coupled to the source of the mass spectrometer. The following are suggested columns; an alternative column may be used as long as sufficient peak resolution and separation is achieved.

- Restek Rxi-1ms Fused Silica Capillary Column; 30m x 0.25mm ID 1.0µm film thickness

  OR

- Restek Rxi-1ms Fused Silica Capillary Column; 60m x 0.25mm ID 1.0µm film thickness

8.6 Data Systems

IBM-compatible PC with Windows 95/98/NT/XP/7 (Microsoft Office EXCEL version 2003 or newer) and Hewlett Packard Chemstation software including EnviroQuant with Extracted Ion Current Profile (EICP), National Institute of Standards and Technology (NIST) library (2011 version or newer) or equivalent.

8.7 Canister Pressurization Station

Vacuum/Pressure Gauge [0 to –30 inHg; 0-90 or 100 psig]

8.8 Canister Sampling Devices

Refer to the *SOP for Flow Controllers and Critical Orifices* for specific calibration and other pertinent information.

- VICI Condyne Model 300 Flow Controller
- Critical Orifices (Laboratory manufactured)

8.9 Gas Collection Devices

- Lab Commerce, Aerosphere Model S6L, 6.0L Passivated Canisters or equivalent
- Lab Commerce, Stabilizer Model 22.4L, 2.4L Canisters or equivalent
- Restek Corporation, #24203, 3.0L Silco Canisters or equivalent
- Tedlar bags – 0.5L, 1L, 3L, 5L, 10L, 25L, and 40L (other sizes are available; however, the volumes that are listed encompass the majority of the bags supplied and the samples submitted to the laboratory).
- Entech Instrument, SiloniteTM Canisters or equivalent
- Entech Instruments, Bottle Vacs or equivalent

8.10 Dynamic Dilution System

- Entech Dynamic Diluter Model 4620A
- Toshiba laptop computer Model 2210CDT/6.0 and Software NT460

9) Standards, Reagents, and Consumable Materials

9.1 Reagents and Equipment

9.1.1 UHP Grade Helium (99.999%) (GC carrier gas, preconcentrator purge/sweep gas, pressurization gas)

9.1.2 Cryogen - Liquid nitrogen from bulk tank or 50 psig dewars (used to cool preconcentrator traps)

9.1.3 UHP/Zero Grade Air (canister pressurization)

9.1.4 ASTM Type II Water, DI water or equivalent

9.1.5 UHP Grade Nitrogen (99.999%) (additional pressurization gas, based on other methods requested – modification to method)

9.2 Standards

Standards are prepared for both SCAN and Selective Ion Monitoring (SIM) modes according to the procedures detailed in this section. The preparation of standards for the analysis of air samples is carried out by following the procedure, “Preparation of Gas Phase Standards for Ambient Air Analysis”, Application Note, Spring 96, Vol. 6.5, *Tekmar*-DOHRMANN AutoCan User’s Manual. Neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

9.2.1 Instrument Performance Check, Internal Standard and Surrogate Spiking Mixture
Prepare a standard solution of p-Bromofluorobenzene (BFB-used as both a tune check and surrogate compound), bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene, 1,2-dichloroethane-d4(surrogate), and toluene-d8(surrogate) at 500µg/m^3 each in humidified zero air (Section 8.2.1.2). Prepare this standard according to the procedure outlined in Volume 6.5 of the *Tekmar*-

DOHRMANN Application Note. This standard may also be prepared from a neat cocktail as in Section 9.2.2.2.1 or as stated in Section 9.2.1.3.

9.2.1.1 An intermediate standard is prepared from neat compounds in a glass static dilution bottle (SDB). After the volume of the SDB is determined, calculate the mass of each compound to be spiked to achieve a final concentration of 5.0μg/ml. Then use the density of each neat compound to calculate the microliter amount to be spiked into the SDB. The SDB is then heated for a minimum of one hour at ~60°C to completely volatilize all components.

Concentration of the intermediate standard prepared in a SDB is 5.0μg/mL. The amount required to achieve this concentration is determined through the use of the following equation.

$$A = \frac{(C)(V)}{D} \qquad \text{(Equation 1)}$$

Where:

A Amount of each compound required to achieve the desired concentration of the standard in the SDB (μL)
C Desired concentration of SDB (μg/mL)
V Actual volume of the SDB (mL)
D Density of the compound in question (μg/μL)

Example:

Calculate the amount of neat bromochloromethane needed to achieve the final concentration of 5.0μg/mL of that compound in the SDB.

V = 2010mL
D = 1934.4μg/μL
C = 5.0μg/mL

$$A = \frac{\left(5.0\,\frac{\mu g}{mL}\right) 2010\,mL}{1934.4\,\frac{\mu g}{\mu L}} = 5.2\mu L$$

Density (μg/μL)	Compound
1934.4	Bromochloromethane
1170.1	1,4-Difluorobenzene
1157	Chlorobenzene-d5
1307	1,2-Dichloroethane-d4
943	Toluene-d8
1593	BFB

9.2.1.2The Working standard is prepared in a canister by spiking an aliquot of the stock SDB standard (Section 9.2.1.1) using a heated gastight syringe. Connect a cleaned, evacuated canister to a source of pure diluent gas (humidified zero air) using a Teflon line with a stainless steel tee directly above the canister valve. One port of the tee is fitted with a septum. Spike the SDB stock and following removal of syringe a small flow of diluent gas to flush the spike into the can. Pressurize the can to positive 83.3 psig with humid zero air, and allow the contents to equilibrate for approximately 24 hours before using.

Concentration of the working standard prepared in a canister is 500ng/L. The final pressure of the canister is 83.3psig; therefore, the pressurized volume is 40L, which is obtained through the use of the following equation.

$$PV = PDF(V) \qquad \text{(Equation 2)}$$

Where:

PV Pressurized canister volume (L)

PDF Pressure Dilution Factor, where PF = $\dfrac{P_{atm} + P_f}{P_{atm} + P_i}$

P_f Final Canister Pressure

P_i Initial Canister Pressure

V Volume of canister at 1atm

P_{atm} Atmospheric Pressure = 14.7psig

Example:

$$\frac{14.7 + 83.3}{14.7 + 0}(6L) = 40\text{L}$$

In order to prepare the canister with a concentration of 500ng/L, it must be determined how much of the intermediate standard is required. This is achieved through the use of the following equation.

$$A = \frac{(F)(V)}{(C)\left(1000\frac{ng}{\mu g}\right)} \qquad \text{(Equation 3)}$$

Where:

F Desired concentration of working standard (ng/L)

V Pressurized Volume of Canister (L)

C Concentration of prepared SDB (µg/mL)

A Amount of standard (mL) of the SDB required to obtain the desired working standard concentration

Example:

$$A = \frac{500\frac{ng}{L}(40L)}{\left(5.0\frac{\mu g}{mL}\right)\left(1000\frac{ng}{\mu g}\right)} = 4mL$$

9.2.1.3 Currently the working standard is purchased in a cylinder at a certified concentration of 500ng/L (prepared by Linde SPECTRA Environmental Gases, Alpha, NJ).

The internal standard (IS) cylinder comes from the vendor with a one year expiration date. These compounds should be stable in the high-pressure cylinder for five years or longer so the laboratory will extend the expiration date to two years from the date of preparation. The working standards are canisters filled directly from the main cylinder and are given a two month expiration when prepared in a 6L canister and a six month expiration when prepared in a 30L or greater canister. The method utilized relative response factors for target analyte quantitation so the IS concentrations are factored out since they appear in the numerator and denominator of the final calculation.

A quantitation report with chromatogram of a TO-15 blank run will be printed as soon as a new IS cylinder is put into use and again after one year. The latter will be checked for any unexpected peaks to look for possible degradation of the IS compounds in the cylinder. These shall be kept on file with the original certificate of analysis.

9.2.1.3.1 For SCAN analyses, the working standard is filled directly into a canister to a pressure of 70 to 80 psig.

9.2.1.3.2 For SIM analyses, the working standard is diluted and pressurized with humid zero air to the desired concentration using Equation 2 in Section 9.2.1.2. Typical concentrations will be 20ng/L, 40ng/L or 50ng/L.

9.2.2 Initial Calibration (ICAL) Standard Prepare the primary source calibration standards in canisters with nominal concentrations of 1ng/L (optional), 20ng/L and 200ng/L for analyses in SCAN mode and 0.1ng/L, 5.0ng/L, and 200ng/L for analyses in Selective Ion Monitoring (SIM) mode for each of the target analytes. Differing injection volumes will create the standard concentrations listed in Tables 3 (SCAN) and 3A (SIM) of this document. The full list of analytes which are analyzed according to this method can also be found in Tables 2 (SCAN) and 2A (SIM).

Standards are prepared by diluting the stock standard with humid zero air into a canister. The stock standard is a certified custom-blended cylinder (prepared by Linde SPECTRA Environmental Gases, Alpha, NJ). Refer to Tables 3 and 3A for the list of analytes and certified concentrations in the purchased cylinder.

9.2.2.1 Working standards are prepared into canisters using the Entech Dynamic Diluter. Turn on the power to the diluter one hour prior to using to allow for the components to come to thermal equilibrium. Connect the computer and start the software. Connect a Zero Air source to the humidification chamber (flow controller #1). Connect stock standard cylinder#1 to flow controller #2 inlet. Open the cylinder valves. Adjust the inlet pressures to 50 to 60psig.

Standard Concentration Selection: The concentration of the three working standards prepared in canisters should be 200ng/L, 20ng/L and 1ng/L (depending on the dynamic range of the initial calibration include 1ng/L if a 0.08ng and 0.4ng on column standard is desired <u>or</u> this standard may be used for the 0.5ng/L concentration as well) for SCAN and 0.2ng/L, 4.0ng/L, and 200ng/L for SIM.

Position 1 – Total Air Flow (Zero Air)
Position 2 – Standard Flow (Purchased Standard One)
Position 3 – Standard Flow (Purchased Standard Two if Applicable)
Position 4 – Total Air Flow (Zero Air) (utilized if preparing a two dilution standard)
Position 5 – Diluted Standard Flow (utilized if preparing a two dilution standard)

<u>Step1</u>: Determine the required flow rate of the stock standards (positions #2 and #3). The range must be from 5 to 50sccm (standard cubic centimeters per minute, same as ml/min). The flows listed below are guidelines to be used for the default standard flow (based on the desired standard concentration) and were chosen based on the ultimate final dilution required and limitations of the Dynamic Diluter (flows must be from 150 to 2000ml/min.).

Desired Standard Conc.	Default Standard Flow
200ng/L	50ml/min
100ng/L	50ml/min
20ng/L	20ml/min
5.0ng/L	10ml/min
4.0ng/L	8ml/min
1ng/L	50ml/min; 20ml/min (See Note 1 below)
0.2ng/L	10ml/min; 20ml/min (See Note 1 below)

<u>Note 1</u>: For the 1ng/L and 0.2ng/L standards (or any standard requiring more than a 400X dilution of the stock), a slightly different procedure is performed. In order to prepare these standards, a double dilution must be performed which involves taking the primary dilution flow and making a secondary dilution of that using the diluent gas. Unscrew the cover of the dilutor and connect the first mass flow controller as well as the tubing to re-route the first dilution output from the final standard canister to the 2nd dilution chamber. Refer to example 2 for the calculation guidelines to prepare a two dilution standard.

<u>*Example 1*</u>: Prepare a 200ng/L working standard. The concentration of each stock standard is 1000ng/L.

<u>Step 2</u>: Determine the required dilution factor for each stock.
Dilution factor = Stock Conc. (ng/L) / Desired Standard Conc. (ng/L)
Dilution Factor = 1000ng/L / 200ng/L = 5

Step 3: Calculate Total Flow
Total Flow= (stock std. flow-see table above)*(Dilution Factor)
Total Flow=50ml/min*5 = 250ml/min

Step 4: Calculate Diluent Air Flow
Air Flow=Total Flow-(Sum of stock std. flows-purchased cylinders)
Air Flow=250ml/min-(50+50)ml/min = 150ml/min

Example 2: Prepare a 0.2ng/L working standard. The concentration of each stock standard is 1000ng/L.

Step 2: Determine the required total dilution factor for the 0.2ng/L standard.
Dilution factor = Stock Conc. (ng/L) / Desired Standard Conc. (ng/L)
Dilution Factor = 1000ng/L / 0.2ng/L = 5,000

The two dilutions must be performed which total the dilution factor calculated above. Since the flow for the Diluter is restricted to a maximum of 2000ml/min, the total flow (as calculated in Step 3 below) cannot exceed 2000ml/min; therefore, the dilutions must be chosen accordingly.

Step 3: Calculate Total Flow
Total Flow = (stock std. flow-see table above)*(Dilution Factor)
Total Flow (Dilution 1) = 10ml/min*200 = 2000ml/min

For the 2nd dilution take the stock standard flow selected for dilution 1 for the two purchased cylinders (10ml/min each based on the desired final concentration) and add them together (10ml/min + 10ml/min for 20ml/min) to get the stock standard flow for the 2nd dilution.

2nd Dilution Factor Needed = Total Dilution/1st Dilution
2nd Dilution Factor = 10000/200(1st dilution) = 50
Total Flow (Dilution 2) = 20ml/min*50 = 1000ml/min

Step 4: Calculate Diluent Air Flow
Air Flow=Total Flow-(Sum of stock std. flows-purchased cylinders)
Air Flow=2000ml/min-(10+10)ml/min = 1980ml/min (Dilution 1)
Air Flow=1000ml/min-20ml/min = 980ml/min (Dilution 2)

Position 1 = 1980ml/min
Position 2 = 10ml/min
Position 3 = 10ml/min
Position 4 = 980ml/min
Position 5 = 20ml/min

Step 5: Enter flow rates in the appropriate fields in the Entech software. Start flows by clicking the "GO" button in the top right of the window. Allow flows to equilibrate for at least fifteen minutes, then attach an empty canister to the outlet port and open the valve. The outlet pressure will be displayed in the lower right of the window, in units of psia. Close the canister valve when the pressure reaches 30psia. There is a relief valve on the diluter that will open when the pressure reaches 35psia, so the canister will still be usable if the valve is not closed in time.

9.2.2.2When analysis of additional (extra) compounds are requested which are not in the purchased stock cylinders, the following preparation instructions should be used. In addition, the internal standard / surrogate standard may also be prepared in this manner (Sections 9.2.2.2.1 – 9.2.2.2.2) as mentioned in Section 9.2.1.

9.2.2.2.1 _Equi-mass “soup”_ (contains compounds in equal mass amounts) or _cocktail_ prepared from the neat compounds for a large number of components. If additional SIM compounds are requested, the same cocktail may be used.

Cocktail Preparation:

Step 1: This cocktail is prepared by combining 25mg of each neat compound into a small glass vial. Use a microliter syringe to transfer each compound, cleaning with solvents in between. Put the vial in the freezer between aliquots to minimize volatilization. Take the density of each compound into account to determine the actual amount of each compound to spike into the cocktail by using the following equation.

$$S = \frac{A}{D} \qquad \text{(Equation 4)}$$

Where:

S Actual spike amount (µL)
A Desired amount for each compound (mg)
D Density (mg/µL); refer to Table 2 for the density

Example: The actual volume of acrolein to add to the cocktail is calculated by the following.

$$S(\text{Acrolein}) = \frac{25mg}{\left(0.840\,\frac{mg}{\mu l}\right)} = 29.8\mu L$$

Step 2: The concentration of each compound in the cocktail is determined by the following equation.

$$C = \frac{A}{V}\left(1000\,\frac{\mu g}{mg}\right) \qquad \text{(Equation 5)}$$

Where:

C Concentration of cocktail (µg/µL)
A Amount of each compound (mg)

V Final volume of cocktail (total spike volumes of each compound) (µL)

Example:

$$C = \frac{25mg}{631.8\mu L}\left(1000\frac{\mu g}{mg}\right) = 39.569\mu g/\mu L$$

9.2.2.2.2 *An intermediate standard* is prepared from neat compounds by spiking individual compounds into a glass static dilution bottle (SDB) as described in Section 9.2.1.1 or spiking an aliquot of a cocktail into the SDB. The spike amount of a cocktail is determined by using the following equation.

$$S = \frac{C_1 V}{C_2} \qquad \text{(Equation 6)}$$

Where:

S Spike amount required in order to obtain the desired concentration (µL)
C_1 Desired concentration of SDB (µg/mL)
C_2 Concentration of cocktail (µg/µL)
V Volume of SDB (L)

Example: Determine the spike amount of the cocktail required to achieve the desired intermediate standard concentration.

$$S = \frac{\left(1\frac{\mu g}{ml}\right)(2010ml)}{27.81\frac{\mu g}{\mu L}} = 72.28\mu L$$

9.2.2.2.3 *Intermediate Standard Preparation (Gaseous Compounds)* As an alternative to the glass SDB method, if the extra compounds needed to be analyzed are gases at room temperature, use a gastight syringe to prepare an intermediate standard in a 1L Tedlar bag filled with humidified zero-grade air. Use the molecular weight of the compound to calculate the microliter amount to be spiked into the bag to achieve desired concentration. The spike amount is determined by using the following equation.

$$S = \frac{C * V * 24.46}{M * \left(1000\frac{ng}{\mu l}\right)}$$

S	Spike amount required in order to obtain the desired concentration (µl)
C	Desired concentration (ng/L)
V	Volume of the Tedlar Bag (1L)
M	Molecular Weight of the compound
24.46	Molar Volume of gas at 25°C, 1atm

Example:

Make a 100,000ng/L intermediate standard of Chlorodifluoromethane (Freon22) in a Tedlar Bag, where M=86

$$S = \frac{100{,}000\frac{ng}{L} * 1L * 24.46}{86 * \left(1000\frac{ng}{\mu l}\right)} = 28.44\mu l$$

9.2.2.2.4 *The Working standard* for extra compounds is prepared in a canister by spiking an aliquot of the intermediate standard (glass SDB or Tedlar bag) using a heated gastight syringe. The preparation of these standards shall follow the instructions detailed in Section 9.2.1.2. The concentrations for working standards are usually 20 and 200ng/L, however different concentrations can be chosen which work best for a particular project.

9.2.3 Initial Calibration Verification (ICV) - (Laboratory Control Sample - LCS) Prepare a secondary source standard (either a different manufacturer or different lot from the same manufacturer as the initial calibration standard) using the same procedures as the primary source. The ICV/LCS working standard should contain each target analyte present in the calibration working standard. Prepare the ICV/LCS working standard at a concentration of 200ng/L. Differing injection volumes account for the allowed concentrations listed in Table 4 for SCAN and 4A for SIM. The preparation of this standard shall follow the instructions detailed in Section 9.2.2, using the certified second-source standard cylinder.

9.2.4 Continuing Calibration Verification (CCV) Standard The CCV is the same as the initial calibration working standards detailed in Section 9.2.2.

9.2.5 Screening Standards Recommended procedure: Prepare a 0.5ug/mL and/or a 3.0ug/mL concentration standard so that the GC may be calibrated utilizing a few levels (may include approximately 0.5ng, 150ng and 600ng). However, other concentrations can be prepared depending on the desired range.

Any of the desired standard concentrations (primary and secondary) may change as long as the equations and the appropriate densities remain the same.

9.3 Storage and Expiration Dates

- All standards that are to be stored in a freezer shall be stored at ≤-10°C for DoD projects.

- Neat Stock Liquids are stored at < -10˚C (-10˚C to -20˚C) as specified by the manufacturer or for a period of five years.
- Equi-Mass Primary Stock Standard is a cocktail or soup of neat compounds (containing compounds in equal mass amounts) used to in preparing intermediate gas phase standards and shall be stored in the freezer at < -10˚C (-10˚C to -20˚C) for up to six months. This is assuming that the soup is sealed with a septum-containing screw cap or Mininert™ valve. The selection of the compounds for the soup should be performed in accordance with the guidelines in Volume 6.5 of the *Tekmar*-DOHRMANN Application Note.
- Purchased Stock Standards Cylinders must be stored at laboratory temperature for a period of 2 years or as specified by the manufacturer before vendor re-certification or purchase of new standards. Expiration dates of the cylinders must be entered into the yearly wall calendar located next to the cylinders. Analysts must verify that the assigned expiration dates of prepared standard canisters do not exceed the parent standard expiration date.
- Intermediate Calibration Standards prepared by static dilution must be stored in an oven at a temperature of approximately 60°C to ensure analyte vaporization. Every time a standard is prepared from the static dilution bottle (SDB), the concentration changes. To increase the useful lifetime of an SDB standard, remove volumes of 25mL or less. The volume removed can be manipulated by increasing the SDB concentration or by adjusting the canister final volume/pressure. Depending upon the volume removed, an SDB intermediate standard is stable for approximately two months as long as new working standards made from this standard continue to meet acceptance criteria. These bottles must be in the oven for a minimum of one hour prior to use in preparing working standards. The guidelines for the storage and expiration date for the intermediate calibration standards are stated in Volume 6.5 of the *Tekmar*-DOHRMANN Application Note.
- Prepared Stock / Intermediate Calibration Standards prepared in canisters (1000ng/L) may be stored at laboratory conditions for up to three months in an atmosphere free of potential contaminants. Upon preparation, canister standards should be allowed to sit for approximately 24 hours prior to use in order for equilibration to take place. Shorter equilibration periods may be necessary and acceptable as long as performance criteria are met.
- Calibration or Working Calibration Standards prepared in canisters may be stored at laboratory conditions for one month in an atmosphere free of potential contaminants. Upon preparation, canister standards should be allowed to sit for approximately 24 hours prior to use in order for equilibration to take place. Shorter equilibration periods may be necessary and acceptable as long as performance criteria are met.

10) Preventive Maintenance

10.1 A maintenance log will be kept documenting maintenance performed on each analytical system. The serial numbers of each instrument shall be recorded, and each log entry must include a description of the maintenance performed and be initialed by the analyst performing or observing/authorizing maintenance by an outside contractor.

The instrument maintenance log must be kept current. An entry shall be made in the appropriate log every time maintenance is performed (no matter the extent). The entry in the log must include.

(a) The date of maintenance
(b) Who did the maintenance
(c) Description of the maintenance
(d) Proof that the maintenance activity was successful

A notation of a successful tune and continuing calibration or initial calibration and the file number that accompanies the data will serve as proof that the maintenance is complete and the instrument is in working order.

The extent of the maintenance is not important, however, it is important that a notation be included for each maintenance activity such as changing a column, tuning the instrument, changing the pump oil, cleaning the source, ordering a part. In addition, a notation should be made in the logbook stating that no samples were analyzed during the days that the instrument was down and no active maintenance was being conducted (i.e., where no other notation was made in the logbook for those days).

10.2 Concentrating Trap

Routine maintenance includes periodic solvent cleaning of the Silco steel lines in the valve oven if contamination is suspected. Also, periodic replacement of the multi-sorbent or partial replacement of the trap if analyte specific deterioration is detected is required. See Attachment 5 for trap packing instructions. For specific trap information refer to the instrument maintenance logbook.

After repacking, the trap should be baked at 265°C for a minimum of three hours (or until a clean blank is generated) and a partial repacking requires baking (at 265°C) the trap for a minimum of 20 minutes (or until a clean blank is generated).

10.3 GC System

Column performance is monitored by observing both peak shapes and column bleed. Over time, the column will exhibit a poor overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced (see Section 8.5). Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column.

Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column-cutting tool. When removing any major portion of the column, which will affect the retention times and elution characteristics, a change in instrument conditions may be required to facilitate nominal analytical activity.

Declining performance can also be due to ineffective column ferrules, which should be replaced when a tight seal around the column is no longer possible. This can be detected with the use of a leak detector.

10.4 Mass Spectrometer

The Mass Selective Detector (MSD) ion source requires periodic cleaning to maintain proper performance. Symptoms of a dirty ion source include difficulty keeping the MSD in tune and fluctuating internal standard areas. The vacuum system should be serviced every six months, including changing the pump oil and checking the molecular sieve in the back-streaming trap.

10.5 Instrument Tuning

The instrument is tuned with guidance from the procedure described in the HP Operations Manual, when necessary.

10.6 Computer Troubleshooting

Computer care and troubleshooting is conducted by the IT department. Refer to Section 8.6 for the computer hardware and software requirements.

Computers are selected to meet or exceed operating system and or acquisition software requirements. Periodic upgrades of memory are performed to maintain or improve system performance and reliability. Upgrades may be performed on systems until instrument hardware configurations become the limiting factor.

Basic Troubleshooting Outline:

1) Document occurrence and severity in IT Log
2) Interview user(s)
3) Investigate any available logs (Event Logs, Acquisition Logs, etc.)
4) Determine if problem is isolated (single user or acquisition) or widespread (multi user or network).
5) If multiple possibilities exist for cause, then eliminate in systematic manner.
6) Hardware issues are addressed with component replacement (beginning with most suspect portion).
7) Software issues are addressed first with internet investigation (user blogs, software source updates/findings).
8) Network issues are investigated from the Server, to Switch, to Network Card; utilizing all available managed devices to help discover possible failure points.
9) In some cases, system corruption may require reload or complete system replacement.
10) Finalize documentation in IT Log with actions taken
11) Perform periodic follow-up with User and review any log found to have suspect events that suggested source of issue.

11) Procedure

11.1 Initial Calibration

The initial calibration is performed to determine instrument sensitivity and the linearity of the GC/MS response for the target compounds.

Initial calibration requirements are as follows:

1. A minimum of 5 concentrations must be used to calculate the calibration curve.
2. An initial calibration must be performed at a minimum initially per instrument, annually thereafter or whenever the continuing calibration verification standard does not meet the acceptance criteria.
3. Highest concentration, together with the lowest concentration, defines the calibration range.
4. The method reporting limit for any reported analyte must be at >/= the lowest calibration point.
5. The initial calibration event may not be interrupted by maintenance.

6. Only one value per concentration may be used.
7. Analyze calibration standards from lowest to highest concentration.
8. All ICAL analyses must be completed within the 24-hour tune window.
9. If 5 calibration standards are in the ICAL, one standard may be re-analyzed. If 6 to 10 calibration standards are in the ICAL, two calibration standards may be re-analyzed.
10. One of the calibration points from the initial calibration curve must be at the same concentration as the continuing calibration verification standard.
11. The upper end of the calibration range must not exhibit any peak saturation for any analyte or the range must be lowered accordingly.
12. The initial calibration model must be linear calibration using average of response factors and cannot be changed for any reason.
13. Point dropping policy
    - Minimum of 5 consecutive concentrations must be used to calculate the calibration curve.
    - Lowest concentration must be at or below the MRL (LOQ) and may not be dropped unless the MRL is changed to the concentration of the remaining lowest standard.
    - Points at the high end may be dropped, but doing so lowers the calibration range.
    - Points may not be dropped from the interior of the curve unless an assignable cause (i.e., gross dilution error, missing internal standards, purge malfunction, standard preparation error, or instrument malfunction) is accounted for and documented. In these instances, all the analytes in that calibration standard must be dropped from the calibration curve as the corrective action (the reason must be documented and the results maintained with the documentation for the final ICAL).
    - Dropping individual compound points from the upper or lower end of the calibration range to improve linearity is not considered an error correction. The reason for dropping these points does not need to be documented but the ICAL documentation must state the revised calibration range if the MRL must be adjusted or the calibration range is lowered for a particular compound. This must be documented on the ICAL Review Checklist.

      When an individual compound point is dropped from an ICAL both the response and concentration fields in the compound database of the method must be cleared. This ensures the average ICAL RRF calculates correctly when executing the CCV check routine.

    - A calibration standard may be re-analyzed if the first analysis of the standard has been dropped and other requirements in this policy are met (i.e., still within 24 hours).
    - Once the ICAL has been used to calculate and report sample results it MUST not to be changed for any reason.
    - It is recommended that if an analyte has a higher MRL than the lowest concentration analyzed that the low standard be automatically dropped from the curve (i.e., acetone MRL is 5, drop at least the 0.4ng point).

11.1.1 <u>Calibration Points</u> Analyze the calibration standards (analyze low to high) that span the monitoring range of interest of the samples. For SCAN, the range is typically 0.5ng-100ng on column; however, 0.1ng on column may be added if low level analyses are requested. For SIM, the range is 20pg on column to 50,000pg on column. The dynamic range is dependent on the sensitivity of a particular instrument as well as the required reporting limit for a given project and may be adjusted accordingly. Refer to Table 3 (SCAN) and Table 3A (SIM) for the concentrations of the compounds of interest in the initial calibration at each particular calibration concentration level.

Note: Refer to the EXCEL TO-15 Standard Concentration templates, located on the network at Q:\\TO15 Std. Concentrations\Std. Conc. Templates for both the SIM and SCAN templates. These templates must be utilized for the documentation of the standard canister concentration selection, final ICAL level concentrations and the determination of the correct injection volumes for the selected standard canister concentrations. If the primary or secondary stock standard cylinder concentrations are revised (upon re-certification or new purchases), the EXCEL spreadsheet templates, injection amounts and the ICAL concentrations in each instrument method must be adjusted accordingly. Other templates may be employed as long as they are validated and provide at least the same information.

SCAN

1. Determine if the lower end of the calibration range is to be 0.1ng or 0.5ng on column. If the low end is 0.1ng, then the 1ng/L standard must be utilized.
2. Determine if the 1ng/L or 20ng/L standard canister is to be used for the 0.5ng on column point.
3. Follow the instructions in the spreadsheet and save the file under the correct instrument folder and the initial calibration method identification.
4. Print the final ICAL concentration sheets and place into the corresponding ICAL folder

11.1.2 Recalibration Each GC/MS system must be recalibrated following any instrument maintenance which may change or effect the sensitivity or linearity of the instrument, if the continuing calibration verification acceptance criteria are not met and at least annually. The following procedure must be followed when updating an initial calibration method.

1. Open the most recent method.
2. Save the method with the new ICAL method ID using the “Save Method As” option. Date used in the method ID must be the date files were analyzed.
3. Quantitate midpoint standard and check retention times and integrations. Update retention times if necessary using QEdit or Easy ID (Tools → Easy ID). Requant if any changes are made and verify all peaks are identified correctly. Print.
   a. While midpoint standard is loaded update reference spectra (Continuing Calibration → Update Reference Spectra).
   b. With midpoint standard loaded update qualifier ion ratios and retention times (Initial Calibration → Update Levels → Select Update Level and then select Retention Times (Replace) and Replace Qualifier Ion Relative Responses).
   c. If necessary adjust integration parameters prior to processing remaining ICAL points.
4. Quantitate remaining ICAL standards. Review each peak for retention time, integration, and print. Review low level standards for acceptable signal to noise ratios and high level standards for saturation.
5. All responses must be cleared from ICAL before updating (Initial Calibration → Clear All Calibration Responses).

6. Update responses for each standard level (Initial Calibration → Update Levels) or (Initial Calibration → Quick Levels Update). If Quick Levels Update is used do not requant datafiles.
7. Save method.
8. Check Response Factor Report and evaluate whether any points should be dropped following the criteria outlined in this SOP.
9. Save method if any changes are made.
10. Verify calibration files listed on Response Factor Report are correct.
11. Verify file ID, acquisition time, quant time, update time, and last update information is correct on the Calibration Status Report.

11.1.3 Analytical Window If time remains in the tune window after meeting the acceptance criteria for the initial calibration, samples may be analyzed according to the procedure described in this document (see Section 11.5.2). If time does not remain in the analytical window, a new sequence shall commence with the analysis of the instrument performance check compound (BFB) and the continuing calibration verification standard.

11.1.4 Procedure The system should be operated using temperature and flow rate parameters equivalent to those in Section 11.6. Use the standard prepared in accordance with Section 9.2.2 of this SOP. Attach the calibration standard and internal standard/surrogate canisters to the designated inlets on the preconcentrator and open the canister valves. Analyzing different volume aliquots of the calibration standards produces differing concentrations.

Analyte responses (target ion areas) are tabulated and recorded using the Enviroquant program. Quantitation ions for the target compounds are shown in Table 2 and 2A and the primary ion should be used unless interferences are present, in which case the secondary ion may be used, but the reason documented in the initial calibration file and all subsequent quantitations utilizing that ICAL must be performed using the same ion selections. Refer to Section 13.2 for the required calculations and Section 12.4 for the acceptance criteria.

11.1.4.1 Additional Requirements The procedure for performing and generating a new initial calibration method must follow a few additional requirements.

1. If any analyte lacks the appropriate sensitivity (3 to 1 signal to noise ratio) at the low end of the calibration range, this point must be dropped from the curve and the MRL/LOQ raised accordingly.
2. No detector saturation may occur for any compound; the upper calibration level must produce no saturated peaks. Exhibited by:
   - The flattening of the response for the higher concentration standards as shown on the plot;
   - The presence of a reverse tail or rise on the front part of the peak;
   - The observed actual percent ratio of the secondary ion presence is lower than the expected percent ratio; or
   - The presence of a flat topped peak and again by the decline or saturation of the secondary ion compared with the expected % recovery.

11.1.4.2 LOQ Establishment, Verification and Acceptance Criteria

1. The LOQ must be set within the calibration range (≥ low std. of the current passing ICAL) prior to sample analysis.
2. The LOQ is verified by analyzing an LOQ verification QC sample containing the analyte at 1-2 times the claimed LOQ.
2. The LOQ for each analyte must be > the analyte's LOD.
3. The verification is acceptable if:
   a. The S/N ratio is at least 3:1 for each analyte.
   b. All ion abundances are acceptable per the requirements in this document.
   c. The % recovery for each analyte is within the laboratory generated control limits or 70-130% recovery for the annual Navy LOQ verification.
4. Using from 2 to 4 LOQ verification points, calculate the ongoing %RSD to demonstrate precision at the LOQ.
5. If the LOQ verification check fails, determine and document the cause. Additional LOQ verification checks must be performed at a higher level to set a higher LOQ.
6. Turn in all LOQ verification data (quantitation reports and software reports/checks) to QA regardless of pass or fail.
7. Verify the LOQ on each instrument quarterly. Navy accreditation requires an annual LOQ verification.

11.1.5 Initial Calibration Review Analyst's calculation and assessment along with a peer review of all ICAL data and documentation as stated in Attachment 2 is required before the ICAL may be used to analyze samples. In the case where samples are placed on the autosampler and allowed to run overnight, the sample results may only be reported if the ICAL is reviewed and found to be acceptable. The ICAL checklist in Attachment 2 must be used to document the review and approval process.

Perform a review of specific aspects of the calibration which might compromise data quality such as inappropriate extension of the calibration range with detector saturation and/or a lack of sensitivity for any analyte. Analyte concentrations which do not meet the signal to noise ratio or exhibit saturation are not to be reported and must be eliminated from the initial calibration. These instances should be followed by a short explanation regarding the reason for the omission.

11.1.6 Initial Calibration File An ICAL file is to be created for each initial calibration performed per instrument into which is placed the following ICAL documents. The file shall remain in the laboratory and be filed by instrument and date.

- ICAL Checklist filled out, reviewed and approved
- BFB tune analysis report
- Calibration status report (aka Calibration History)
- Relative Response Factor Report / Percent Relative Standard Deviation
- Quantitation report for each calibration standard (including manual integration documentation – before and after manual integration)
- ICV quantitation report and % recovery report.
- TO-15 Standard Concentration Spreadsheet (exact ICAL level concentrations and ICV concentrations)
- Any manual integration documentation

11.2 Initial Calibration Verification Standard

Verify the initial calibration by analyzing an initial calibration verification standard (ICV). This standard shall be obtained or prepared from materials acquired from a different manufacturer or lot from that of the initial calibration and prepared according to Section 9.2.3.

Analyze 50ng or less (refer to Table 4 for the secondary source standard concentrations) of the ICV standard depending on the dynamic range of a given instrument and refer to Section 13.4 for the required calculations.

11.3 Sample Preparation

The pressure/vacuum is checked and the canister pressurized upon receipt by the laboratory, as needed. When necessary, canisters shall be pressurized with humidified zero grade air. However, if the samples are to be analyzed in accordance with EPA Method 3C then the samples must be pressurized with UHP Helium (refer to Section 11.11 for additional information). The client must be made aware of this in advance and given the option of either submitting two canisters for analysis or receiving a report with qualified results (TO-15 Modified).

Depending on the size of the canister and location of sampling and as specified in the SOP below, samples may be pressurized to approximately 1.0psig to 3.5psig. Additional information may be found in the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters*. Initial and final pressures are recorded in LIMS and should be repeated on the back of the sample tag. The dilution factor created by filling the sample canister is calculated using equation number 12 in Section 13.7.

11.4 Screening

The analyst must screen a sample or subset of samples if the source is of unknown origin. Typically, if the source is known to be indoor or ambient outdoor air, no screening is necessary. However, if screening is required make sure that the instrument is calibrated. A single point calibration is sufficient; however, the instrument may be calibrated utilizing a two point calibration. The ICAL points are recommended to be at approximately 0.5ng, 150ng and/or 600ng spanning the desired dynamic range. Refer to Section 9.2.5 for additional information.

Inject a 1mL or smaller aliquot of each sample into a GC/flame ionization detector (FID) system that has been calibrated with a standard containing a subset of the target analytes. This subset represents the most commonly found compounds in air samples, such as acetone, trichloroethylene, and toluene. Use the results to determine the maximum volume of sample to be analyzed by TO-15 by utilizing the following equation. Dilutions may be prepared as necessary according to Section 11.11.1.

$$I = \frac{C}{H}$$

Where:

I	Injection volume (mL)
C	Maximum calibration level (ng on column)
H	Compound screening concentration (ng/mL)

Example: Select the compound with the highest concentration (toluene = 1.0ng/mL). If the upper calibration level is 100ng on column, then the following calculation determines the maximum injection volume to analyze.

$$\frac{100ng}{1.0ng/mL} = 100\text{mL maximum injection volume}$$

11.5 Analytical Sequence and Data System Setup

11.5.1 Data System For the Tekmar AUTOCAN, fill in the sequence log of the Teklink program with the appropriate information. Refer to the Section 11.6.1 for the operating parameters.

For HP Chemstation, load the appropriate acquisition method for the GC/MS in the top window of the Chemstation program. Suggested GC/MS operating parameters are given in Section 11.6.2.

11.5.2 Analytical Sequence The analytical sequence must be completed for the analysis of ≤20 field samples. Re-runs, dilutions, and sample duplicates are not counted as separate samples. A method blank (MB) shall be run to monitor for laboratory introduced contamination. There must be at a minimum a laboratory duplicate (LD) analyzed in each batch to assess batch precision. The following generalized analytical sequence is to be followed:

Analytical Sequence Guideline

With Calibration	Tune Check[1] Calibration Standards (5 Standards Minimum) ICV Standard[2] (Acts as the ICV and LCS) QC Canister Checks[6] MB[7] Sample(s) – 1-20 Laboratory Duplicate[4]
With Continuing	Tune Check[1] CCV Standard[5] QC Canister Checks[6] MB[7] LCS[3] MRL Check Standard[8] Sample(s) – 1-20 Laboratory Duplicate[4]

[1] The instrument performance check solution must be analyzed initially and once per 24 hour (or as specified by the project) time period (sequence / tune window) of operation. All analyses for a sequence must be initiated (injected) prior to the expiration of the tune window.

[2] In this scenario, the ICV may also be evaluated as the LCS (differing acceptance criteria).

[3] An LCS shall be analyzed at a rate of 1 in 20 or fewer samples. The LCS is the second source calibration check standard analyzed at the lower end of the calibration curve (below the midpoint).

[4] A laboratory duplicate must be analyzed at a rate of 1 per 20 or fewer samples. The duplicate must be rotated among clients, whenever possible. Also, a duplicate laboratory control sample may be analyzed to assess precision to meet project requirements or due to sample matrix effects.

[5] A CCV must be analyzed at the beginning of every analytical sequence.

[6] Any number of QC check canisters may be analyzed in the sequence to determine a canister cleaning batch or batches acceptability.

[7] Any of the QC Check Canisters may serve as the method blank as long as the minimum requirements detailed in this document are met. A method blank shall be analyzed at a rate of 1 in 20 or fewer samples.

[8] A MRL check standard may be analyzed with each batch of 20 or fewer samples (when an initial calibration is not analyzed within the same batch). Additional information is included in Section 11.17.

<u>Note</u>: Client project batch specifications may require certain modifications to the analytical sequence; however, a batch may not be more lenient than that which is specified in this document.

11.6 Conditions

11.6.1 Sample Collection Conditions

The suggested settings and system parameters are as follows:

Adsorbent Trap

Set Point:	35°
Sample Volume:	up to 1L
Dry Purge:	300mL
Sampling Rate:	100mL/min (utilize for a sample injection volume of >100mL); 40mL/min (utilize for a sample injection volume of 25-100mL)
Desorb Temp.:	200°C to 230°C
Desorb Flow Rate:	8-10mL/min He, measured at refocuser split vent
Desorb Time:	3.0 minutes

Refocusing Trap

Temperature:	-180°C
Injection Temp.:	160°C
Injection Time:	1.0 min

Adsorbent Trap Reconditioning Conditions

Temperature:	265°C
Initial Bakeout:	3 hours or until clean blank is obtained
After each run:	5-8 minutes

Sample Run Time

Each analytical run is approximately 20 minutes long; the total cycle time is about 30 minutes between injections.

11.6.2 GC/MS System

Optimize GC conditions for compound separation and sensitivity.

Item	Condition
Carrier Gas	Helium
Flow Rate	1.0-1.6mL/minute
Temperature Program	Initial Temperature: ~20°C Initial Hold Temperature: 3 minutes Ramp Rate: 5°C/min to 80°C 2nd Ramp: 10°C/min to 160°C 3rd Ramp: 20°C/min to 240°C for 5 min hold
Detector B (MSD *Interface)*	260°C
Electron Energy	70 Volts (nominal)
Mass Range (Scan mode)	34 to 280 amu
Mass Range (SIM mode)	Scan masses corresponding to the target analytes
Scan Time	To give at least 10 scans per peak, not to exceed 1 second per scan.

Note: *The instrument may be operated in Selective Ion Monitoring (SIM) mode if requested by the client.*

11.7 Instrument Performance Check

Since the BFB tuning compound is included in the internal standard and surrogate standard canister and an autosampler is used, it is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to the reduction and approval of any data collection. The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or continuing calibration verification criteria) begins at the injection of the BFB, which shall be documented in laboratory records. Upon completion of the successful BFB tune, the tune report must be printed and retained on file for future reference.

The mass spectrum of BFB must be acquired in the following manner.

- Inject 50ng or less (on column)
- Three scans (peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.
- Background subtraction is conducted using a single scan prior to the elution of BFB.
- All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.
- The ion abundance criteria must not be changed from the requirement stated in this document (TO-15 or TO-14A, as requested).

All subsequent standards, samples and QC samples associated with a BFB analysis must use identical instrument conditions.

11.8 Continuing Calibration Verification Standard

Verify the calibration each working day, where necessary (e.g., an ICAL was not analyzed or the tune window has closed) by analyzing a continuing calibration verification (CCV) standard from the initial calibration standard canister. The concentration of the calibration verification may be varied between the low calibration standard and the midpoint of the calibration range; however, the concentration must be at one of the levels analyzed in the initial calibration. Refer to Table 3 for the standard concentrations. Refer to Section 13.3 for the required calculations.

DoD QSM Requirement: A CCV standard must be analyzed daily before sample analysis; after every 24 hours of analysis time; and at the end of the analytical batch run.

11.9 Canister Quality Control Check and Method Blank

The method blank must be a sample of a matrix similar to the batch of associated samples that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure, and in which no target or interferences are present at concentrations that impact the analytical results for sample analyses. Prepare a canister that has not left the building by pressuring with humidified zero air. Analyze an aliquot of one liter along with the same volume of internal standard and surrogate as standards and samples. Additionally, a blank must be analyzed whenever a high concentration sample is encountered and carryover is suspected. For all method blanks the unique laboratory barcode for the canister must be included in the sample analysis identification.

A Quality Control (QC) check canister pressurized with humidified zero air may serve as a method blank as long as the analyte concentration requirements stated in the canister quality control check section (Sections 12.7 and 12.8) and other requirements (refer to Section 12.12 for internal standard requirements) are met. Assuming continuing failure, another QC canister or a new canister must be prepared and analyzed in order to verify that no system contamination exists. For tracking purposes the unique laboratory barcode given to a canister shall be the information included in the sample analysis identification.

11.9.1 Sampling Systems Section 7.1 and 8.4 of Method TO-15 describe the setup and certification procedure for a specific sampling apparatus that has been used by the EPA for several of its large air monitoring programs. These systems are rarely used for the types of projects that make up the bulk of the laboratory's work. The vast majority of samples analyzed by the laboratory are taken into canisters either as grab samples or using a simple time integrated sampling device (flow controller), as in Section 8.2.1 of the method, so these procedures are not part of the typical protocol for providing sampling materials to clients. The laboratory has developed an SOP for the cleaning and certification of the materials it provides its clients for obtaining air samples to be analyzed by method TO-15. Refer to the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters* for additional information.

It is this laboratory's interpretation that the sampler system certification procedure described in Section 8.4.4 of the TO-15 method applies to the specific sampling apparatus described in the method and not to the sampling procedures used by our clients. The laboratory does not maintain a dynamic calibration manifold or canister sampler apparatus as described in the method and thus performance of the relative accuracy certification procedure described in section 8.4.4 is not possible.

11.10 Laboratory Control Sample

The laboratory control sample is a sample matrix, which is free from the analytes of interest and spiked with a standard containing known amounts of analytes. The laboratory control sample is an injection of the initial calibration verification standard. Inject the LCS (ICV) at concentrations below the midpoint of the calibration curve. Make sure that all of the pertinent information is included on the quantitation report including the sample identification (LCS), concentration, standard used, and analyst.

11.11 Sample Analysis

Prior to analysis, all sample containers (canisters and bags) should be at temperature equilibrium with the laboratory.

- Attach sample canisters to Tekmar AUTOCan using a 9/16" wrench. Bottle Vacs use a proprietary quick connect fitting (Micro-QT, Entech Instruments). Tedlar bags can be connected using soft silicone tubing or a 3/16" fitting with a reusable ferrule.
- Before opening the valve, check for leaking fittings by running the leak check program in the Teklink software. Quick connect fittings must be leak checked before connecting the sample container.
- If system is leak tight, open the canister valves and start the automated preconcentration procedure. Make sure the Chemstation data acquisition software has been readied.
- Maintain the trap at an elevated temperature until the beginning of the next analysis.

Check all target compounds using the QEdit routine in Enviroquant, making sure all extracted ion chromatogram peaks are integrated properly (see Section 11.15).

Note 1: The secondary ion quantitation is only allowed if there is sample matrix interference with the primary ion. If the secondary ion quantitation is performed, document the reasons in the instrument run logbook and/or on the quantitation report (initial and date any notation).

Note 2: Each female Micro-QT fitting must be purged after use to remove any remaining sample residue and prevent contamination from subsequent usage. Connect a male Micro-QT fitting to a source of ultrapure or carbon-filtered gas. Adjust the pressure to about 10 psig using an inline regulator. Connect the female fitting for several seconds, then remove and place in an oven kept at 60ºC until the next use. Do not heat the fitting higher than 80ºC.

SCAN Mode - The instrument is normally operated in the SCAN mode, where the following procedure may be followed.

- Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic range from 34 to 270 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning allows identification of unknown compounds in the sample through searching of library spectra. See operating conditions in Section 11.6.
- Generate a quantitation report for each run.
- If reporting Tentatively Identified Compounds (TICs), refer to Section 11.11.2 for identification criteria.

SIM Mode - When the client requests SIM mode, select SIM instead of SCAN mode and identify a minimum of two ions per analyte of interest. Also, a minimum of two ions for each internal standard and surrogate compound should be selected.

Helium Pressurization – If a canister is pressurized with helium, a correction factor is applied to sample volumes extracted from the canister via auto sampler. This is due to the difference in thermal properties between helium and air. A correction factor worksheet has been generated to determine the exact volume taken from a canister and may be found at J:\\A-GCMS\Helium Pressurization. Save file, print the sheet and include with the data. Refer to the instruction page in the template for all of the instructions and calculations including backfilled canisters.

AutoCAN Leak Checks – Canisters should be put on at least two different AutoCAN positions to confirm a “leak”. In addition, the valve threads should be inspected for defects which may prevent a good seal with the AutoCAN. Once a canister has “failed” the leak check it must be tagged, an NCAR initiated, and the PM notified. Regardless of what the client or PM specifies as the fate of the sample, the canister must be put on maintenance hold to complete a full 24-hour leak check. The leaking canister must be documented on the Sample Review Checklist (or yellow sheet). This is a fixed QA procedure with no allowance for deviation.

11.11.1 Sample Dilution If any target analyte results are above the highest level of the initial calibration, a smaller sample aliquot should be analyzed. The dynamic range of volume aliquots for the automatic cryogenic concentrator is 15ml to 1L. If a volume smaller than 15ml is to be analyzed, a dilution should be made in a Tedlar bag, or the sample directly injected using a gastight syringe. Guidance in performing dilutions and exceptions to this requirement are given below.

- Refer to Section 11.6.1 (Adsorbent Trap Sampling Rate) for the required sampling rate if less than 100mL is to be analyzed.
- Use results of the original analysis to determine the approximate dilution factor required and get the largest analyte peak within the initial calibration range.
- The dilution factor must be documented (and included in the final report) and chosen in such a way as to keep the response of the analyte peak for a reported target compound in the upper half of the initial calibration range of the instrument.

Tedlar bag dilution:

- Make a dilution by filling a Tedlar bag with 1.0 liter of humidified zero air using a one-liter gas syringe.
- Calculate the volume of balance gas needed to obtain the required dilution.
- Remove the difference in the balance gas using a syringe.
- Add the calculated sample amount using a gastight syringe.

Direct injection:

- Make a direct injection by attaching a clean, humidified zero air filled canister to the preconcentrator autosampler using 1/4” stainless steel or teflon tubing with a “tee” septum port. This canister should be the same canister that may be used as the method blank.
- Inject the sample through the septum while the preconcentrator withdraws a 200cc aliquot from the canister.

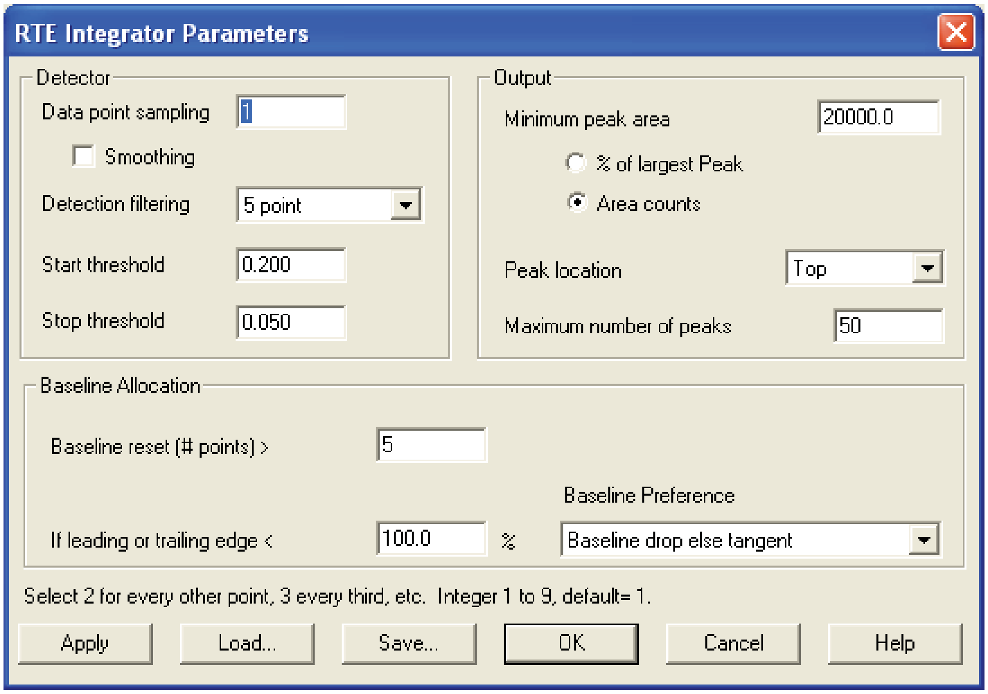
11.11.2 Tentatively Identified Compounds When requested, a mass spectral library search may be made for the purpose of tentatively identifying sample components not associated with the calibration standards. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system mass spectral library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

Certain programs may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. The following guidelines are used for making tentative identifications.

- Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. For example, for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30 and 70%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.
- The concentration of the tentatively identified compound is estimated by assuming a response factor of 1.0 and comparing the response of the tentatively identified compound to the response of the nearest internal standard.
- If non-target analytes are not Q-deleted from the quant report, the analyst must evaluate whether these compounds should be reported as TICS.

<u>Procedure for Reporting Tentatively Identified Compounds (TICs) for samples and associated Method Blanks</u>

1. Load the datafile in the main Enviroquant window.
2. Load the TIC integration parameters (LSCINT.p). Typical setpoints are as shown below.



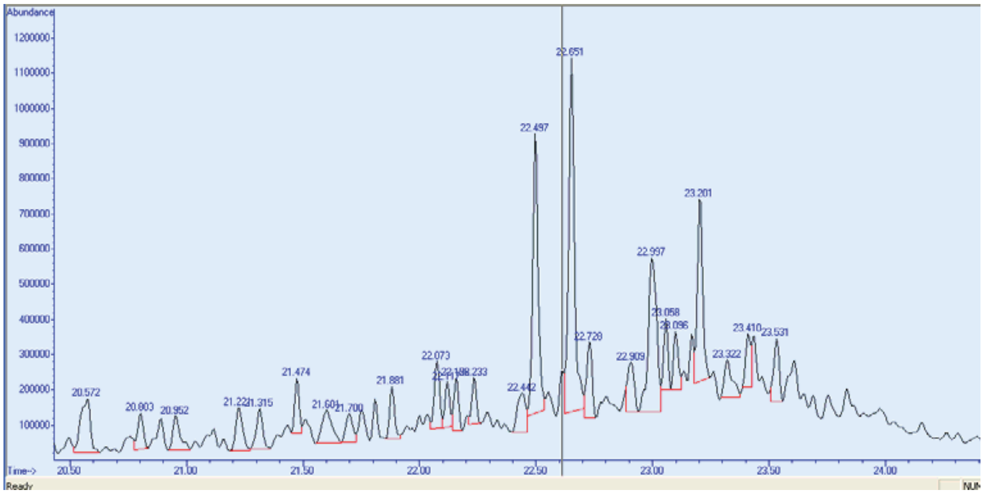
Detector
Data point sampling: 1
☐ Smoothing
Detection filtering: 5 point
Start threshold: 0.200
Stop threshold: 0.050

Output
Minimum peak area: 20000.0
○ % of largest Peak
● Area counts
Peak location: Top
Maximum number of peaks: 50

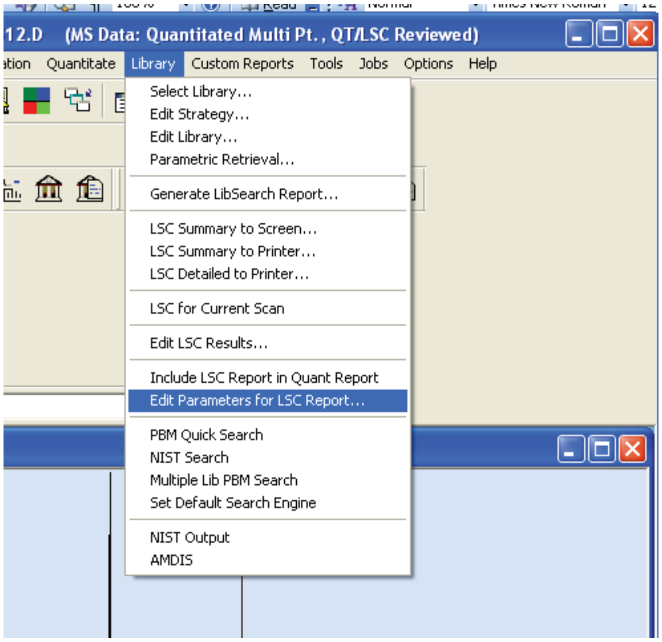
Baseline Allocation
Baseline reset (# points) > 5
If leading or trailing edge < 100.0 %
Baseline Preference: Baseline drop else tangent

Select 2 for every other point, 3 every third, etc. Integer 1 to 9, default= 1.

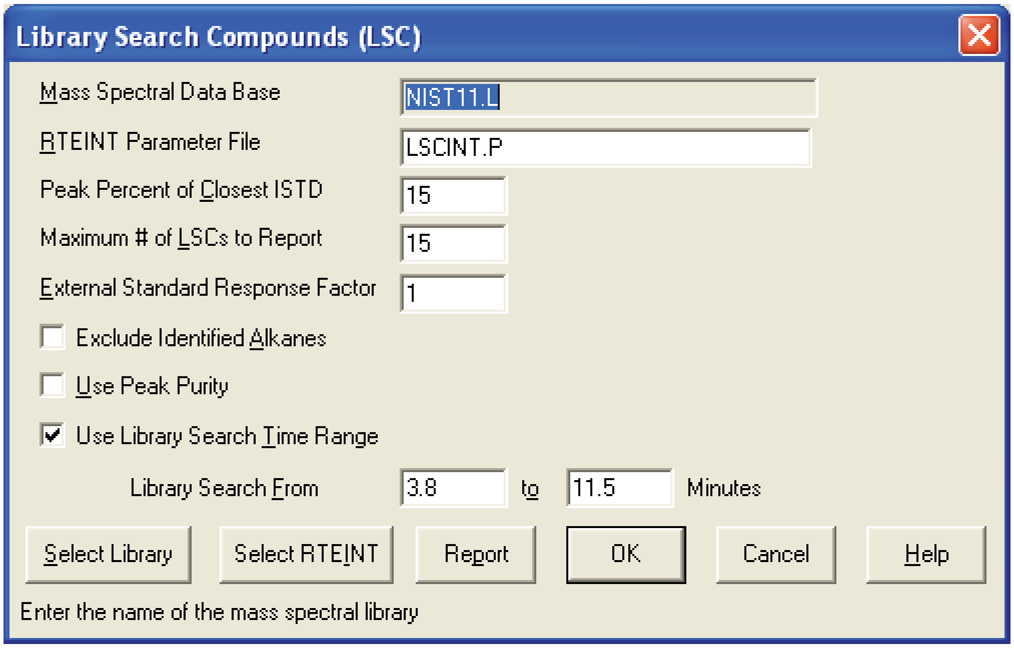
3. Integrate the chromatogram and inspect the peak integrations. Adjust the parameters as needed to achieve integration that will:
   - Resolve closely-eluting peaks that only have a small valley separating them.
   - Not include excess area below the peak in a complex matrix with an elevated baseline.
   - Include peak tailing when necessary.
   - Yield a sufficient number of peaks that will ensure that the internal standards are included.



4. Edit the parameters to be used in generation the library search report:



Select the most current mass spectral library database available, the correct integration parameters file, the area threshold (as a percent of IS area), number of peaks to report, and a time range of the chromatogram to search (set to start after the CO2 peak).



Mass Spectral Data Base: NIST11.L
RTEINT Parameter File: LSCINT.P
Peak Percent of Closest ISTD: 15
Maximum # of LSCs to Report: 15
External Standard Response Factor: 1
☐ Exclude Identified Alkanes
☐ Use Peak Purity
☑ Use Library Search Time Range
Library Search From 3.8 to 11.5 Minutes

Enter the name of the mass spectral library

5. Run the LSC routine from the Library menu. You may choose 'LSC Summary to Screen' (Calculate/Generate Report) to get a quick view of the results and then proceed if they seem acceptable. Set the default printer to 'Adobe PDF' and then choose 'LSC Detailed to Printer'.
6. Open the pdf file and inspect the LSC summary (last page). Check the internal standard areas and confirm that they are correct. If any IS area is biased high due to a coeluting peak use the 'Edit LSC Results' routine to switch all associated TICs to use a different IS. If all three IS peaks have coelutions substitute the areas from the daily method blank in the calculations.
7. Use the LSC Summary as a guide and inspect the chromatogram in the data analysis window. Integrate the chromatogram from the Integrate menu and look for peaks that may have been missed by the LSC routine. Possible reasons for missed peaks are excessive tailing (organic acids), RT close to a target compound, coeluting peaks with no valley between them. These will need to be added manually.
8. Use the DOSCAN routine from the Tools menu to search individual missed peaks one by one. This will add them to the LSC list.
9. Go back into the Edit LSC Results routine and make any necessary changes to compound names and/or the internal standard used for quantitation.
10. Run the macro "QT '0,0,C' by clicking the Custom Tool 1 button. This will update the LSC list to the quant.csv file.
11. Run the LSC Detailed to Printer routine from the Library menu (Generate Report *only*). This will print the file to pdf.
12. Excel Reporting
    1. In Excel, open the TIC reporting template (I:\A-GCMS\TICS\System\StarLIMS_TICQ).
    2. Enter the service request number and click ok.
    3. Click the Get Samples button. Select the samples to be reported. Delete any samples that are not to be reported (right click/delete row).
    4. Click the Update PEF button.
    5. Click the Get TICs from CSV button. Enter the date analyzed and select the instrument ID.
    6. Click the Apply to all Samples button. Change the date for any sample that was analyzed on a different date.
    7. Click the Apply Instrument to all Samples button.
    8. Enter file number in column E (i.e. enter 07 for file 12301507.d).
    9. Click the Copy Data button. This copies the TIC info to the report sheets.

11.12 Duplicate

A duplicate must be analyzed to assess laboratory precision and samples selected for duplicate analysis shall be rotated among client samples, where applicable. Some projects or sample matrix issues may require the analysis of a duplicate laboratory control sample (DLCS).

11.13 Internal Standard (IS)

The concentration of internal standard added to each standard, field sample and QC sample must be consistent from that of each current ICAL standard.

11.14 Surrogates

Internal standards/surrogates must be added at the same volume for every standard, sample and QC sample. Surrogate compound recoveries are requested by a number of clients, but are more appropriately used as system monitoring compounds. This is due to the fact that the compounds are introduced directly into the analytical system and not into the canisters or bags. It is for this reason that they are not considered to be true surrogates and a fixed window is applied. Additionally, surrogates are not included in the ICAL because they are not required by the method and are only system monitoring compounds.

11.15 Manual Integration and Q Deletion

A list of abbreviations (codes) that may be used to give a reason for performing either of these procedures are listed in the *SOP for Data Review and Reporting*.

11.15.1 Manual Integration The integration for each peak must be legally defensible and shall be checked to ensure that it has been integrated properly and consistently between samples, standards and QC samples. All peak reviews and manual integrations must follow the requirements specified in the *SOP for Manual Integration Policy* and the *SOP for Laboratory Ethics and Data Integrity.* The requirements in the above stated procedure include when manual integrations are performed, raw data records shall include a complete audit trail for those manipulations (i.e., chromatograms showing both the integration prior to any manual integrations and those depicting the corresponding manually integrated peaks), and notation of rationale, date, and initials of person performing the manual integration operation. In addition, manual integrations must be reviewed and approved by a second reviewer and the manual integrations maintained in the appropriate job file.

Reporting Requirements Certain project requirements including samples which are submitted under the Department of Defense (DoD) QSM require that the case narrative include an identification of samples and analytes for which manual integration is required. Refer to project requirements to determine if this is necessary.

11.15.2 Q Deletion Q deleting may be performed to either delete a false positive or delete non-target compounds.

11.16 Detection Limits and Limits of Detection

The MDL shall be performed in accordance with the procedure outlined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.* The detection limit shall be used to determine the LOD for each analyte.

11.16.1 Performance and Acceptance Criteria

1. The MDL must be <0.5ppbV for each analyte (Method 11.11.1).
2. Following the MDL study perform a Limit of Detection (LOD) verification on all instruments (performing this method). Spike the LOD at 2-4x the MDL; the spike level establishes the LOD.
3. LOD Acceptance
    - Analyte must be detected reliably and identified by the method-specific criteria (i.e, ion confirmation) and produce a signal that is at least 3 times the instrument's noise level (3:1 signal to noise ratio).
    - It is specific to each combination of analyte, matrix, method and instrument configuration.

- The LOD must be verified quarterly on each instrument (spiked at LOD) using the criteria listed above.

4. If the LOD verification fails (per #3), repeat the detection limit determination and LOD verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.
5. The laboratory shall maintain documentation for all detection limit determinations and LOD verifications (regardless of pass or fail).

11.17 Method Reporting Limit Check Standard

It is recommended to analyze a MRL check standard at the current MRL or required MRL for the batch (per client requirements) of twenty or fewer samples if the CCV fails low for any target compound. A MRL check standard may also be required per client specifications.

This check standard can also serve as the LOQ verification if it meets the specific requirements listed in Section 11.1.4.2. Apply the requirements and retain all documentation accordingly. Refer to Attachment 4 for Minnesota specified MRL check standard criteria.

11.18 Method Modifications

Method modifications are not allowed under TNI standards; therefore, a statement, however worded, must be included in the final report indicating that data reported does not fall under the laboratory's NELAP certificate of approval. In addition, the following items are considered to be method modifications and must be reported accordingly.

- Sample collection in gas collection bags
- The pressurization of canisters with nitrogen or helium (if EPA Method 3C is requested) refer to Section 11.11.

12) Quality Control Requirements and Corrective Action

12.1 To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.2 Corrective actions shall follow the procedures outlined in the *SOP for Nonconformance and Corrective Action*, where appropriate. Any maintenance which may alter instrument sensitivity or linearity must result in the re-analysis of the entire sequence including the tune compound, ICAL or CCV or any batch QC.

12.3 Instrument Performance Check

12.3.1 Acceptance Criteria

Refer to Tables 1 and 1A for the required ion abundance criteria.

12.3.2 Corrective Action Perform auto tune or manual tune and then re-analyze BFB. If the BFB acceptance criteria are still not met, the MS must be retuned according to the procedure outlined in the instrument user's manual. Perform necessary maintenance and make notations in the instrument maintenance logbook. It may be necessary to clean the ion source, or quadrupole, or take other necessary actions to achieve the acceptance criteria. An acceptable tune is required for sample results to be calculated and reported.

12.4 Initial Calibration

12.4.1 Acceptance Criteria Refer to the following acceptance criteria for the initial calibration.

- The RRT for each target compound at each calibration level must be within 0.06RRT units of the mean RRT for the compound.
- The calculated %RSD for the RRF for each compound in the calibration standard must be less than 30% with at most two exceptions up to a limit of 40% (this may not be true for all projects).

  DoD QSM/Navy Requirement: The two exceptions of %RSD up to 40%, allowed by the method, are not allowed.

- For each Internal Standard the area response (Y) at each calibration level must be within 40% of the mean area response $\overline{Y}$ over the initial calibration range.
- The retention time shift for each of the internal standards at each calibration level must be within 20s of the mean retention time over the initial calibration range for each internal standard.

  Navy Requirement: The absolute retention time for each of the internal standard and calibrated analytes must be within ±0.20 minutes (12 seconds) of the mean retention time for the corresponding internal standard or analyte over the initial calibration range.

- All of the following information must be retained to permit reconstruction of the initial instrument calibration: calibration date, test method, instrument, analysis date, analyte identification, analyst's initials, concentration and responses, and response factors.
- All initial instrument calibrations must be verified with an acceptable ICV.

12.4.2 Corrective Action Follow the initial calibration requirements detailed in Section 11.1 for information on re-analyzing or dropping points and the restriction of maintenance performed during the analysis of the initial calibration standards.

If the initial calibration results are outside the established acceptance criteria, corrective actions must be performed and all associated samples reanalyzed, if reanalysis of the samples is not possible, data associated with an unacceptable initial calibration shall be reported as estimated with the appropriate data qualifiers.

12.5 Initial Calibration Verification Standard (ICV)

12.5.1 Acceptance Criteria The percent recovery for each compound in the ICV must be between 70%-130% for all analytes except vinyl acetate, which must be within 50-150%. Exceptions to this allowance for the vinyl acetate recovery are project specific requirements and any DoD type project, which shall adhere to the 70-130% requirement for all target compounds.

12.5.2 Corrective Action If the initial calibration verification technical acceptance criteria are not met, reanalyze and if it fails again, prepare a new canister and analyze. If the criteria are still not met inspect the system for possible sources and perform any necessary maintenance and make a notation in the maintenance logbook of any steps taken. It may be necessary to clean the ion source or change the column. Perform a new initial calibration if any performed maintenance has altered instrument linearity and/or sensitivity. Perform another initial calibration or if reanalysis is not possible, data associated with an unacceptable ICAL/ICV shall be reported as estimated with the appropriate data qualifiers.

12.6 Continuing Calibration Verification (CCV)

12.6.1 Acceptance Criteria All compounds must be evaluated prior to rounding. The percent difference for each target analyte must be within plus or minus 30% of the initial calibration average RRFs.

12.6.2 Corrective Action If the continuing calibration verification technical acceptance criteria are not met, reanalyze and if it fails again, prepare a new canister and analyze. If the criteria are still not met inspect the system for possible sources of the problem and perform any necessary maintenance and make a notation in the maintenance logbook of any steps taken. It may be necessary to clean the ion source or change the column.

If any corrective action and/or reanalysis fails to produce continuing calibration verification within acceptance criteria (analyzed immediately following the initial failure), then either two consecutive successful verifications must be performed following corrective action or a new initial calibration must be performed; however, refer to 16.6.2.1 below.

DOD Requirement: If a CCV fails, the laboratory must immediately analyze two additional consecutive CCVs (The two consecutive CCVs must be analyzed within one hour).

- Both of these CCVs must meet acceptance criteria in order for samples to be reported without reanalysis.
- If either of these two CCVs fail or if the laboratory cannot immediately analyze two CCVs, the associated samples cannot be reported and must be reanalyzed.
- Corrective action(s) and recalibration must occur if the above scenario fails.
- Flagging data for a failed CCV is only appropriate when the affected samples cannot be reanalyzed. The laboratory must notify the client prior to reporting data associated with a failed CCV.

12.6.2.1 Method Reporting Limit Check Standard

If a per batch MRL check standard is analyzed due to a failing CCV or client requirement and is unacceptable for any compound (sensitivity; ratio or %D), reanalyze at the same or higher level within the same batch and report data with the CCV flag and case narrative notes accordingly. Reporting data with these conditions must be acceptable per project and client requirements otherwise corrective action must be initiated and samples reanalyzed.

Refer to Section 11.1.4.2 for annual (NELAP and Navy) and quarterly (DoD) LOQ verification requirements.

12.7 Canister Quality Control Check

The actual cleaning procedure, number of cans to select for analysis (to release a cleaning batch) and corrective actions are covered in the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters* and are not covered in this section. However, the procedure for analyzing and certifying a cleaning batch is included. If a canister passes as a QC canister it meets all of the requirements for a method blank (Method, TNI Standards, and Department of Defense Quality Systems Manual – DoD QSM, etc.).

12.7.1 Scan Analyses A canister is considered "clean" for normal SCAN analyses if the analysis shows <0.2ppbv of any target analyte (analyte exceptions listed in table below). If a canister passes as a QC canister it meets all of the requirements for a method blank (Method, TNI Standards, and Department of Defense Quality Systems Manual - DoD QSM, etc.).

Low Level SCAN Analyses For those analytes with a MRL of 0.1ug/m3, the QC criteria of <MRL is acceptable; otherwise, <0.2ppbV is required (analyte exceptions listed in table below).

SIM Analyses Results <MRL will be acceptable as this complies with the <0.2ppbV method requirement.

DoD QSM Requirement Each canister must be individually certified. A canister is considered clean if no reported analytes are detected at >1/2 the LOQ.

ANALYTE EXCEPTION LIST					
Compounds	ppbV	On Column (ng)	Compounds	ppbV	On Column (ng)
Target Analytes	0.2	0.50	Acrylonitrile	0.2	0.43
Chloromethane	0.2	0.41	Acetone	1.5	3.5
1,3-Butadiene	0.2	0.44	Ethanol	1.9	3.5
Acetonitrile	0.2	0.33	Vinyl acetate	0.99	3.5
Acrolein	0.65	1.5	1-Butanol	0.23	0.70
Isopropanol	0.28	0.70	Carbon Disulfide	1.1	3.5
2-Butanone	1.2	3.5			

Document the status of the check in LIMS and return the canister to the canister conditioning room. Additionally, if the check was found to be acceptable, the quantitation report must be kept on file for future reference

12.7.2 Tentatively Identified Compounds (TIC) If the batch of canisters are to be used for tentatively identified compounds (TIC) analysis, any non-target peaks present in the QC check canister analysis must be evaluated and determined to be less than the TIC reporting limit (10% of the internal standard). The concentration is estimated by assuming a RRF of 1.0 and comparing the response of the TIC to the response of the nearest internal standard.

12.8 Method Blank

12.8.1 Acceptance Criteria

- The concentration of a targeted analyte in the blank cannot be at or above the MRL, AND be greater than 1/10 of the amount measured in any associated sample. For any project that requires reported results less than the MRL, all associated measurements found in the MB should result in a qualifier; however, project requirements may differ and must be followed. Refer to DoD requirements listed below.

- The method blank should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.
- For DoD samples, the method blank will be considered to be contaminated if:

    1. The concentration of any target analyte in the blank exceeds 1/2 the reporting limit or is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);
    2. The concentration of any common laboratory contaminant (acetone, ethanol, carbon disulfide, and methylene chloride) in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
    3. The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

The laboratory shall evaluate whether reprocessing of the samples is necessary based on the above criteria.

12.8.2 Corrective Action If the analyte concentration results in the blank do not meet the acceptance criteria repeat analysis with remaining QC canisters until results are acceptable or prepare a canister per Section 11.9. If the analyte results in the blank still do not meet the acceptance criteria the source of the problem must be investigated and measures taken to eliminate the source. Each method blank must be critically evaluated as to the nature of the interference and the effect on the analysis of each sample within the batch. Determine whether the contamination is from the instrument or due to contamination in the blank container (if results from the new can are not acceptable then the system is probably contaminated). In all cases, the corrective action (reprocessing or data qualifying codes) must be documented. However, the specific corrective action depends on the type of project the blank is utilized for; therefore, refer (below) to the reporting/reprocessing requirements.

DEPARTMENT OF DEFENSE (DoD) QSM PROJECT: Any sample associated with a blank that fails the criteria shall be reprocessed in the same or subsequent analytical batch, except when the sample analysis resulted in a non-detect. If reanalysis is not performed, the results shall be reported with appropriate data qualifier.

OTHER PROJECT TYPE: Appropriate corrective measures must be taken and documented before sample analysis proceeds. However, if this is not a possibility and the results must be reported follow the reporting requirements stated in Section 16.4.

12.9 Laboratory Control Sample (LCS)

12.9.1 Acceptance Criteria Round all results to the nearest whole number prior to determining if the acceptance criteria have been met. The percent recoveries must be within the laboratory-generated limits and are referenced in the electronic TO-15 Method Manual. However, Arizona requires the percent recovery for each compound in the LCS to be 70%-130% (to match the ICV requirement). Therefore, the ICV exception for vinyl acetate stated in Section 12.5 requires the percent recovery for AZ samples to be 50-150%.

Note: Client project requirements and DoD requirements shall take precedence over the AZ requirement for AZ samples. Meaning if a sample is collected for a

DoD project in AZ, DoD requirements specified in this document and the project specific QAPP (if supplied) are to be followed.

DoD Requirement: In the absence of client specified LCS reporting criteria, the LCS control limits outlined in the DoD QSM Appendix C tables shall be used when reporting data for DoD projects.

12.9.2 Corrective Action If the LCS criteria are not met, determine whether the cause is instrumentation or the result of a poor injection. If the problem is instrumentation, perform maintenance and if the problem is with the injection re-analyze the LCS. DoD considers the same analyte exceeding the LCS control limits two out of three consecutive LCS to be indicative of non-random behavior; therefore, this trend should be monitored and the appropriate corrective action taken when it occurs.

12.10 Sample Results

12.10.1 Acceptance Criteria

- Sample results must be quantitated from the initial instrument calibration and may not be quantitated from any continuing instrument calibration verification.
- The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, initial calibration verification technical acceptance criteria described in this document.
- All target analyte peaks must be within the initial calibration range, diluted or reported with the appropriate data qualifier.

12.10.2 Corrective Action

- If the retention time for any internal standard within the sample changes by more than 20 sec from the latest daily calibration or initial calibration mid-point standard, the GC/MS system must be inspected for malfunctions, and maintenance performed as required. Repeat sample analysis as needed.

  Navy Requirement: The absolute retention time for each of the internal standard and calibration analytes must be within ±0.20 minutes (12 seconds) of the mean retention time for the corresponding internal standard or analyte over the initial calibration range.

- If the area for any internal standard changes by more than ±40 percent between the sample and the most recent calibration, check for possible matrix interferences and re-analyze at a greater dilution. If the requirement is still not met and matrix interference is not detected the GC/MS system must be inspected for malfunction and maintenance made where necessary.
- When corrective actions are made, samples analyzed while the instrument was not functioning properly must be re-analyzed or the appropriate data qualifiers must be attached to the results.

  To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.11 Laboratory Duplicate

12.11.1 Acceptance Criteria The relative percent difference must fall within ±25%. This RPD criterion also applies to duplicate laboratory control samples (DLCS).

12.11.2 Corrective Action If the duplicate results do not meet the technical acceptance criteria, perform another duplicate analysis. If the results are still unacceptable and the associated samples are not reanalyzed then all of the sample results in the associated batch must be flagged accordingly.

12.12 Internal Standards

12.12.1 Acceptance Criteria The following acceptance criteria must be applied to each run (except the ICAL – see Section 12.4).

- The area response for each internal standard in the blank must be within ±40 percent of the area response for each internal standard in the most recent valid calibration. (CCV or mid-point from the initial calibration, whichever is most current).
- The retention time for each internal standard must be within ±0.33 minutes of the retention time for each internal standard in the most recent valid calibration. (CCV or mid-point from the initial calibration, whichever is most current).

  Navy Requirement: The absolute retention time for each of the internal standard and calibration analytes must be within ±0.20 minutes (12 seconds) of the mean retention time for the corresponding internal standard or analyte over the initial calibration range.

12.12.2 Corrective Action

- Internal Standard Responses If the problem is with the instrument, perform maintenance. If the problem is with a sample, check for interferences. If the response is high, it is likely that interference is present. In this case, lower the volume or aliquot of the sample and re-analyze. If the problem persists, report the results with the best quality and qualify the results. If the problem is corrected with the lower volume analysis, report those results.
- Internal Standard Retention Times If the retention time for any internal standard within the sample changes by more than 20 sec from the latest daily calibration or initial calibration mid-point standard, the GC/MS system must be inspected for malfunctions, and maintenance performed as required. Repeat sample analysis where required.

12.13 Surrogates

12.13.1 Acceptance Criteria Since the matrix precludes the use of true surrogates and there is no established method criterion, acceptable surrogate recoveries are based on a fixed window of 70 - 130%. This is the typical requirement from clients. Additionally, these limits are referenced in SW-846 for use as guidance in evaluating recoveries. These limits are sufficient for evaluating the effect indicated for the individual sample results.

12.13.2 Corrective Action Poor surrogate recovery should be followed by re-analyzing a smaller aliquot to mitigate any matrix interferences. Evaluate the out of control surrogate for the effect on individual sample results.

12.14 Method Reporting Limit Check Standard

12.14.1 Acceptance Criteria Per client requirements or if the CCV is biased low for any compound, then evaluate the MRL check standard. Analyte must be detected reliably and identified by the method-specific criteria (i.e, ion confirmation) and produce a signal that is at least 3 times the instrument's noise level (3:1 signal to noise ratio). A percent difference +/-50% is recommended but program and client specific requirements must be followed if applicable.

12.15 Sample Holding Time Expired

The customer is to be notified that the sample's holding time was missed and the customer is to decide if the sample analysis is to continue. The documentation of missed holding time and the client's decision to proceed must be included in the corresponding job file. A statement dictating all holding time occurrences must accompany the sample results in the final report.

13) Data Reduction and Reporting

13.1 This method has specific requirements including the use of canisters; any modification must be reported accordingly. All reports that fall under the laboratory's certificate of approval (in accordance with TNI standards) must include a statement(s) clarifying any deviations from the scope of this certification. Refer to Section 13.10 for additional information and specific items, which require this clarification.

13.2 Initial Calibration

Tabulate each of the following:

13.2.1 Equation Number 1 - **Relative Response Factor (RRF):**

$$\text{RRF} = \frac{A_x C_{is}}{A_{is} C_x}$$ where:

A_x is the area response of the analyte quantitation ion.
A_{is} is the area response of the corresponding internal standard quantitation ion.
C_{is} Internal standard concentration, ng.
C_x Analyte concentration, ng.

Note: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC samples is the same from run to run.

13.2.2 Equation Number 2 - **Average (or Mean) RRF:**

$$\overline{RRF} = \frac{\sum_{i=1}^{N} RRF_i}{N}$$ where:

RRF_i are the individual RRFs from each concentration level in the initial calibration curve.

N is the number of calibration concentration levels.

13.2.3 Equation Number 3 - **Standard Deviation, SD:**

$$SD = \sqrt{\sum_{i=1}^{N} \frac{\left(RRF_i - \overline{RRF}\right)^2}{N-1}}$$ where:

RRF_i are the individual RRFs from each concentration level in the initial calibration curve.
$\overline{RRF}$ Average (or Mean) RRF of all concentration levels in the initial calibration curve.
N total number of calibration concentration levels

13.2.4 Equation Number 4 - **Percent Relative Standard Deviation, %RSD:**

$$\%RSD = \frac{SD}{\overline{RRF}}(100)$$ where:

SD Standard Deviation calculated in equation number 3
$\overline{RRF}$ Average or Mean RRF

13.2.5 Equation Number 5 - **Relative Retention Time (RRT):**

$$RRT = \frac{RT_C}{RT_{is}}$$ where:

RT_C Retention time of the target compound, seconds.
RT_{is} Retention time of the internal standard, seconds.

13.2.6 Equation Number 6 - **Mean Relative Retention Time ($\overline{RRT}$):**

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT_i}{n}$$ where:

$\overline{RRT}$ Mean relative retention time (seconds) for the target compound for all initial calibration levels.
RRT_i Relative retention time for the target compound in level i.
n Number of calibration levels

13.2.7 Equation Number 7 - **Mean Area Response ($\overline{Y}$):**

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$ where:

Y_i Area response for the primary quantitation ion for the internal standard for each initial calibration standard.
n number of calibration concentration levels

13.2.8 Equation Number 8 - **Mean Retention Times ($\overline{RT}$):**

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

where:

$\overline{RT}$ Mean retention time, seconds
RT_i Retention time for the internal standard for each initial calibration standard, seconds.
n number of initial calibration levels

13.3 Continuing Calibration Verification

- Calculate the (RRF) of each target compound using equation number 1.

13.3.1 Equation Number 9 - **Percent Difference, %D:**

$$\%D = \frac{RRFx - \overline{RRF}}{\overline{RRF}}(100)$$

where, for any given analyte:

RRF_x is the RRF from the CCV being evaluated.
$\overline{RRF}$ is the mean RRF from the current calibration curve.

13.4 Percent Recovery – ICV, LCS, Surrogates, MRL Check Standard

13.4.1 Equation Number 10 - **Percent Recovery (%R):**

%R = X/TV x 100

where
X = Concentration of the analyte recovered
TV = True value of amount spiked

13.5 Duplicate Analysis

13.5.1 Equation Number 11 - **Relative Percent Difference (RPD):**

$$\frac{x_1 - x_2}{\bar{x}}(100)$$

where:

x_1 First measurement value
x_2 Second measurement value
$\bar{x}$ Average of the two values

13.6 Internal Standards (IS)

- Calculate the mean area response $\overline{Y}$ for each internal standard using equation number 7.
- Calculate the mean of the retention times for each internal standard using equation number 8.

13.7 Pressure Dilution Factor (PDF)

13.7.1 Equation Number 12 - **PDF**, for samples collected in canisters:

$$PDF = \frac{P_{atm} + P_f}{P_{atm} + P_i}$$

where:

P_{atm} is the ambient atmospheric pressure, 14.7 psi at sea level.
P_f is the final sample canister pressure, in psig.
P_i is the initial sample canister pressure, in psig. This will most often be a negative value (sub-ambient initial pressure).

13.8 Results

If a canister has been pressurized with Helium and the Tekmar AutoCan was utilized, refer to Section 11.11.

13.8.1 Equation Number 13 - For calculating analyte concentrations in a sample, the starting point is the nanogram amount generated by the HP Enviroquant software, which appears on the quantitation report.

$$ng_x = \frac{A_x ng_{is}}{A_{is} \overline{RRF}}$$

where:

ng_x is the nanogram amount of analyte *x.*
A_x is the area response of the analyte's quantitation ion.
A_{is} is the area response of the corresponding internal standard's quantitation ion.
ng_{is} is the internal standard amount, in nanograms.
$\overline{RRF}$ is the average or mean RRFs

13.8.2 Equation Number 14 - The final analyte concentration, C_x, in units of micrograms per cubic meter (µg/m^3), is then calculated from the following:

$$C_x = \left(\frac{ng_x PDF}{V}\right)\left(\frac{1\mu g}{1000ng}\right)\left(\frac{1000l}{1m^3}\right)$$

where:

V is the sample volume analyzed, in liters.
PDF is the sample canister pressure dilution factor.

13.8.3 Equation Number 15 - To convert to units of parts per billion volume (ppbv):

$$ppbv = \frac{\mu g / m^3}{MW} x24.46 \qquad \mu g / m^3 = \frac{ppbv}{24.46} xMW$$

where:

MW is the molecular weight (Table 2) of the analyte, in g/mole.

24.46 is the molar volume of an ideal gas at 298 K (25 °C) and 760 mmHg (1 atm), in liters per mole (l/mol).

C_x the final analyte concentration in micrograms per cubic meter.

13.8.4 Equation Number 16 – Helium Pressurization (Injection Amount)

Applicable to canisters pressurized with helium and injected utilizing the mass flow controller of the AutoCAN. For full instructions and calculations, refer to the 1st tab of the template located at: J:\A-GCMS\Helium Pressurization\System\HE Pressurization Template.

13.9 Data Review

The analyst must review data on a real time basis for all calibration and QC data. The QC data must be evaluated by analytical sequence following the Daily QC review checklist (Attachment 3). The data shall be reviewed and the sample results calculated and assessed by one analyst and reviewed by a second qualified analyst. The Sample Review checklist (Attachment 3) is used to document sample review per service request and once completed, initialed and dated must be filed with each job file.

Initial calibrations must be reviewed in the same manner as QC data with all ICAL documentation retained in a separate file organized by instrument and date. Refer to the initial calibration checklist in Attachment 2 for the review guideline. The ICAL file must contain all the pertinent information stated in Section 11.1.6.

13.10 Reporting

The results of each test shall be reported clearly, unambiguously and objectively, and shall include all the information necessary for the interpretation of the test results and information required by this laboratory's policy, TNI standards, DoD Manual (applicable version, see reference section), client projects, and the TO-15 method including modifications, observances, data qualifiers, and certification information.

If the project requires that results be reported below the MRL (LOQ), but above the LOD all of the requirements specified for normal reporting apply (3:1 S/N ratio and ion abundance). This is regardless of the fact that the results will be qualified as estimated.

13.10.1 Analysis Observations / Case Narrative Summary Form

This form, which is included in the *SOP for Laboratory Storage, Analysis and Tracking*, may be generated when there are specific sample composition information or analysis issues and/or observations. In addition, during the analysis, specific identification information or problems, interferences, calibration issues, flags, and additional/expanded explanation of flags should be added to the form. This form may be modified as long as the sections and basic concepts are reserved. All data qualifiers and flags should follow those listed in the most recent Quality Assurance Manual or as defined in any client requirements.

This form may be used as a means for documentation. This form, among other information, will be reviewed when compiling the final report and case narrative. Alternatively, information may be included on the Daily QC and Sample Review Checklists (Attachment 3). All information regarding the job shall remain in the file, in order that sufficient documentation is available to recreate the job from sample receipt through analysis, data reduction, and reporting.

13.10.2 NELAP\TNI Requirements

The following items do not comply with TNI standard requirements and must be reported accordingly. A statement, however worded, must be included in the final report indicating that data reported does not fall under the laboratory's NELAP certificate of approval.

- Reporting any compound which is not included in the second source standard (ICV or LCS) does not meet NELAP requirements.
- In addition, a report that contains a compound not included on the NELAP certificate of approval must also include the statement listed above.

13.10.2.1 Modifications

Method modifications are also not allowed under TNI standards; therefore, a statement, however worded, must be included in the final report indicating that data reported does not fall under the laboratory's NELAP certificate of approval. In addition, the following items are considered to be method modifications and must be reported accordingly.

- Sample collection in gas collection bags
- The pressurization of canisters with nitrogen or helium (if EPA Method 3C is requested) refer to Section 11.11.

13.10.3 Surrogates

Only report surrogates at the request of the client. If any surrogate is out of control, all samples results (with surrogates requested) associated with the surrogate must be reported with the appropriate data qualifier.

13.10.4 DoD Requirements

Report results with the appropriate data qualifiers, if samples cannot be reanalyzed for any reason. In addition and at a minimum, the following situations are to be noted in the case narrative: manual integrations, CCV out of control, and results exceeding the calibration range.

13.11 Storing Electronic Data

The initial calibration data must be stored in a quantitation method (on the server) using a unique filename and may not be overwritten at any time in order to maintain an accurate audit trail. There are multiple quantitation methods, which are subsets of the compound list in Table 2. Therefore, files will be named with a notation indicating the compound list and the date of the corresponding initial calibration. In addition, all data files including method blanks, continuing calibration verification, laboratory control samples and client submitted samples files are saved in a unique sub-directory on the server.

13.12 Sufficient raw data records must be retained on file of all laboratory analyses described in this document including passing QC canister checks, tune checks, instrument calibrations, verifications, sample analyses and dilutions, QC checks, and method detection limit studies. The information that is required includes: analysis/calibration date and time, test method, instrument, sample identification, analyte identification, analyst's initials, concentrations and responses, as well as standards used for the analysis and calibrations, all manual calculations including sample dilutions and manual integrations to permit reconstruction of analyses. Information entered and reported on the quantitation report and instrument run log must be complete and accurate. All data shall be obtained following defensible and ethical practices in accordance with the most recent Quality Assurance Manual and the *SOP for Laboratory Ethics and Data Integrity*.

Note: All data records must explicitly connect data to the initial instrument calibration. This includes all samples, continuing calibrations and QC samples.

13.13 The essential information to be associated with analysis, such as computer data files, run logs, etc. shall include: Sample ID code, date and time (if the holding time is 72 hours) of analysis, instrument operating conditions/parameters (or reference to such data), analysis type, all manual calculations including dilutions and manual integrations, analyst's initials, sample preparation (pressure readings and balance gas if pressurized with helium), standard and reagent origin, receipt, preparation, and use, as well as calibration criteria, frequency and acceptance criteria, data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions.

14) Method Performance

14.1 An on-going assessment of method performance is conducted in order to ensure that the laboratory is capable of reporting results which are acceptable for its intended use. Validation of the method is confirmed by the examination and provision of objective evidence that these requirements are met.

14.2 Method Detection Limit (MDL)

The procedure used to determine the method detection limits are as stated in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as defined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation*. The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is distinguishable from method blank results. The MDL concentrations are listed in Tables 2 and 2A for both SCAN and SIM modes and were obtained using spiked canisters prepared with humidified zero air, making at least seven replicate measurements of the compounds of interest, computing the standard deviation, and multiplying this value by the appropriate Student's t value for 99 percent confidence. Additionally, at least seven method blank results were processed according to the procedure described in this document. Refer to the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* for the method blank MDL calculation and additional requirements for establishing the MDL. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. All MDLs, regardless of the mode of operation, meet the method performance criteria of <0.5ppbV.

14.3 Accuracy and Precision

Refer to Section 11.4 in the referenced method for information on replicate precision criteria for method performance. Single laboratory accuracy is presented as the second source initial calibration verification standard, which meets the method performance criteria of 30%. Additionally, laboratory generated control limit data for LCSs are presented for the analytes of interest and may be referenced in the electronic TO-15 Method Manual. Refer to Section 11.1.4.2 for the accuracy and precision requirements for concentrations at the LOQ/MRL.

14.4 Selectivity

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification.

It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak must be acquired. Scanning also allows identification of unknown compounds in the sample by searching through library spectra.

The sample analysis using the GC/MS is based in part on a combination of retention times and relative abundances of selected ions. The retention time of each chromatographic peak should be ±0.10 minutes of the library/reference retention time of the compound. The acceptance level for relative abundance should be set at ±20% of the expected abundance. The data should be manually examined by the analyst to determine the reason for the # flag [(#) = qualifier out of range], if present and whether the compound should be reported as found or if there is matrix interference. A background subtraction may aid in this determination. Manual inspection of the qualitative results should also be performed to verify concentrations outside the expected range.

Specific selectivity information is provided in this section and document (such as relative retention time) as well as in the referenced method. Refer to the method for additional information on selectivity.

- Use NIST Library 2011 or newer version
- The *reference spectra updates* must be performed with every new ICAL utilizing the mid-level standard (minimum). If needed, the reference spectra may be updated sooner with the continuing calibration standard.
- *Retention time updates* must be performed using EasyID and not by updating to the method (InitCal \ Update Calibration). Refer to the Help selection of the software.

14.5 Demonstration of Capability

This laboratory has continuously performed this method since before July 1999. Therefore, ongoing demonstration of capable shall be performed and documented; however, the initial demonstration of method capability is not required.

14.6 Proficiency Testing (PT) Program

The laboratory shall participate in an air and emissions PT study for TO-15. The testing shall be performed in accordance with this document and meet the frequency and proficiency requirements detailed in the DoD QSM.

Proficiency testing samples including all accredited compounds are not available. Therefore, in addition to third party PT samples, intra laboratory comparisons must be performed biannually to meet the DoD QSM proficiency testing requirements. Eight QC analyses from various analysts and instruments shall be compiled and statistical validity evaluated using a Z-score.

15) Pollution Prevention and Waste Management

15.1 All waste disposals shall be carried out in accordance with the requirements detailed in the *SOP for Waste Disposal.* In addition, canisters must be cleaned in accordance with the requirements detailed in the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters.*

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 The following is specific information on how to report unacceptable data. If the data requires a data qualifier flag, as specified in this SOP, refer to Appendix D of the most recent version of the Quality Assurance Manual for the appropriate data qualifier.

16.2 Initial Calibration and/or Initial Calibration Verification

All results reported with an unacceptable ICAL must be reported as estimated and all data shall be reported using defined qualifiers or flags or explained in the case narrative accordingly.

16.3 Continuing Calibration Verification

All results associated with an unacceptable CCV (other than #1 below) must be reported with the appropriate data qualifier, flag and/or explained in the case narrative.

1. When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported without a qualifier.
2. When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples with detects, then those detects must be reported with a qualifier, flag and/or explained in the case narrative.
3. If however, the acceptance criteria for the continuing calibration verification are exceeded low, i.e., low bias, and there are associated samples that are non-detects, then those non-detects must be reported with qualifiers, flags and/or explained in the case narrative as having less certainty. However, along with the data qualifiers, the case narrative may include information stating the fact that the results were not significantly affected if:
    a. *An MRL check standard was analyzed and found to be acceptable. The MRL must be the same as that analyzed in the MRL check standard for those analytes that were biased low in the CCV. Adjust MRLs (if required), flag data and state the certainty in the case narrative where the sensitivity of the instrument was demonstrated at the MRL; therefore, results were not significantly affected.*
    b. *With the reporting limit adjusted to the next level in the calibration curve (typically 5 times higher) to prove the nonexistence of a false negative and note procedure in case narrative.*
4. If the acceptance criteria was exceeded (biased high) for the CCV and there were detectable results in a sample, the results may be "qualified" if the results exceeded the regulatory/decision limit (this is to be stated in the case narrative along with the data qualifiers or flags).
5. Data associated with a biased low CCV may be fully useable if the results reported exceed a maximum regulatory limit/decision level.

16.4 Method Blank

- If an analyte in the blank is found to be out of control and the analyte is also found in associated samples, those sample results shall be "flagged" in the report and the method blank results reported.
- If the analyte is found in the blank but not in the sample then the results for the sample may be reported without a qualifier.

16.5 Laboratory Control Sample

All results associated with an out of control laboratory control sample must be reported with the appropriate data qualifier. An indication of whether the LCS was out high or low should also be included.

16.6 Surrogate

Report sample results with the appropriate data qualifier.

16.7 Laboratory Duplicate

All batch sample results associated with an out of control laboratory duplicate must be flagged with the appropriate data qualifier.

16.8 Internal Standard

All target analytes associated with an out of control internal standard must be flagged with the appropriate data qualifier.

16.9 Estimated Sample Results

16.9.1 Sample Hold Time All occurrences of missed holding times must be included on the final report including those samples received and/or analyzed outside of the specified hold times detailed in this SOP.

16.9.2 Matrix Interference Sample data associated with matrix interference must be flagged with the appropriate data qualifier.

16.9.3 Results Outside Initial Calibration Range All sample results not bracketed by initial calibration standards (within calibration range) must be reported as having less certainty by reporting with the appropriate data qualifier.

17) Training

17.1 Demonstration of Capability

All analysts must be trained in accordance with the guidelines detailed in the *SOP for Training Policy*. Demonstrations shall also be performed in accordance with the TNI Standards and DoD Quality Systems Manual. Attachment 1 shall be used to document the training plan for new analysts' initial demonstration. Additionally, these demonstrations are performed anytime there is a change in instrument type, personnel or method.

Once performance is found to be acceptable, a required certification statement must be completed by the QA Manager and either the immediate supervisor or Laboratory Manager and retained on file as a demonstration of compliance.

17.1.1 Quarterly Demonstration A demonstration of method sensitivity must be performed *quarterly on each instrument* performing this method.

1) A spike at the current LOD must be analyzed.

2) Verification of precision and bias at the LOQ must be performed.

Refer to Section 11.1.4.2 (LOQ) and 12.14.1 (LOD) for additional information on how these demonstrations are to be performed as well as the acceptance criteria.

17.1.2 Annual Demonstration Each analyst must perform a demonstration of capability initially and annually. For the initial demonstration analyze four LCS standards at 1-4x the MRL (LOQ) either concurrently or over a period of days as a verification of precision and bias of the quantitation range. The standard deviation (n-1) and average percent recovery of the four replicates are compared against the method requirement for precision (±25%) and current laboratory control limits for bias/LCS.

17.1.3 Change in Personnel, Instruments, Method and/or Matrix The requirements in Sections 17.1.1 and 17.1.2 must be performed per the schedule noted and when there is a change in personnel, instruments, method or matrix. "Change" refers to any change in personnel, instrument, test method, or sample matrix that potentially affects the precision and bias, sensitivity, or selectivity of the output (e.g., a change in the detector, column type, matrix, or other components of the sample analytical system, or a method revision).

All completed attempts at this demonstration must be turned into the QA department for retention.

18) Summary of Changes

Table 18.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
25.0	08/18/2018	C. Arend	Applied updated SOP formatting style to first two pages and header/footer. Sections renamed and reorganized to align with *SOP for Preparing Standard Operating Procedures*. Section references updated throughout.
			1.1 – second paragraph - removed reference to Note 1 (note previously removed from SOP
			5.1 – removed "Summa" from section heading
			6 – removed table and sections and replaced with new sections 6.1 – 6.6
			6.1 – removed reference to Environmental Health and Safety Manual as document is being spilt into multiple documents
			7.1 – changed "stainless steel pressure vessel" to "passivated stainless steel canister"
			7.4 – last sentence – minor revision to wording
			8.9 – added last two bullets; removed "Summa" from first bullet
			9.2.1.3 – changed "Summa canister" to "canister"
			9.2.1.3.1 – added six month expiration when prepared in 30L or greater canister; changed "Summa canister" to "canister"
			9.2.2 – changed "Summa canister" to "canister" throughout

			9.2.2.1 - changed “Summa canister” to “canister” throughout
			9.2.2.2.4 – changed “Summa canister” to “canister”
			10.2 – removed reference to electronic method manual
			10.2.1.2 – changed “Summa canister” to “canister” throughout
			10.2.2.1 – changed “Summa canister” to “canister”
			10.3 – changed “Summa canister” to “canister”
			11.1.1 – revised low points of ranges
			11.5.2 – changed “Sample(s) – 1-19” to “Sample(s) – 1-20” since sample duplicate does not count as a separate sample. Revised first two sentences to add clarification.
			11.8 – changed “DoD QSM 5.1” to “DoD QSM”
			11.9.1 – changed “Summa canister” to “canister”
			12.4.1 – 4th bullet – added Nay specific requirement; changed “DoD QSM 5.1” to “DoD QSM”
			12.7.1 – changed “DoD QSM 5.1” to “DoD QSM”
			12.9 – minor revision to AutoCAN Leak Checks box
			12.9.1 – Direct Injection box – changed “Summa canister” to “canister”; removed “AFFCEE”
			12.10.2 – included Navy requirement
			12.12.1 – included Navy requirement
			Information previously in section 13 removed – redundant to information covered in section 12
			13.7.1 – changed “Summa canister” to “canister”
			13.11 – removed “eight-character” naming convention requirement
			14.2 – updated MDL procedure
			Information previously in section 17 removed – redundant to information covered in administrative SOPs
			17.1 – removed reference to specific section in TNI Standard
			19.5 – added 2016 TNI Standards
			19.7 – updated
			Table 2 – updated MDLs and MRLs
			Table 2A – updated MRL for 1,2,4-Trichlorobenzene; added Bromobenzene
			Table 3 – updated
			Table 3A – updated; added Bromobenzene
			Table 4 – updated
			Table 4A – updated; added Bromobenzene
			Attachment 3 – Sample Review Checklist – removed questions 3 and 4 from APH section

19) References and Related Documents

19.1 EPA Method TO-14A, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA/625/R-96/010b, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1997.

19.2 EPA Method TO-15, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA/625/R-96/010b, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1997.

19.3 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, January 1999.

19.4 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Addendum, January 17, 2002.

19.5 2009 TNI Standards; 2016 TNI Standards

19.6 *Preparation of Gas Phase Standards for Ambient Air Analysis,* Tekmar-DOHRMANN Application Note, Spring 96, Vol. 6.5.

19.7 DoD/DoE Quality Systems Manual Version 5.1, 2017; and Version 5.1.1, 2018.

19.8 Arizona Administrative Code, Title 9. Health Services, Chapter 14. Department of Health Services Laboratories, October 1, 2016.

19.9 Florida Department of Environmental Protection, Chapter 62-160.

19.10 Minnesota Department of Health, 4740.2065, *Standard Operating Procedures*, Statutory Authority: MS s 144.97; 144.98; History: 31 SR 446, Posted: October 09, 2006, Revised April 16, 2010.

20) Attachments

20.1 Tables

Table 1: Instrument Tune Check Ion Abundance Criteria (TO-15)

Table 1A: Instrument Tune Check Ion Abundance Criteria (TO-14A)

Table 2: Volatile Organic Compounds, EPA Compendium Method TO-15 (SCAN)

Table 2A: Volatile Organic Compounds, EPA Compendium Method TO-15 (SIM)

Table 3: Standard Concentrations (SCAN) (Primary Sources)

Table 3A: Standard Concentrations (SIM) (Primary Sources)

Table 4: Standard Concentrations (SCAN) (Secondary Sources)

Table 4A: Standard Concentrations (SIM) (Secondary Sources)

20.2 Attachments

Attachment 1 – Training Plan

Attachment 2 – Initial Calibration Checklist

Attachment 3 – Daily QC and Sample Review Checklists

Attachment 4 – State and Project Specific Requirements

Attachment 5 – Tekmar AutoCan Trap Packing Instructions

TABLE 1

Required BFB Key Ions and
Ion Abundance Criteria for Method TO-15

Mass	Ion Abundance Criteria[1]
50	8.0 to 40.0 percent of m/e 95
75	30.0 to 66.0 percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/e 95
173	Less than 2.0 Percent of m/e 174
174	50.0 to 120.0 Percent of m/e 95
175	4.0 to 9.0 Percent of m/e 174
176	93.0 to 101.0 Percent of m/e 174
177	5.0 to 9.0 Percent of m/e 176

[1] All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 1A

Required BFB Key Ions and
Ion Abundance Criteria for Method TO-14A

Mass	Ion Abundance Criteria
50	15 to 40 percent of m/e 95
75	30 to 60 percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5 to 9 Percent of m/e 95
173	Less than 2 Percent of m/e 174
174	>50 Percent of m/e 95
175	5 to 9 Percent of m/e 174
176	>95 and <101 Percent of m/e 174
177	5 to 9 Percent of m/e 176

Note: The criteria listed in Tables 1 and 1A shall be met or exceeded in order for EPA Compendium Methods TO-15 or TO-14A to be referenced.

TABLE 2 - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	**CAS Number**	**Molecular Weight**	**Density**	**Primary Ion[2]**	**Secondary Ion(s)[2]**	**MRL[3] $(\mu g/m^3)$**	**MDL[3] $(\mu g/m^3)$**	**IS[4]**
Bromochloromethane (IS1)	74-97-5	-	-	130	128, 132	-	-	-
Propene	115-07-1	42.08	NA	42	39,41	0.52	0.13	IS1
Dichlorodifluoromethane (CFC 12)	75-71-8	120.9	1.329	85	87, 101, 103	0.52	0.087	IS1
Chloromethane	74-87-3	50.49	0.911	50	52	0.50	0.086	IS1
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	76-14-2	170.9	1.455	135	137	0.51	0.084	IS1
Vinyl Chloride	75-01-4	62.50	0.9106	62	64	0.52	0.057	IS1
1,3-Butadiene	106-99-0	54.09	0.6149	54	39, 53	0.53	0.088	IS1
Bromomethane	74-83-9	94.94	1.6755	94	96	0.50	0.074	IS1
Chloroethane	75-00-3	64.52	0.8902	64	66	0.51	0.066	IS1
Ethanol	64-17-5	46.07	0.7893	45	46	5.3	0.37	IS1
Acetonitrile	75-05-8	41.05	0.7857	41	40	0.53	0.13	IS1
Acrolein	107-02-8	56.06	0.840	56	55	2.1	0.15	IS1
Acetone	67-64-1	58.08	0.7845	58	43	5.3	1.2	IS1
Trichlorofluoromethane	75-69-4	137.4	NA	101	103	0.53	0.081	IS1
Isopropyl Alcohol	67-63-0	60.10	0.7809	45	43	5.3	0.22	IS1
Acrylonitrile	107-13-1	53.06	0.8060	53	52	0.53	0.11	IS1
1,1-Dichloroethene	75-35-4	96.94	1.213	96	61	0.53	0.074	IS1
tert-Butanol	75-65-0	74.12	0.7887	59	57,41,43	1.1	0.16	IS1
Methylene Chloride	75-09-2	84.94	1.3266	84	49	0.53	0.15	IS1
Allyl Chloride	107-05-1	76.53	0.9376	41	76	0.53	0.072	IS1
Trichlorotrifluoroethane	76-13-1	187.38	1.5635	151	101	0.53	0.076	IS1

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)

Compound[1]	CAS Number	Molecular Weight	Density	Primary Ion[2]	Secondary Ion(s)[2]	MRL[3] (µg/m^3)	MDL[3] (µg/m^3)	IS[4]
Carbon Disulfide	75-15-0	76.14	1.2632	76	78	5.3	0.16	IS1
trans-1,2-Dichloroethene	156-60-5	96.94	1.2565	61	96	0.54	0.074	IS1
1,1-Dichloroethane	75-34-3	98.96	1.1757	63	65	0.51	0.078	IS1
Methyl tert-Butyl Ether	1634-04-4	88.15	0.7402	73	57	0.54	0.063	IS1
Vinyl Acetate	108-05-4	86.09	0.9317	86	43	5.3	1.2	IS1
2-Butanone (MEK)	78-93-3	72.11	0.7999	72	43	5.3	0.11	IS1
cis-1,2-Dichloroethene	156-59-2	96.94	1.2837	61	96	0.53	0.075	IS1
Diisopropyl Ether	108-20-3	102.18	0.7241	87	45,59,43	0.53	0.070	IS1
Ethyl Acetate	141-78-6	88.106	0.9003	61	70	1.1	0.28	IS1
n-Hexane	110-54-3	86.18	0.6548	57	86	0.53	0.11	IS1
Chloroform	67-66-3	119.4	1.4832	83	85	0.53	0.071	IS1
1,2-Dichloroethane-d4(S)	17060-07-0	-	-	65	67	-	-	IS1
Tetrahydrofuran	109-99-9	72.11	0.8892	72	71,42	0.53	0.067	IS1
Ethyl tert-Butyl Ether	637-92-3	102.176	0.7519	87	59,57	0.53	0.064	IS1
1,2-Dichloroethane	107-06-2	98.96	1.2351	62	64	0.53	0.059	IS1
1,4-Difluorobenzene(IS2)	540-36-3	-	-	114	88	-	-	-
1,1,1-Trichloroethane	71-55-6	133.4	1.3390	97	99, 61	0.54	0.066	IS2
Isopropyl acetate	108-21-4	102.13	0.8718	61	87,43	1.1	0.17	IS2
1-Butanol	71-36-3	74.1224	0.8098	56	41	1.1	0.14	IS2
Benzene	71-43-2	78.11	0.8765	78	77	0.53	0.077	IS2
Carbon Tetrachloride	56-23-5	153.8	1.5940	117	119	0.53	0.074	IS2

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)

Compound[1]	CAS Number	Molecular Weight	Density	Primary Ion[2]	Secondary Ion(s)[2]	MRL[3] (μg/m³)	MDL[3] (μg/m³)	IS[4]
Cyclohexane	110-82-7	84.16	0.7739	84	69,56	1.1	0.15	IS2
tert-Amyl Methyl Ether	994-05-8	102.176	0.7703	73	87,55,43	0.53	0.065	IS2
1,2-Dichloropropane	78-87-5	113	1.1560	63	62	0.53	0.066	IS2
Bromodichloromethane	75-27-4	163.8	1.980	83	85	0.53	0.077	IS2
Trichloroethene	79-01-6	131.4	1.4642	130	132	0.53	0.072	IS2
1,4-Dioxane	123-91-1	88.11	1.0337	88	58	0.53	0.063	IS2
Isooctane	540-84-1	114.23	0.6877	57	41	0.53	0.080	IS2
Methyl Methacrylate	80-62-6	100.12	0.944	100	69	1.1	0.19	IS2
n-Heptane	142-82-5	100.2	0.6837	71	57,100	0.53	0.085	IS2
cis-1,3-Dichloropropene	10061-01-5	111	1.224	75	77	0.56	0.083	IS2
4-Methyl-2-Pentanone	108-10-1	100.2	0.7965	58	85	0.53	0.073	IS2
trans-1,3-Dichloropropene	10061-02-6	111	1.217	75	77	0.53	0.11	IS2
1,1,2-Trichloroethane	79-00-5	133.4	1.4397	97	83	0.53	0.054	IS2
Chlorobenzene-d5(IS3)	3114-55-4	-	-	82	117	-	-	-
Toluene-d8(S)	2037-26-5	-	-	98	100	-	-	IS3
Toluene	108-88-3	92.14	0.8669	91	92	0.53	0.065	IS3
2-Hexanone	591-78-6	100.16	0.8113	43	58	0.53	0.066	IS3
Dibromochloromethane	124-48-1	208.3	2.451	129	127	0.53	0.070	IS3
1,2-Dibromoethane	106-93-4	187.9	2.1791	107	109	0.53	0.062	IS3
n-Butyl Acetate	123-86-4	116.16	0.8825	43	56, 73	0.53	0.073	IS3
n-Octane	111-65-9	114.23	0.6986	57	114	0.53	0.12	IS3

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)

Compound[1]	CAS Number	Molecular Weight	Density	Primary Ion[2]	Secondary Ion(s)[2]	MRL[3] (µg/m^3)	MDL[3] (µg/m^3)	IS[4]
Tetrachloroethene	127-18-4	165.8	1.6227	166	164	0.53	0.069	IS3
Chlorobenzene	108-90-7	112.6	1.1058	112	114	0.53	0.071	IS3
Ethylbenzene	100-41-4	106.2	0.8670	91	106	0.53	0.075	IS3
m-, p-Xylenes	179601-23-1	106.2	0.8642, 0.8611	91	106	1.1	0.14	IS3
Bromoform	75-25-2	252.8	2.899	173	175	0.53	0.11	IS3
Styrene	100-42-5	104.1	0.9060	104	78, 103	0.53	0.086	IS3
o-Xylene	95-47-6	106.2	0.8802	91	106	0.53	0.077	IS3
n-Nonane	111-84-2	128.26	0.7176	43	57, 85	0.53	0.089	IS3
1,1,2,2-Tetrachloroethane	79-34-5	167.9	1.5953	83	85	0.53	0.074	IS3
4-Bromofluorobenzene(S)	460-00-4	-	-	174	176	-	-	IS3
Cumene	98-82-8	120.2	0.8618	105	120	0.53	0.077	IS3
alpha-Pinene	80-56-8	136.24	0.8582	93	77	0.52	0.082	IS3
n-Propylbenzene	103-65-1	120.1938	0.8670	91	120,65	0.53	0.077	IS3
3-Ethyltoluene	620-14-4	120.2	0.8645	105	120	0.53	0.072	IS3
4-Ethyltoluene	622-96-8	120.2	0.8614	105	120	0.52	0.085	IS3
1,3,5-Trimethylbenzene	108-67-8	120.2	0.8652	105	120	0.52	0.077	IS3
alpha-Methylstyrene	98-83-9	118.19	0.9106	118	103,117	0.52	0.085	IS3
2-Ethyltoluene	611-14-3	120.2	0.8807	105	120	0.53	0.068	IS3
1,2,4-Trimethylbenzene	95-63-6	120.2	0.8758	105	120	0.53	0.074	IS3
n-Decane	124-18-5	142.28	0.7300	57	71,85	0.53	0.072	IS3
Benzyl Chloride	100-44-7	126.59	1.1004	91	126	1.1	0.12	IS3

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)

Compound[1]	CAS Number	Molecular Weight	Density	Primary Ion[2]	Secondary Ion(s)[2]	MRL[3] (µg/m³)	MDL[3] (µg/m³)	IS[4]
1,3-Dichlorobenzene	541-73-1	147	1.2884	146	148	0.54	0.080	IS3
1,4-Dichlorobenzene	106-46-7	147	1.2475	146	148	0.53	0.082	IS3
sec-Butylbenzene	135-98-8	134.2206	0.8601	105	134,91	0.53	0.073	IS3
p-Isopropyltoluene	99-87-6	134.2206	0.8573	119	134,91	0.51	0.081	IS3
1,2,3-Trimethylbenzene	526-73-8	120.1938	0.8944	105	120	0.51	0.073	IS3
1,2-Dichlorobenzene	95-50-1	147	1.3059	146	148	0.54	0.079	IS3
d-Limonene	5989-27-5	136.24	0.8402	68	93	0.50	0.11	IS3
1,2,Dibromo-3-Chloropropane	96-12-8	236.33	2.093	157	75, 39	0.53	0.10	IS3
n-Undecane	1120-21-4	156.31	0.7402	57	71, 85	0.53	0.14	IS3
1,2,4-Trichlorobenzene	120-82-1	181.5	1.459	180	182, 184	0.55	0.13	IS3
Naphthalene	91-20-3	128.17	1.0253	128	129	0.53	0.13	IS3
n-Dodecane	112-40-3	170.34	0.7487	57	71,85	0.53	0.15	IS3
Hexachlorobutadiene	87-68-3	260.8	1.556	225	227	0.53	0.11	IS3
Cyclohexanone	108-94-1	98.14	0.9478	55	42, 98	0.52	0.083	IS3
tert-Butylbenzene	98-06-6	134.22	0.867	119	134	0.53	0.080	IS3
n-Butylbenzene	104-51-8	134.22	0.867	91	134	0.53	0.077	IS3

(S) = Surrogate (IS1) = Internal Standard 1 (IS2) = Internal Standard 2 (IS3) = Internal Standard 3
NA = Not Available

Note 1: Additional compounds may be reported as long as the minimum requirements of this document are met. The compounds listed in this table are reported using TO-15 SCAN. The Selected Ion Monitoring (SIM) compounds are a subset of this list and are included in Table 2A.

Note 2: These are suggested primary and secondary ions. However, any ions in the analyte spectra that are sufficient enough in response to reach the desired reporting limit and having a limited amount of interference, is acceptable for both the primary and secondary ion selection. Analyst experience should be utilized in determining appropriate ions.

Note 3: The laboratory performs three concentration level analyses (SIM, SCAN and Low Level SCAN). The method reporting limit listed is the standard SCAN limit (at or above lowest concentration in the initial calibration curve), but may change with each new initial calibration performed. Therefore, current reporting limits for the three analysis levels, MRLs in ppbv, and those from the Low Level SCAN should be reviewed in the electronic TO-15 Method Manual.

Note 4: The listing of the internal standard by which the compounds are quantitated is for TO-15 SCAN only. SIM compounds (SCAN subset) and their corresponding ions and internal standards are listed in Table 2A.

Note 5: m/e 101 is ~10% or less of m/e 85 (the base peak) and may not be present for low level results. Retention times must be carefully verified.

Table 2A – Volatile Organic Compounds, EPA Compendium Method TO-15 (SIM)

Compound	Primary Ion[1]	Secondary Ion[1]	MRL[2] (ug/m3)	MDL[2] (ug/m3)	IS
Dichlorodifluoromethane	85	87	0.050	0.017	IS1
Chloromethane	52	50	0.050	0.019	IS1
Vinyl Chloride	62	64	0.025	0.0076	IS1
1,3-Butadiene	54	39	0.050	0.014	IS1
Bromomethane	94	96	0.025	0.0093	IS1
Chloroethane	64	66	0.025	0.0085	IS1
Acrolein	56	55	0.20	0.039	IS1
Acetone	58	43	2.5	0.056	IS1
Freon 11	101	103	0.050	0.015	IS1
1,1-Dichloroethene	96	98,61	0.025	0.0086	IS1
Methylene Chloride	84	49	0.10	0.013	IS1
Trichlorotrifluoroethane	151	153	0.025	0.0089	IS1
trans-1,2-Dichloroethene	96	98,61	0.025	0.0073	IS1
1,1-Dichloroethane	63	65	0.025	0.0061	IS1
Methyl tert-Butyl Ether	73	57	0.025	0.0093	IS1
cis-1,2-Dichloroethene	96	98,61	0.025	0.0092	IS1
Chloroform	83	85	0.10	0.018	IS1
1,2-Dichloroethane	62	64	0.025	0.0084	IS1
1,1,1-Trichloroethane	97	99	0.025	0.0059	IS1
Benzene	78	77	0.075	0.020	IS1
Carbon Tetrachloride	117	119	0.025	0.012	IS1
1,2-Dichloropropane	63	62,76	0.025	0.0073	IS2
Bromodichloromethane	83	85	0.025	0.0069	IS2
Trichloroethene	130	132	0.025	0.0085	IS2
1,4-Dioxane	88	58	0.10	0.0085	IS2
cis-1,3-Dichloropropene	75	77,39	0.025	0.0062	IS2
trans-1,3-Dichloropropene	75	77,39	0.025	0.0055	IS2
1,1,2-Trichloroethane	83	97,61	0.10	0.0079	IS2
Toluene	91	92	0.10	0.011	IS2
Dibromochloromethane	129	127	0.025	0.0088	IS3
1,2-Dibromoethane	107	109	0.025	0.0079	IS2
Tetrachloroethene	166	164	0.025	0.0082	IS2
Chlorobenzene	112	114	0.10	0.0092	IS3
Ethylbenzene	91	106	0.10	0.0097	IS3
m-&-p-Xylene	91	106	0.10	0.019	IS3
Styrene	104	103	0.10	0.0074	IS3
o-Xylene	91	106	0.10	0.0089	IS3
1,1,2,2-Tetrachloroethane	83	85	0.025	0.0072	IS3
1,3,5-Trimethylbenzene	105	120	0.10	0.0073	IS3
1,2,4-Trimethylbenzene	105	120	0.10	0.0083	IS3
1,3-Dichlorobenzene	146	148	0.025	0.0085	IS3
1,4-Dichlorobenzene	146	148	0.025	0.0081	IS3
1,2-Dichlorobenzene	146	148	0.025	0.0083	IS3
1,2-Dibromo-3-chloropropane	157	75	0.10	0.0095	IS3
1,2,4-Trichlorobenzene	182	184	0.050	0.013	IS3
Naphthalene	128	129	0.10	0.016	IS3
Hexachlorobutadiene	225	227	0.10	0.0092	IS3
Bromobenzene	77	156, 158	0.10	0.0042	IS3

NA = Not Available (IS1) = Internal Standard 1 (IS2) = Internal Standard 2 (IS3) = Internal Standard 3

Note 1: These are suggested primary and secondary ions. However, any ions in the analyte spectra that is sufficient enough in response to reach the desired reporting limit and having a limited amount of interference, is acceptable

for both the primary and secondary ion selection. Analyst experience should be utilized in determining appropriate ions.
Note 2: The method reporting limit listed is the standard SIM limit (lowest concentration in the initial calibration curve; must be higher than MDL), but may change with each new initial calibration performed. Therefore, current reporting limits should be reviewed. MDLs in ppbV may be reviewed in the electronic TO-15 Method Manual.

Table 3
Standard Concentrations (SCAN) (Primary Sources)[1]

Compound Name	0.1ng	0.2ng	0.5ng	1.0ng	5.0ng	25ng	50ng	100ng
Bromochloromethane (IS1)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Propene	0.1037	0.2074	0.5185	1.037	5.185	25.925	51.85	103.7
Dichlorodifluoromethane (CFC 12)	0.1048	0.2096	0.5240	1.048	5.240	26.200	52.40	104.8
Chloromethane	0.1006	0.2012	0.5030	1.006	5.030	25.150	50.30	100.6
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	0.1021	0.2042	0.5105	1.021	5.105	25.525	51.05	102.1
Vinyl Chloride	0.1032	0.2064	0.5160	1.032	5.160	25.800	51.60	103.2
1,3-Butadiene	0.1059	0.2118	0.5295	1.059	5.295	26.475	52.95	105.9
Bromomethane	0.0993	0.1986	0.4965	0.993	4.965	24.825	49.65	99.3
Chloroethane	0.1012	0.2024	0.5060	1.012	5.060	25.300	50.60	101.2
Ethanol	0.5271	1.0542	2.6355	5.271	26.355	131.775	263.55	527.1
Acetonitrile	0.1059	0.2118	0.5295	1.059	5.295	26.475	52.95	105.9
Acrolein	0.1054	0.2108	0.5270	1.054	5.270	26.350	52.70	105.4
Acetone	0.5322	1.0644	2.6610	5.322	26.610	133.050	266.10	532.2
Trichlorofluoromethane	0.1051	0.2102	0.5255	1.051	5.255	26.275	52.55	105.1
Isopropyl Alcohol	0.2107	0.4214	1.0535	2.107	10.535	52.675	105.35	210.7
Acrylonitrile	0.1056	0.2112	0.5280	1.056	5.280	26.400	52.80	105.6
1,1-Dichloroethene	0.1061	0.2122	0.5305	1.061	5.305	26.525	53.05	106.1
tert-Butanol	0.2120	0.4240	1.0600	2.120	10.600	53.000	106.00	212.0
Methylene Chloride	0.1058	0.2116	0.5290	1.058	5.290	26.450	52.90	105.8
Allyl Chloride	0.1054	0.2108	0.5270	1.054	5.270	26.350	52.70	105.4
Trichlorotrifluoroethane	0.1053	0.2106	0.5265	1.053	5.265	26.325	52.65	105.3
Carbon Disulfide	0.1063	0.2126	0.5315	1.063	5.315	26.575	53.15	106.3
trans-1,2-Dichloroethene	0.1081	0.2162	0.5405	1.081	5.405	27.025	54.05	108.1
1,1-Dichloroethane	0.1022	0.2044	0.5110	1.022	5.110	25.550	51.10	102.2
Methyl tert-Butyl Ether	0.1070	0.2140	0.5350	1.070	5.350	26.750	53.50	107.0
Vinyl Acetate	0.5281	1.0562	2.6405	5.281	26.405	132.025	264.05	528.1
2-Butanone (MEK)	0.1052	0.2104	0.5260	1.052	5.260	26.300	52.60	105.2
cis-1,2-Dichloroethene	0.1067	0.2134	0.5335	1.067	5.335	26.675	53.35	106.7
Diispropyl Ether	0.1065	0.2130	0.5325	1.065	5.325	26.625	53.25	106.5
Ethyl Acetate	0.2136	0.4272	1.0680	2.136	10.680	53.400	106.80	213.6
n-Hexane	0.1066	0.2132	0.5330	1.066	5.330	26.650	53.30	106.6
Chloroform	0.1061	0.2122	0.5305	1.061	5.305	26.525	53.05	106.1
1,2-Dichloroethane-d4 (S)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Tetrahydrofuran	0.1064	0.2128	0.5320	1.064	5.320	26.600	53.20	106.4
Ethyl tert-Butyl Ether	0.1059	0.2118	0.5295	1.059	5.295	26.475	52.95	105.9
1,2-Dichloroethane	0.1055	0.2110	0.5275	1.055	5.275	26.375	52.75	105.5
1,4-Difluorobenzene(IS2)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
1,1,1-Trichloroethane	0.1077	0.2154	0.5385	1.077	5.385	26.925	53.85	107.7
Isopropyl acetate	0.2113	0.4226	1.0565	2.113	10.565	52.825	105.65	211.3
1-Butanol	0.2114	0.4228	1.0570	2.114	10.570	52.850	105.70	211.4

Table 3 - Continued
Standard Concentrations (SCAN) (Primary Sources)[1]

Compound Name	0.1ng	0.2ng	0.5ng	1.0ng	5.0ng	25ng	50ng	100ng
Benzene	0.1057	0.2114	0.5285	1.057	5.285	26.425	52.85	105.7
Carbon Tetrachloride	0.1060	0.2120	0.5300	1.060	5.300	26.500	53.00	106.0
Cyclohexane	0.2135	0.4270	1.0675	2.135	10.675	53.375	106.75	213.5
tert-Amyl Methyl Ether	0.1057	0.2114	0.5285	1.057	5.285	26.425	52.85	105.7
1,2-Dichloropropane	0.1066	0.2132	0.5330	1.066	5.330	26.650	53.30	106.6
Bromodichloromethane	0.1067	0.2134	0.5335	1.067	5.335	26.675	53.35	106.7
Trichloroethene	0.1061	0.2122	0.5305	1.061	5.305	26.525	53.05	106.1
1,4-Dioxane	0.1063	0.2126	0.5315	1.063	5.315	26.575	53.15	106.3
Isooctane	0.1060	0.2120	0.5300	1.060	5.300	26.500	53.00	106.0
Methyl Methacrylate	0.2112	0.4224	1.0560	2.112	10.560	52.800	105.60	211.2
n-Heptane	0.1065	0.2130	0.5325	1.065	5.325	26.625	53.25	106.5
cis-1,3-Dichloropropene	0.1120	0.2240	0.5600	1.120	5.600	28.000	56.00	112.0
4-Methyl-2-Pentanone	0.1059	0.2118	0.5295	1.059	5.295	26.475	52.95	105.9
trans-1,3-Dichloropropene	0.1067	0.2134	0.5335	1.067	5.335	26.675	53.35	106.7
1,1,2-Trichloroethane	0.1064	0.2128	0.5320	1.064	5.320	26.600	53.20	106.4
Chlorobenzene-d5 (IS3)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Toluene-d8 (S)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Toluene	0.1054	0.2108	0.5270	1.054	5.270	26.350	52.70	105.4
2-Hexanone	0.1060	0.2120	0.5300	1.060	5.300	26.500	53.00	106.0
Dibromochloromethane	0.1061	0.2122	0.5305	1.061	5.305	26.525	53.05	106.1
1,2-Dibromoethane	0.1064	0.2128	0.5320	1.064	5.320	26.600	53.20	106.4
n-Butyl Acetate	0.1068	0.2136	0.5340	1.068	5.340	26.700	53.40	106.8
n-Octane	0.1060	0.2120	0.5300	1.060	5.300	26.500	53.00	106.0
Tetrachloroethene	0.1063	0.2126	0.5315	1.063	5.315	26.575	53.15	106.3
Chlorobenzene	0.1066	0.2132	0.5330	1.066	5.330	26.650	53.30	106.6
Ethylbenzene	0.1052	0.2104	0.5260	1.052	5.260	26.300	52.60	105.2
m- & p-Xylene	0.2123	0.4246	1.0615	2.123	10.615	53.075	106.15	212.3
Bromoform	0.1063	0.2126	0.5315	1.063	5.315	26.575	53.15	106.3
Styrene	0.1058	0.2116	0.5290	1.058	5.290	26.450	52.90	105.8
o-Xylene	0.1055	0.2110	0.5275	1.055	5.275	26.375	52.75	105.5
n-Nonane	0.1054	0.2108	0.5270	1.054	5.270	26.350	52.70	105.4
1,1,2,2-Tetrachloroethane	0.1057	0.2114	0.5285	1.057	5.285	26.425	52.85	105.7
4-Bromofluorobenzene (S)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Cumene	0.1052	0.2104	0.5260	1.052	5.260	26.300	52.60	105.2
alpha-Pinene	0.1046	0.2092	0.5230	1.046	5.230	26.150	52.30	104.6
n-Propylbenzene	0.1064	0.2128	0.5320	1.064	5.320	26.600	53.20	106.4
3-Ethyltoluene	0.1050	0.2100	0.5250	1.050	5.250	26.250	52.50	105.0
4-Ethyltoluene	0.1049	0.2098	0.5245	1.049	5.245	26.225	52.45	104.9
1,3,5-Trimethylbenzene	0.1049	0.2098	0.5245	1.049	5.245	26.225	52.45	104.9
alpha-Methylstyrene	0.1049	0.2098	0.5245	1.049	5.245	26.225	52.45	104.9
2-Ethyltoluene	0.1060	0.2120	0.5300	1.060	5.300	26.500	53.00	106.0
1,2,4-Trimethylbenzene	0.1051	0.2102	0.5255	1.051	5.255	26.275	52.55	105.1

Table 3 - Continued
Standard Concentrations (SCAN) (Primary Sources)[1]

Compound Name	0.1ng	0.2ng	0.5ng	1.0ng	5.0ng	25ng	50ng	100ng
n-Decane	0.1059	0.2118	0.5295	1.059	5.295	26.475	52.95	105.9
Benzyl Chloride	0.1074	0.2148	0.5370	1.074	5.370	26.850	53.70	107.4
1,3-Dichlorobenzene	0.1071	0.2142	0.5355	1.071	5.355	26.775	53.55	107.1
1,4-Dichlorobenzene	0.1064	0.2128	0.5320	1.064	5.320	26.600	53.20	106.4
sec-Butylbenzene	0.1055	0.2110	0.5275	1.055	5.275	26.375	52.75	105.5
p-Isopropyltoluene	0.1026	0.2052	0.5130	1.026	5.130	25.650	51.30	102.6
1,2,3-Trimethylbenzene	0.1026	0.2052	0.5130	1.026	5.130	25.650	51.30	102.6
1,2-Dichlorobenzene	0.1083	0.2166	0.5415	1.083	5.415	27.075	54.15	108.3
d-Limonene	0.1005	0.2010	0.5025	1.005	5.025	25.125	50.25	100.5
1,2-Dibromo-3-Chloropropane	0.1051	0.2102	0.5255	1.051	5.255	26.275	52.55	105.1
n-Undecane	0.1053	0.2106	0.5265	1.053	5.265	26.325	52.65	105.3
1,2,4-Trichlorobenzene	0.1097	0.2194	0.5485	1.097	5.485	27.425	54.85	109.7
Naphthalene	0.1056	0.2112	0.5280	1.056	5.280	26.400	52.80	105.6
n-Dodecane	0.1056	0.2112	0.5280	1.056	5.280	26.400	52.80	105.6
Hexachlorobutadiene	0.1057	0.2114	0.5285	1.057	5.285	26.425	52.85	105.7
Methacrylonitrile	0.1067	0.2134	0.5335	1.067	5.335	26.675	53.35	106.7
Cyclohexanone	0.1039	0.2078	0.5195	1.039	5.195	25.975	51.95	103.9
tert-Butylbenzene	0.1050	0.2100	0.5250	1.050	5.250	26.250	52.50	105.0
n-Butylbenzene	0.1054	0.2108	0.5270	1.054	5.270	26.350	52.70	105.4

Note 1: The concentrations detailed in this table may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Table 3A - Standard Concentrations (SIM) (Primary Sources)[1]

Compound Name	20pg	50pg	100pg	500pg	1000pg	2000pg	5000pg	10,000pg	25,000pg	50,000pg
Freon-12	20.96	52.40	104.8	524.0	1048	2096	5240	10480	26200	52400
Chloromethane	20.12	50.30	100.6	503.0	1006	2012	5030	10060	25150	50300
Vinyl Chloride	20.64	51.60	103.2	516.0	1032	2064	5160	10320	25800	51600
1,3-Butadiene	21.18	52.95	105.9	529.5	1059	2118	5295	10590	26475	52950
Bromomethane	19.86	49.65	99.3	496.5	993	1986	4965	9930	24825	49650
Chloroethane	20.24	50.60	101.2	506.0	1012	2024	5060	10120	25300	50600
Acrolein	21.08	52.70	105.4	527.0	1054	2108	5270	10540	26350	52700
Acetone	106.44	266.10	532.2	2661.0	5322	10644	26610	53220	133050	266100
Freon-11	21.02	52.55	105.1	525.5	1051	2102	5255	10510	26275	52550
1,1-Dichloroethene	21.22	53.05	106.1	530.5	1061	2122	5305	10610	26525	53050
Methylene Chloride	21.16	52.90	105.8	529.0	1058	2116	5290	10580	26450	52900
Freon-113	21.06	52.65	105.3	526.5	1053	2106	5265	10530	26325	52650
trans-1,2-Dichloroethene	21.62	54.05	108.1	540.5	1081	2162	5405	10810	27025	54050
1,1-Dichloroethane	20.44	51.10	102.2	511.0	1022	2044	5110	10220	25550	51100
Methyl tert-Butyl Ether	21.40	53.50	107.0	535.0	1070	2140	5350	10700	26750	53500
cis-1,2-Dichloroethene	21.34	53.35	106.7	533.5	1067	2134	5335	10670	26675	53350
Chloroform	21.22	53.05	106.1	530.5	1061	2122	5305	10610	26525	53050
1,2-Dichloroethane	21.10	52.75	105.5	527.5	1055	2110	5275	10550	26375	52750
1,1,1-Trichloroethane	21.54	53.85	107.7	538.5	1077	2154	5385	10770	26925	53850
Benzene	21.14	52.85	105.7	528.5	1057	2114	5285	10570	26425	52850
Carbon Tetrachloride	21.20	53.00	106.0	530.0	1060	2120	5300	10600	26500	53000
1,2-Dichloropropane	21.32	53.30	106.6	533.0	1066	2132	5330	10660	26650	53300
Bromodichloromethane	21.34	53.35	106.7	533.5	1067	2134	5335	10670	26675	53350
Trichloroethene	21.22	53.05	106.1	530.5	1061	2122	5305	10610	26525	53050
1,4-Dioxane	21.26	53.15	106.3	531.5	1063	2126	5315	10630	26575	53150
cis-1,3-Dichloropropene	22.40	56.00	112.0	560.0	1120	2240	5600	11200	28000	56000
trans-1,3-Dichloropropene	21.34	53.35	106.7	533.5	1067	2134	5335	10670	26675	53350
1,1,2-Trichloroethane	21.28	53.20	106.4	532.0	1064	2128	5320	10640	26600	53200
Toluene	21.08	52.70	105.4	527.0	1054	2108	5270	10540	26350	52700
Dibromochloromethane	21.22	53.05	106.1	530.5	1061	2122	5305	10610	26525	53050
1,2-Dibromoethane	21.28	53.20	106.4	532.0	1064	2128	5320	10640	26600	53200
Tetrachloroethene	21.26	53.15	106.3	531.5	1063	2126	5315	10630	26575	53150
Chlorobenzene	21.32	53.30	106.6	533.0	1066	2132	5330	10660	26650	53300
Ethylbenzene	21.04	52.60	105.2	526.0	1052	2104	5260	10520	26300	52600
m,p-Xylenes	42.46	106.15	212.3	1061.5	2123	4246	10615	21230	53075	106150
Styrene	21.16	52.90	105.8	529.0	1058	2116	5290	10580	26450	52900
o-Xylene	21.10	52.75	105.5	527.5	1055	2110	5275	10550	26375	52750
1,1,2,2-Tetrachloroethane	21.14	52.85	105.7	528.5	1057	2114	5285	10570	26425	52850
1,3,5-Trimethylbenzene	20.98	52.45	104.9	524.5	1049	2098	5245	10490	26225	52450
1,2,4-Trimethylbenzene	21.02	52.55	105.1	525.5	1051	2102	5255	10510	26275	52550
1,3-Dichlorobenzene	21.42	53.55	107.1	535.5	1071	2142	5355	10710	26775	53550
1,4-Dichlorobenzene	21.28	53.20	106.4	532.0	1064	2128	5320	10640	26600	53200
1,2-Dichlorobenzene	21.66	54.15	108.3	541.5	1083	2166	5415	10830	27075	54150
1,2-Dibromo-3-chloropropane	21.02	52.55	105.1	525.5	1051	2102	5255	10510	26275	52550
1,2,4-Trichlorobenzene	21.94	54.85	109.7	548.5	1097	2194	5485	10970	27425	54850
Naphthalene	21.12	52.80	105.6	528.0	1056	2112	5280	10560	26400	52800
Hexachloro-1,3-butadiene	21.14	52.85	105.7	528.5	1057	2114	5285	10570	26425	52850

Table 3A - Standard Concentrations (SIM) (Primary Sources)[1] – Continued

Compound Name	20pg	50pg	100pg	500pg	1000pg	2000pg	5000pg	10,000pg
Bromobenzene	21.2	53.0	106	530	1060	2120	5300	10600

Note 1: The concentrations detailed in Table 3A may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Table 4 - Standard Concentrations (SCAN) (Secondary Sources)[1]

Compound Name	25ng	Compound Name	25ng	Compound Name	25ng
Bromochloromethane (IS1)	**12.5**	1,1,1-Trichloroethane	26.525	alpha-Pinene	26.600
Propene	26.275	Isopropyl acetate	53.275	n-Propylbenzene	26.750
Dichlorodifluoromethane (CFC 12)	26.600	1-Butanol	53.300	3-Ethyltoluene	26.450
Chloromethane	26.250	Benzene	26.625	4-Ethyltoluene	26.425
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	26.325	Carbon Tetrachloride	26.700	1,3,5-Trimethylbenzene	26.500
Vinyl Chloride	26.350	Cyclohexane	53.150	alpha-Methylstyrene	26.525
1,3-Butadiene	26.225	tert-Amyl Methyl Ether	26.550	2-Ethyltoluene	26.700
Bromomethane	26.225	1,2-Dichloropropane	26.525	1,2,4-Trimethylbenzene	26.550
Chloroethane	26.250	Bromodichloromethane	26.700	n-Decane	26.625
Ethanol	130.375	Trichloroethene	26.550	Benzyl Chloride	26.550
Acetonitrile	26.200	1,4-Dioxane	26.600	1,3-Dichlorobenzene	26.475
Acrolein	26.075	Isooctane	26.525	1,4-Dichlorobenzene	26.750
Acetone	131.825	Methyl Methacrylate	52.950	sec-Butylbenzene	26.575
Trichlorofluoromethane	26.025	n-Heptane	26.625	p-Isopropyltoluene	26.600
Isopropyl Alcohol	52.775	cis-1,3-Dichloropropene	26.025	1,2,3-Trimethylbenzene	26.600
Acrylonitrile	26.450	4-Methyl-2-Pentanone	26.650	1,2-Dichlorobenzene	26.750
1,1-Dichloroethene	26.675	trans-1,3-Dichloropropene	26.625	d-Limonene	26.625
tert-Butanol	53.350	1,1,2-Trichloroethane	26.500	1,2-Dibromo-3-Chloropropane	26.300
Methylene Chloride	26.600	**Chlorobenzene-d5 (IS3)**	**12.5**	n-Undecane	26.775
Allyl Chloride	26.525	**Toluene-d8 (S)**	**12.5**	1,2,4-Trichlorobenzene	27.200
Trichlorotrifluoroethane	26.750	Toluene	26.400	Naphthalene	26.125
Carbon Disulfide	26.725	2-Hexanone	26.425	n-Dodecane	26.825
trans-1,2-Dichloroethene	26.700	Dibromochloromethane	26.450	Hexachlorobutadiene	26.550
1,1-Dichloroethane	26.525	1,2-Dibromoethane	26.425	Methacrylonitrile	26.500
Methyl tert-Butyl Ether	26.625	Butyl Acetate	26.850	Cyclohexanone	26.150
Vinyl Acetate	132.750	n-Octane	26.525	tert-Butylbenzene	26.525
2-Butanone (MEK)	26.450	Tetrachloroethene	26.500	n-Butylbenzene	26.575
cis-1,2-Dichloroethene	26.475	Chlorobenzene	26.525		
Diisopropyl Ether	26.600	Ethylbenzene	26.475		
Ethyl Acetate	53.300	m- & p-Xylene	52.975		
n-Hexane	26.625	Bromoform	26.525		
Chloroform	26.500	Styrene	26.350		
1,2-Dichloroethane-d4 (S)	**12.5**	o-Xylene	26.400		
Tetrahydrofuran	26.550	n-Nonane	26.500		
Ethyl tert-Butyl Ether	26.525	1,1,2,2-Tetrachloroethane	26.450		
1,2-Dichloroethane	26.500	**4-Bromofluorobenzene (S)**	**12.5**		
1,4-Difluorobenzene(IS2)	**12.5**	Cumene	26.525		

Note 1: The concentrations detailed in this table may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Table 4A – ICV/LCS Standard Concentrations (SIM) (Secondary Sources)[1]

Compound Name	500pg
Freon-12	532.0
Chloromethane	525.0
Vinyl Chloride	527.0
1,3-Butadiene	524.5
Bromomethane	524.5
Chloroethane	525.0
Acrolein	521.5
Acetone	2636.5
Freon-11	520.5
1,1-Dichloroethene	533.5
Methylene Chloride	532.0
Freon-113	535.0
trans-1,2-Dichloroethene	534.0
1,1-Dichloroethane	530.5
Methyl tert-Butyl Ether	532.5
cis-1,2-Dichloroethene	529.5
Chloroform	530.0
1,2-Dichloroethane	530.0
1,1,1-Trichloroethane	530.5
Benzene	532.5
Carbon Tetrachloride	534.0
1,2-Dichloropropane	530.5
Bromodichloromethane	534.0
Trichloroethene	531.0
1,4-Dioxane	532.0
cis-1,3-Dichloropropene	520.5
trans-1,3-Dichloropropene	532.5
1,1,2-Trichloroethane	530.0
Toluene	528.0
Dibromochloromethane	529.0
1,2-Dibromoethane	528.5
Tetrachloroethene	530.0
Chlorobenzene	530.5
Ethylbenzene	529.5
m,p-Xylenes	1059.5
Styrene	527.0
o-Xylene	528.0
1,1,2,2-Tetrachloroethane	529.0
1,3,5-Trimethylbenzene	530.0
1,2,4-Trimethylbenzene	531.0
1,3-Dichlorobenzene	529.5
1,4-Dichlorobenzene	535.0
1,2-Dichlorobenzene	535.0
1,2-Dibromo-3-chloropropane	526.0
1,2,4-Trichlorobenzene	544.0
Naphthalene	522.5
Hexachloro-1,3-butadiene	531.0
Bromobenzene	1060

Note 1: The concentrations detailed in this table may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Attachment 1

Training Plan

Training Plan for Analysis of VOCs by GC/MS

Trainee ________________ Trainer _________________ Instrument _____ Training Completion Date ___________

1. Read SOP *Training Duration* ______________ Trainer ___ Trainee ___ Date _________

2. Read Methods TO-14A & TO-15A *Training Duration* ______________ Trainer ___ Trainee ___ Date _________

3. Demonstrated understanding of the scientific basis of the analysis Trainer ___ Trainee ___ Date _________
   Whole air sample preconcentration techniques
   Gas chromatography *Training Duration* ________________
   Mass spectrometry

4. Demonstrated familiarity with related SOPs Trainer ___ Trainee ___ Date _________
   SOP for Batches and Sequences; Rev. ___
   SOP for Making Entries onto Analytical Records; Rev. ___ *Training Duration* ________________
   SOP for Manual Integration Policy; Rev. ____
   SOP for Significant Figures; Rev. ____
   SOP for Nonconformance and Corrective Action; Rev. ____
   SOP for Performing MDL Studies and Establishing Limits of Detection and Quantitation; Rev. ____
   SOP for Cleaning and Certification of Summa Canisters; Rev. ____

5. Observe performance of SOP *Training Duration* ______________ Trainer ___ Trainee ___ Date _________
   ___sample preparation/dilution and sample loading and analysis
   ___analytical sequence setup
   ___standard preparation
   ___BFB tuning evaluation
   ___initial calibration (model, calculations, manual integrations)/initial calibration verification
   ___manual integrations
   ___continuing calibration verification
   ___EnviroQuant introduction (recognizing saturation and sensitivity issues)
   ___data reduction and reporting including reporting req. for various agencies, autotexts, documentation
   ___canister and bag handling (including leakers)

6. Perform SOP with supervision *Training Duration* ______________ Trainer ___ Trainee ___ Date _________
   ___sample preparation/dilution and sample loading and analysis
   ___analytical sequence setup
   ___standard preparation
   ___BFB tuning evaluation
   ___initial calibration (model, calculations, manual integrations)/initial calibration verification
   ___manual integrations
   ___continuing calibration verification
   ___EnviroQuant use (recognizing saturation and sensitivity issues)
   ___data reduction and reporting including reporting req. for various agencies, autotexts, documentation
   ___canister and bag handling (including leakers)

7. Independent performance of the SOP *Training Duration* ______________ Trainer ___ Trainee ___ Date _________
   ___sample preparation/dilution and sample loading and analysis
   ___analytical sequence setup
   ___standard preparation
   ___BFB tuning evaluation
   ___initial calibration (model, calculations, manual integrations)/initial calibration verification
   ___manual integrations
   ___continuing calibration verification
   ___EnviroQuant proficiency (recognizing saturation and sensitivity issues)
   ___data reduction and reporting including reporting req. for various agencies, autotexts, documentation
   ___canister and bag handling (including leakers)
   ___initial demonstration of competency (4 Laboratory Control Samples)

8. Instrument operation and maintenance Trainer ___ Trainee ___ Date _________
   ___autosampler *Training Duration* ________________
   ___GC and capillary column installation *Training Duration* ________________
   ___mass spectrometer *Training Duration* ________________
   ___data system *Training Duration* ________________

Attachment 2

Initial Calibration Checklist

Initial Calibration Review Checklist - EPA Compendium Method TO-15

ICAL Date:________________________ ICAL ID:____________________ LIMS ICAL ID:____________________

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan Scan Low Level (0.1ng): ☐ Yes ☐ No

Analyst **Reviewer**

☐ 1. Is the required documentation in the ICAL file? ☐
  ☐ BFB Tune analysis Report ☐
  ☐ Calibration Status Report (aka Calibration History) ☐
  ☐ Response Factor Report/Percent RSD ☐
  ☐ Quant Report for each calibration std (including manual integration documentation) ☐
  ☐ ICV Quantitation Report ☐
  ☐ TO-15 Standard Calculation Spreadsheet ☐
☐ 2. Was the ICAL performed continuously (not interrupted for maintenance or sample analysis)? ☐
☐ 3. Have all the calibration standards been analyzed within 24 hours of each other? ☐
☐ 4. Does the BFB tune check standard analysis at the start meet the tune criteria? ☐
☐ 5. Are all the analytes in the blank analysis <MRL? ☐
☐ 6. Does each analyte's ICAL include a minimum of 5 concentrations at 5 consecutive levels? ☐
☐ 7. Were the standards analyzed from low concentration to high concentration? ☐
☐ 8. For each analyte, are there no levels skipped? ☐
☐ 9. For each analyte, is there only one value used for each calibration level? ☐
☐ 10. For each analyte, is the lowest standard's concentration at or below the analyte's MRL? ☐
☐ 11. For each analyte, is the corresponding signal to noise ratio at least 3:1 at the lowest point on the curve? ☐
☐ 12. For each analyte, are the corresponding upper levels free from saturation? ☐
☐ 13. If a calibration level is dropped, are all the responses for each target analyte dropped and is the information noted in the ICAL explaining the reason? ☐
☐ 14. Is the average RSD ≤30% for all analytes, with no more than two exceptions ≤40%? ☐
☐ 15. DoD/Navy: Is the average RSD ≤30% for all analytes? ☐
☐ 16. Is the response Y at each calibration level within 40% of the mean area response over the initial calibration range for each internal standard? ☐
☐ 17. Percent recovery for each analyte in the ICV 70%-130% (AZ: 50-150% for VA)? ☐
☐ 18. Was the RRT for each target compound at each calibration level within 0.06RRT units of the mean RRT for the compound? ☐
☐ 19. Is the retention time shift for each of the internal standards at each calibration level within 20s of the mean retention time over the initial calibration range for each standard? ☐
☐ 20. If there are any manual integrations, are they performed correctly according to the corresponding SOP? If so, initial and date the appropriate pages. ☐
☐ 21. Is the ICAL good at 0.5ng (or 0.1ng)–100ng (Scan) or 10-20000pg (SIM) for all compounds?
  ☐ Yes ☐ No Note exceptions and corresponding MRLs below – *Specify applicable range...* ☐
☐ 22. Are ALL of the peak selections for each analyte correct according to retention time (all RTs must be checked by both the initial and peer reviewer)? ☐

COMMENTS:

Analyst: ______________________________ Secondary Reviewer: ______________________________

Attachment 3

Daily QC and Sample Review Checklists

EPA Compendium Method TO-15 - Daily QC Review Checklist

(Note exceptions in Comments and include Analysis Observations/Case Narrative Summary Form as appropriate)

Method: ☐ EPA TO-15 ☐ EPA TO-14A **Analysis Date:** ____________________

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan **Scan Low Level (0.1ng):** ☐ Yes ☐ No **DOD:** ☐ Yes ☐ No

Analyst **Reviewer**

☐ 1. Is the required documentation present? .... ☐
- ☐ CORRECT BFB Tune analysis Report
- ☐ CCV analysis Quantitation Report & %D Report
- ☐ LCS analysis Quantitation Report
- ☐ MB analysis Quantitation Report

☐ 2. BFB **tune** check standard analysis meet the tune criteria for the method indicated above? .... ☐

☐ 3. Analyses within the tune's **24-hr window or** ☐ **Client's 12hr window requirement**? .... ☐

☐ 4. Does the **CCV** have a difference ≤30% for all analytes? .... ☐
[Note all outliers biased high and/or low]

☐ 5. **DoD**: Does the **Closing CCV** have a difference ≤30% for all analytes? .... ☐
[Note all outliers biased high and/or low]

☐ 6. All **IS** retention times within 20 seconds of the CCV RT or the RT from the midpoint (ICAL)? .... ☐

☐ 7. All **IS** responses within ±40% of CCV or the midpoint in the ICAL? .... ☐

☐ 8. All **surrogate** recoveries (in CCVs, MB, LCSs, etc.) within acceptance limits (70%-130%) .... ☐

☐ 9. All analytes in the **MB** <MRL? (DoD <1/2MRL, except Acetone, MeCl2, EtOH, Carbon Disulfide)? .... ☐

☐ 10. **LCS** %R within lab control limits for all analytes except AZ samples (70%-130%, VA 50%-150%)? .... ☐

☐ 11. All analytes in the **Lab Duplicate / DLCS** within ±25% or the client specified limits? .... ☐

☐ 12. **DoD/Navy**: **DLCS** analyzed? .... ☐

Air-Phase Petroleum Hydrocarbons

☐ 1. Does the **CCV** meet the following criteria? .... ☐
- Percent difference ≤30%.
- One compound or range can be >30%, but less than 50%.
- No single analyte or range may be >50%.

[Note outliers biased high and/or low in comments below]

☐ 2. Does lab **duplicate** meet an RPD of ≤30% for results >5x MRL? Repeat analysis if: .... ☐

RPD >30 (where both analyses are >5x RL	1st analysis detect @ >5x MRL, Dup=ND
1st analysis ≤5x RL; Dup=ND (RPD not calculable)	

☐ 3. Are the analytes in the **LCS** within 70%-130% recovery? .... ☐

COMMENTS:

Analyst/LIMS Run Approval: ______________________________ Secondary/LIMS Supervisor Approval: ______________________________

EPA Compendium Method TO-15 - Sample Review Checklist

(Note exceptions in Comments and include Analysis Observations/Case Narrative Summary Form as appropriate)

Method: ☐ EPA TO-15 ☐ EPA TO-14A **Analysis Date:** _______________ **Project #:** _______________

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan **Scan Low Level (0.1ng):** ☐ Yes ☐ No **DOD:** ☐ Yes ☐ No

Analyst **Reviewer**

☐ 1. All analyte hits in the samples within the **calibration range** and/or noted? .... ☐
☐ 2. All **peak integrations** acceptable? .... ☐
☐ 3. All **manual integrations** flagged and documented? .... ☐
☐ 4. Have **Q values** been verified for each peak? .... ☐
☐ 5. All **calculations** correct? .... ☐
☐ 6. Has the analyst initialed and dated each **quantitation report**? .... ☐
☐ 7. For **TICs** are the relative intensity and other requirements met (associated MB reported)? .... ☐
☐ 8. **Auto report** correct? .... ☐
☐ 9. **MRL** = _______ ☐ ng ☐ pg (ethanol, acetone, vinyl acetate = 5.0ng) .... ☐
☐ 10. Pressurized with **Helium**? Is the worksheet completed for all samples? .... ☐
☐ 11. Report to **MDL**? ☐ Yes ☐ No .... ☐
☐ 12. **Global Minimum Detection Limit** = _______ ☐ ng ☐ pg .... ☐
☐ 13. **DOD:** Are **manual integrations** notated in the **case narrative?** .... ☐

Air-Phase Petroleum Hydrocarbons

☐ 1. Are all manual **integrations** flagged and documented (except for HC ranges)? .... ☐
☐ 2. Are the associated ICAL responses correct? .... ☐
☐ 3. Does the lab **duplicate** meet RPD ≤30% for results >5x the MRL? Otherwise, repeat analyses if: .... ☐

RPD >30 (where both analyses are >5x RL	1st analysis detect @ >5x MRL, Dup=ND
1st analysis ≤5x RL; Dup=ND (RPD not calculable)	

COMMENTS:

☐ 1. CASE NARRATIVE COMPLETED? .... ☐

Analyst/LIMS Run Approval: ________________________ Secondary/LIMS Supervisor Approval: ________________________

Attachment 4

State and Project Specific Requirements

Minnesota Requirements	
Item	**Criteria**
Holding Time (HT)	14 days
Tedlar bags	Not allowed for sampling or sample dilution
Canisters and flow controllers	Individually certified Individually leak checked before shipment
	Samples with concentrations outside of the calibration curve will have a zero canister analysis performed to check for carryover. If carryover is detected, system bake out shall be performed and documented. Additionally, in instances where the laboratory has evidence on file that a particular compound when present at a high concentration does not exhibit carry-over, the samples will not be reanalyzed. When samples are analyzed that have a higher concentration than the evidence on file, the above requirements must be followed. Also, samples that have hits below the MRL will not be reanalyzed when analyzed after a sample with concentrations over the calibration range.
Method Reporting Verification Check	Analyze a Method Reporting Verification at the beginning of the sequence prior to analyzing samples. Acceptance criteria ±40%.
Duplicates	10 percent laboratory duplicates
Record retention	MN/NELAP 5 years MPCA (Minnesota Pollution Control Agency) compliant samples 10 years
Tier level	TIII

Arizona Requirements	
Item	**Criteria**
LCS	70-130% (vinyl acetate 50-150%)

Department of Toxic Substances Control (DTSC) Requirements	
Item	**Criteria**
Holding Time (HT)	72 hour hold time for canisters

EPA Region 9 Requirements	
Item	**Criteria**
Holding Time (HT)	14 days

Attachment 5

Tekmar AutoCan Trap Packing Instructions

Tekmar AutoCan Trap Packing Instructions

The internal sample trap on the AutoCan is a 1/8” x 12” thin-walled stainless steel tube, usually coated with fused silica (Silcosteel). It is packed with a combination of graphitized carbon black and carbon molecular sieve adsorbents, with the weakest adsorbent at the top (inlet) and the strongest at the bottom (outlet). Each bed is separated by a small plug of untreated glass wool. Untreated is used because DCMS-treated wool will release siloxanes when heated to the temperatures used for TO-15 analysis.

The adsorbents listed below are further refined at the lab by sifting in an 80-mesh sieve. This removes the smaller particles and leaves a very uniform product of about 60-mesh size. Getting rid of the “fines” helps ensure good flow through the trap during sampling and reduces the pressure drop across the trap. A tightly-packed trap can lead to problems such as poor reproducibility, slowed flow rates, and channeling (small spaces in the beds that let analytes pass through).

Adsorbent	Mesh	Supplier	Catalog #	Packing Amount (mg)
Carbosieve SIII	60/80	Supelco	10184	40
Carbosieve G	60/80	Supelco	10198	30
Carbopack Z	60/80	Supelco	20273	30
Tenax TA	20/30 or 45/60	Supelco	10257	rest of trap

Old traps can be reused if unpacked carefully and cleaned and baked out properly. Use a glass wool puller to remove the wool plugs, and gently tap the sorbent out onto a piece of paper. If necessary, use the other end of the puller to loosen the sorbent bed, being careful not to scratch the inside of the trap. Discard the old sorbent. Rinse the empty trap with methanol, then bake in a GC oven for 30 minutes at 150˚C.

The total length of the adsorbent bed is 12 to 13cm. You want to leave 2 to 3cm of space above the top of the last glass wool layer to ensure that all of the material is within the heated zone of the AutoCan trap heater.

With clean hands (no lotion!) place a small amount of glass wool, about 10-15mg, into the top of the trap and work it in with a piece of wire or tubing. Then use the trap packing tool (the larger steel rod that just barely fits inside the trap) to hold the plug in the trap while you pull away any loose strands of wool. Then use the long steel tube to push the plug down about 15cm. The idea is to keep the plug very compact, so it is a good idea to use the trap packing tool to push up from the bottom while pushing the wool in from the top, meeting 15cm down. The plug should not move too easily when pushed.

Weigh out the first sorbent (Carbosieve SIII) on weighing paper using the analytical balance. Using the glass funnel and a short piece of silicone tubing, pour the sorbent into the top of the trap. Tap on counter to get it all out of the funnel, then remove the funnel and tap some more to settle the sorbent into a compact bed. It is very important that there are no air spaces in the bed. However, it is also very important not to compress the sorbents too much, so be very careful when placing the glass wool plugs.

Place a glass wool plug on top of the first bed, starting as described above for the first plug. Push it gently onto the top of the sorbent with very little pressure.

Proceed with the other three packings in the table above (Carbosieve G, Carbopack Z, and Tenax TA).

After placing the last glass wool plug on top, turn the trap over and gently tap it on a piece of white paper to see if any sorbent comes out. If it does, you need to add more glass wool.

Now the trap needs to be conditioned in the trap heater. The sorbent manufacturers recommend that they be conditioned at succeedingly higher temperatures, with the final temperature being about 20-30˚C higher than the desorb temperature. The reason is that the sieves hold a lot of air and moisture and it is better to drive these off at lower temperatures to avoid damage to the material, such as cracking and oxidation which creates active sites. The temperatures and times are:

80˚C for 30 minutes, 50 to 100ml/min nitrogen or helium flow
200˚C for 30 minutes
265˚C for at least 3 hours

These temperatures are set using the variable power controller and thermocouple meter. Repeat for the other temperatures (low to high). Make sure the gas toggle valve in back is open, and measure flow at the top of the trap.

VOLATILE ORGANIC COMPOUNDS BY GC/MS

DOCUMENT I.D. VOC-8260

Approved By:	______________________________ Organics Manager, Todd Poyfair	Date: 2/23/18
Prepared By:	______________________________ Quality Assurance Manager, Carl Degner	Date: 2/23/18
Prepared By:	______________________________ Laboratory Director, Jeff Grindstaff	Date: 2/23/18

Annual Review:

Reviewed By:	______________________________	Date: ______________
Reviewed By:	______________________________	Date: ______________
Reviewed By:	______________________________	Date: ______________
Reviewed By:	______________________________	Date: ______________
Reviewed By:	______________________________	Date: ______________

Doc Control ID:	________________	Archived Date:	________________

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1) Scope & Applicability

1.1 This procedure is used to determine the concentration of volatile organic compounds in water and soil using USEPA Method 8260C. This method is also applicable to TCLP ZHE leachates and may also be applicable to various types of aqueous and non-aqueous waste samples.

1.2 The analyte reporting list and current Method Reporting Limits (MRL), Method Detection Limits (MDL)/Lower Limits of Quantitation (LLOQ), Limits of Quantitation (LOQ), and Limits of Detection (LOD) can be found in the ALS-Kelso Data Quality Objective (DQO) Tables.

1.3 The nominal quantitation range for water samples is 0.5 – 80 µg/L. The nominal quantitation range for low concentration soils is 5-200 µg/kg. The nominal quantitation range for high concentration soils is 50-8000 µg/kg.

2) Summary of Procedure

2.1 This procedure gives gas chromatographic/mass spectrometric (GC/MS) conditions for the detection of parts per billion (ppb) levels of volatile organic compounds. A sample aliquot is injected into the gas chromatograph (GC) by either the purge and trap method or by direct injection. The compounds are separated on a fused silica capillary GC column. The compounds are detected by a mass selective detector (MSD), which gives both qualitative as well as quantitative information.

2.2 In the purge and trap process an inert gas, helium, is bubbled through the sample aliquot, at room temperature. This gas stream sweeps the volatile organic compounds out of the aqueous phase and into the gas stream - it purges the compounds out of the sample. The gas stream then passes through a sorbent column which selectively adsorbs, (traps) these compounds out of the helium. The preparation and analysis of soil samples uses procedures described in USEPA Method 5030B or 5035/5035A. After the purging sequence is done, the sorbent column (the trap) is heated and desorbed onto the GC column. The GC column separates the compounds and passes then onto the MSD for identification and quantification.

2.3 The sensitivity of this method depends on the level of background contamination (i.e. interferences) rather than on instrumental limitations. Highly contaminated waste samples will require a methanol extraction prior to analysis. This will elevate the reporting levels and may mask low levels of compounds of interest.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The window begins with the injection of the tune verification standard. After this standard has passed the method specific criteria a 12 hour analysis window is started. Next, a calibration curve or a continuing calibration standard (CCV see below) is run. If the CCV meets the specified criteria, sample and QC analyses are run until the 12 hour time limit closes. A new window must then be opened and the sequence repeated.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client’s sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3 Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4 Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5 Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7 Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.3.1 through 3.3.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8 Miscellaneous matrices – Samples of any composition not listed in 3.3.1 – 3.3.7. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4 Internal Standards - Internal standards are organic compounds which are similar to the analytes of interest but which are not found in the samples. The chosen internal standards are used to help calibrate the instrument's response and to compensate for slight instrument variations from injection to injection.

3.5 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at 5-10X the MRL or at levels specified by a project analysis plan.

3.6 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.7 Surrogate - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. The purpose of the surrogates is to evaluate the preparation and analysis of samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

3.8 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.9 Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.10 Independent Verification Standard (ICV) - A standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.11 Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.12 Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.13 Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes:

- To help develop accurate methods of analysis
- To calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a

property at the state-of-the-art limit

- To ensure the long-term adequacy and integrity of measurement quality assurance programs.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

4.2 It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the *ALS-Kelso Training Procedure* (ADM-TRAIN) is also the responsibility of the department supervisor/manager.

5) Interferences

5.1 Interferences by common laboratory extraction solvents, such as Methylene Chloride, Acetone, and Freon 113 can cause problems. The area where volatile organic analyses are performed is kept free of these solvents through the design of the air handling systems and its isolation from other areas of the lab that use these solvent. Laboratory experience has shown that when Methylene Chloride is a problem it is due to maintenance activities or air handling equipment failures. In the rare event this happens, ultra-pure water can be used for all samples and calibration standards for that analytical batch.

5.2 Other interferences include but are not limited to impurities in the inert purge gas, dirty plumbing/purge vessels, cross contamination by highly contaminated samples to clean ones in transport and storage, and carry over from one analysis to subsequent ones.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

6.2 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Environmental, Chemical Hygiene Plan and the appropriate SDS prior to beginning this method.

6.3 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane,tetrachloroethene, trichloroethene, and vinyl chloride. Care must be taken when handling stock standard solutions of these compounds and should be handled in a hood.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Refer to procedures for methods 5030 and 5035 for sample container and collection procedures. Pre-cleaned sample containers are purchased from a lab equipment supplier. All containers should be of glass or amber glass and equipped with a screw top cap and PFTE (Teflon) lined septa.

7.2 Samples collected using EPA Method 5035 should be shipped in Encore sample tubes or collected in VOA vials containing sodium bisulfate (low concentration) and/or methanol (high concentration).

7.3 Collect all samples in duplicate, triplicate when possible. Prepare the proper number of sample bottles/containers prior to the sampling event with preservatives to adjust the samples pH to <2 with 1:1 HCl (water samples).

7.4 Slowly fill sample bottles to just overflowing taking care not to flush out the preservative or to entrain air bubbles in the samples. Seal the bottles with PFTE lined septa toward the sample and invert to check for entrained air bubbles.

7.5 Experimental evidence has shown refrigeration at 4°C alone will not stop biological degradation of some aromatic volatile organics. Adjusting the pH of the replicate samples to less than two (pH <2) with 1:1 HCl (@ 2-3 drops per 40 mL) preserves samples for 14 days after collection. Residual chlorine can also degrade some organic compounds, generating trihalomethanes (THMs).

7.6 All samples must be stored at 4 ± 2°C and must be analyzed within 14 days of collection. See SOP VOC-5035 for additional holding time information. Any free product samples to be tested do not have any set holding times but should be analyzed as soon as possible.

7.7 The analysis of 2-CVE in water by method 8260 requires the collection of an unpreserved sample. 2-Chloroetheyl Vinyl Ether is highly reactive and preservation may accelerate loss by polymerization or other rapid chemical reaction. Therefore, the accuracy of results from a preserved sample cannot be guaranteed. If a client requests 2-CVE they must collect three preserved and three unpreserved vials and the sample must be logged in for a separate 2-CVE analysis.

8) Apparatus and Equipment

8.1 Gas Chromatograph/Mass Spectrometer System

8.1.1 Each GC/MS system is set up with a GC capable of cooling the GC oven/column, injection onto a capillary column, and a transfer line interfaced with the MSD. Each MSD is a 5973, 5975, or 5977 that is controlled by the HP-MSDOS ChemStation software.

Instrument ID	Configuration	Column
MS13, MS18, MS19, MS23, MS24, MS27, MS46, MS30	Split/splitless – capillary direct	RTX-624, 20m, 0.18mm, 1um

8.1.2 Instrument systems and associated test methods are listed below.

Instrument ID	Description	Tests Performed
MS13	6890/5973	8260W, 8260S
MS18	6890/5973	8260W, 8260S, 8260 SIM
MS19	6890/5973	Screening
MS23	6890/5973	624

MS24/MS27	7890/5975	8260W, 8260S
MS46	7890/5977	8260W, 8260S
MS30	7890/5977	8260SIM

8.2 Purge and Trap with Autosampler – Each volatile GC/MS analytical system uses a purge and trap to introduce the sample onto the GC column. Each purge and trap has an autosampler (A/S) attached to run multiple samples, one at a time, and run unattended for extended periods of time. Teledyne Tekmar or EST Analytical autosamplers and Purge and Traps are preferred for extended unattended automated analyses.

8.3 GC Columns

8.3.1 Restek RTX-624 (or equivalent) 20 M x 0.18 mm id fused silica column 1.0 µm film thickness

8.4 Each volatile GC/MS data processing station uses the most recent version of the EPA/NIST Mass Spectral Library. The current version is the NIST98k library.

8.5 Analytical balance - Capable of accurately weighing to 0.001 g, Mettler PE160 or equivalent.

8.6 Syringes, Hamilton Gas-Tight in 10 µL, 25 µL, 100 µL, 500 µL, and 1000 µL sizes.

8.7 Standard storage vials, screw thread with Mini-inert caps.

9) Standards, Reagents, and Consumable Materials

9.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements.

9.2 Methanol, purge and trap grade or equivalent.

9.3 Reagent water, prepared from deionized water, by charcoal filtration and then purging with high purity helium or nitrogen that is set at 4-5 psi for approximately 2 hours prior to use.

9.4 Blank soil matrix – Ottawa sand, AccuStandard specialty sands.

9.5 Helium, compressed high purity grade.

9.6 BFB Tuning Verification Stock Standard – A 25,000 ppm stock standard is purchased (AccuStandard). This stock solution is diluted in methanol to give a working standard of 50 ppm.

9.7 Stock Standard Solutions

9.7.1 Commercially prepared and certified stock standards are used routinely for all the method specified analytes. All such mixtures are also routinely checked against an independent source for both analyte identification and analyte concentration. All such stock standard mixtures have expiration dates given by the manufacturer and must be replaced if the comparison with the independent check standards indicates a problem. Alternatively, stock standards may be prepared from neat chemicals. Store according to manufacturer's instructions. If no storage instructions are provided, store with minimal headspace, at -10˚ to -20˚C and protect from light.

9.7.2 When preparing stock standards from neat chemicals accurately weigh approximately 0.1 g of material and dilute with methanol to 10 mL in a volumetric flask. If the purity of the neat chemical is <96%, adjust the calculated concentration accordingly.

9.8 Working Standards - Prepare these standards from stock solutions. Prepare at concentrations which facilitate ease of preparation of instrument-level standards (calibration standards, etc.). Refer to Table 1 for Standard Expiration Date Guidelines. Store standards with minimal headspace in appropriately sized standard storage vials with mini-inert caps. Solutions should be checked for degradation or evaporation prior to use.

9.9 Calibration Standards

9.9.1 A minimum of five different concentration levels for all the analytes are prepared by diluting working standards into reagent water. The lowest concentration level must be at the method reporting level, or a level corresponding to a sample concentration meeting project-specific data quality objectives, with the remaining four levels defining the working linear range of the analytical system. The permanent gas stock standards used to prepare calibration standards must not be more than one week old.

9.9.2 The suggested levels are 0.5, 2, 10, 20 and 40 ppb for waters; and 5, 20, 50, 100, and 200 ppb for soils. All calibration solutions are made up daily.

9.9.3 The continuing calibration verification (CCV) solution is prepared by adding 10 µL of a 50 ppm working standard to 50 mL of prepared reagent water, resulting in a 10 ppb (nominal concentration) standard. The CCV solution is prepared daily.

9.10 ICV Standard

9.10.1 The independent calibration verification (ICV) solution is prepared by adding 10 µL of a 50 ppm intermediate to 50 mL of prepared reagent water, resulting in a 10 ppb (nominal concentration) standard. Acrolein is added at 50 µL directly from a 100 ppm stock into the 50 mL of prepared reagent water yield a final concentration of 100 ppb in. The ICV solution is prepared with each initial calibration.

9.11 Internal Standards and Surrogates

9.11.1 The surrogates recommended are Dibromofluoromethane, Toluene-d_8 and 4-Bromofluorobenzene. The internal standards recommended are: Fluorobenzene, 1,4-Dichlorobenzene-d_4 and Chlorobenzene-d_5. Other internal standards and surrogates may be used, depending on the analysis requirements. All internal standards are added to every calibration standard. The spike level for samples, blanks, and matrix spikes is 10 µg/L for waters and 50 µg/L for soils.

9.12 Spiking Solutions

9.12.1 Waters are typically spiked at 10 ppb and soils are typically spiked at 50 ppb.

9.12.2 Matrix spike and laboratory control spike solutions should contain the full list of analytes of interest. However, a subset may be reported.

Note: Refer to Table 1 for Standard Expiration Date Guidelines.

10) Preventive Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

10.2 Carrier gas - Inline purifiers or scrubbers should be in place for all sources of carrier gas. These are selected to remove water, oxygen, and hydrocarbons. Purifiers should be changed as recommended by the supplier.

10.3 Purge and Trap /Autosamplers

10.3.1 The purge/trap system should be baked out and back-flushed daily as needed, generally prior to use on a daily basis.

10.3.2 Replace the trap monthly or sooner if performance deteriorates.

10.3.3 The heating cup temperature is checked each time the instrument is calibrated and documented on the calibration run log.

10.4 Gas Chromatograph

10.4.1 Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column cutting tool.

10.4.2 Over time, the column will exhibit poorer overall performance, as indicated by poor peak shape and reduced responses. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in performance is evident, more thorough maintenance is necessary. Some steps are to solvent rinse the split vent and septum lines with a mix of 20% methanol in DCM. When these and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

10.5 Mass Spectrometer

10.5.1 Tune the MS as needed to result in consistent and acceptable performance while meeting the required ion abundance criteria given in section 11.

10.5.2 For units under service contract, certain maintenance is performed by instrument service staff, including pump oil changed, vacuuming boards, etc., as recommended by the manufacturer.

10.5.3 MS source cleaning should be performed as needed, depending on the performance of the unit. This may be done by the analyst or by instrument service staff.

11) Procedure

11.1 Sample Preparation

11.1.1 Water Samples

11.1.1.1 No preparation is generally required, other than dilution with reagent water to bring analytes into the upper half of the calibration range. Thus, a 10 mL sample volume is run straight from the sample vial. See the SOP for *Purge and Trap for Aqueous Samples* (VOC-5030) for details.

11.1.1.2 All water samples must be checked to have a pH $\leq$ 2 after sample analysis has taken place. Narrow range pH paper is used and the results are recorded on the injection log.

11.1.1.3 TCLP ZHE leachates are diluted 1:400 in reagent water prior to analysis. The TCLP samples and method blanks are diluted from the acidified ZHE extract; and the TCLP MS and LCS are diluted from a non-acidified extract, spiked, and poured into an HCL preserved VOA vial.

11.1.2 Soil samples are analyzed as either low concentration (direct purge) or high concentration (methanol preservation/extraction). Refer to the SOP for *Purge and Trap/Extraction for Volatile Organics in Soil and Waste Samples, Close System* (VOC-5035) for details.

11.1.2.1 For low concentration analyses, one of the sampling options given in method 5035 is to be used. Depending on the option used, follow the instructions given in the method. Typically, 1-5 g is weighed out into the sample vial and 5 mL of reagent water is added. QC spikes and internal standards are then added, and the sample is purged at a temperature of 40ºC ± 1º. Calibration standards, LCS, and method blanks require 5 g Ottawa sand as the matrix.

11.1.2.2 In the event that low concentration analyses are specified but samples were not taken using a EPA Method 5035 procedure, a portion of the sample is analyzed via direct heated purge of soil and EPA Method 5030A is cited. The analytical report should also be narrated with a statement indicating that 5030A has been deleted from SW-846. The low concentration analyses require a calibration specific to direct soil analysis.

11.1.2.3 The mid-level type is a methanol extraction method. In general, a 5 g wet weight of soil is extracted with 5 mL of purge-and-trap methanol in a scintillation vial. Place 5 mL of purge-and-trap methanol into vial, tare, and add 5 g of sample, and record the weight. Quickly cap and vortex until the sample is thoroughly mixed. A 1:100 dilution (500 µL to 50 mL) of this extract is then prepared in reagent water and analyzed using the water calibration. The extract weight, volume used, and methanol lot number are recorded on the injection log (or a bench sheet).

NOTE: For soil/solid samples requiring VOA and non-VOA analyses and only one container was submitted to the lab, sample receiving will label the sample container as "VOA Analysis First" and/or attach a "VOA FIRST" tag. The VOA department will remove a sample aliquot first for their analyses. The sample should be handled as if it were a Rush analysis, so that the other non-VOA analyses will not be unduly delayed. The VOA analyst who opens the container will either break the custody seal and will initial and date it when the container was opened or sign and date the "VOA FIRST" tag. A VOA Analysis First note will also be included on the SR.

11.2 The recommended typical operating conditions are listed below. Minor modification may be necessary based off the various instrument combinations which may be used.

Purge & Trap	Purge flow rate: 40 mL/min, "K" (Vocarb 3000) or "9" Trap; Purge 11 min, desorb 2 min at 240ºC, bake 20 min at 260ºC (Tekmar 3000)
Injection Port Temperature	200ºC
Initial Temperature	35ºC for 1.0 min
Temperature Program	15ºC/min to 140ºC; hold 0 min
Final Temperature	20ºC/min to 200ºC; hold 2.5 min
Detector Temperature	200ºC
MS Scanning	~3.0 scans/second
Scan Range	35 - 270
Carrier Gas	He, 22.7 psig head pressure

11.3 Initial Calibration

NOTE: The calibration procedure(s) and options chosen must follow the ALS protocols. Any exceptions to the calibration procedures detailed in the SOP for *Calibration of Instruments for Organics Chromatographic Analyses* (SOC-CAL) are described as follows:

11.3.1 BFB Tuning

11.3.1.1 Prior to calibration and sample analyses, analyze a 25 ng or 50 ng injection of Bromofluorobenzene (BFB). Each volatile GC/MS analytical system set up to run 8260C must meet the criteria listed in Table 2 for the injection of BFB. The analysis time for BFB is used to define the start of the 12-hour window in which all analyses must be performed. Once the instrument is tuned, all subsequent analyses of standards, samples, and QA/QC samples within the same 12-hour window must be analyzed using the identical mass spectrometer operating conditions.

11.3.1.2 Obtain the spectrum for evaluation using one of the following options:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak or part of any other closely eluting peak.

- Use one scan at the apex of the peak. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak or part of any other closely eluting peak.

- Use the average across the entire peak up to a total of 5 scans. Peak integration must be consistent with standard operating procedure. If the peak is wider than 5 scans, the tune will consist of the peak apex scan and the two scans immediately preceding and following the apex. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak or part of any other closely eluting peak.

- Use the average across the entire peak. Peak integration must be consistent with standard operating procedure. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak or part of any other closely eluting peak.

11.3.1.3 Evaluate the spectrum against the criteria specified in Table 2. The criteria used must be the same for all ion abundance criteria checks associated with a given analysis. For example, initial calibration, continuing calibration(s), QC, and sample analyses for a given sample must all use the same criteria.

11.3.2 GC/MS Analytical System Initial Calibrations

11.3.2.1 Prior to conducting any sample analyses, a multi-point (5 point minimum) calibration <u>must</u> be run. Recommended calibration levels are 0.5 - 70 ppb for waters, and 5 - 300 ppb for soils. Analyze each calibration standard and tabulate the area response of the characteristic quantitation ions (Table 3) versus concentration for each compound, internal standard and surrogate. Calculate the response factors (RF) for each compound relative to the specified internal standard by:

$$RF_x = \frac{(A_x)(C_{ISTD})}{(A_{ISTD})(C_x)}$$

Where:

A_x = Area of the characteristic ion for compound being measured.
A_{ISTD} = Area of the characteristic ion for specific internal standard.
C_{ISTD} = Concentration of the specific internal standard (ng/µL).
C_x = Concentration of the compound being measured (ng/µL).

Note: For DoD projects, a multi-point calibration is performed for the surrogates.

11.3.2.2 Calculate the mean response factor $(\overline{RF_x})$ for each analyte from the five calibration levels. Calculate standard deviation (SD) and the percent relative standard deviations (%RSD) for each analyte from the mean with:

$$\%RSD = \frac{SD}{\overline{\overline{RF}}} \text{ x } 100$$

Where:
RSD = relative standard deviation.

$\overline{RF}$ = mean of 5 initial RFs for a compound.
SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - RF)^2}{N - 1}}$$

Where:

RF_i = RF for each of the 5 calibration levels
N = Number of RF values (i.e., 5)

11.3.2.3 The %RSD should be less than 20% for each compound.

11.3.2.4 If the % RSD for any compound is ≤ 20%, linearity can be assumed over the calibration range, and the relative response factor for each analyte and surrogate is used.

11.3.2.5 If the %RSD for a compound is >20%, then alternative calibration models should be used. See the SOP *Calibration of Instruments for Organics Chromatographic* (SOC-CAL) *Analysis* for further guidance.

11.3.2.6 The mean response factor for each target analyte should meet the minimum response factors listed in Table 5. Meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed by this method, some compounds will fail to meet this criterion. For these occasions, the analyte is qualified as not meeting the method recommended response factor criterion.

11.3.2.7 When instrument response does not follow a linear model, a non-linear calibration model may be used. Refer to the SOP for *Calibration of Instruments for Organics Chromatographic Analysis* (SOC-CAL) for alternative curve fit guidance.

11.3.2.8 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too imprecise for analysis to begin and corrective action is necessary. Further preventative maintenance may be required or the system may not be adequately *primed* for initial calibration.

11.3.3 Review of calibration curve

11.3.3.1 The calibration curve must be reviewed to ensure it represents the calibration data. This is done by re-fitting each calibration level against the true concentration of each calibration standard. The % difference between the calculated concentration verses the true concentration should be ≤ 30% for each calibration level and may not exceed 50% for any level.

11.3.3.2 Due to the large number of compounds that may be analyzed, one or more analytes may exceed 20% RSD or 0.99 COD. The initial calibration may still be acceptable if the following conditions are met:

- The % difference between the calculated concentrations verses the true concentration for each level of the initial calibration curve meets the criteria specified in section 11.2.3.1.

- In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit. This is done by re-evaluating the concentrations of the calibrations standards against the calculated concentrations.

NOTE: Certain project plans that fall under the (DoD QSM) contain additional initial calibration acceptance criteria. In these cases, the analyst must refer to the project plan to know if the criteria listed in the DoD QSM or QAPP-specified criteria or EPA method calibration criteria are to be used.

NOTE: The “80/20” criteria allowed under section 11.3.3.2 only applies when the full target compound list is being reported. Individual compounds that are a subset of the entire target analyte list and have ≤20%D may still be reported, e.g. dilutions, reruns, abbreviated reporting lists.

11.3.4 Independent Calibration Verification

11.3.4.1 Following initial calibration, analyze an ICV standard. The ICV solution must be obtained for all analytes that are analyzed and reported. Calculate the percent difference (%D) or % Drift from the ICV true value. The acceptance limits for the ICV are ± 30% of true value.

11.3.4.2 If a second source standard is not available from a second vendor, a second lot number from the same vendor may be used. It is recommended that the lab obtain a written warranty that the lot numbers are prepared from different source materials.

11.3.4.3 After the multi-point calibration has passed all of the above criteria, and the Independent Calibration Verification has been performed, samples can be analyzed. The calibration curve mid-point standard may serve as the CCV for the opening set of samples within the same 12-hour window as the initial calibration.

11.4 Continuing Calibration

11.4.1 The start of a 12-hour analysis window requires a check of the instrument tune via an injection of 25ng or 50 ng of BFB. Refer to section 11.2.1.2 for the procedure. If the criteria found in Table 2 are met, then a check of the initial calibration curve is done. If the first analysis of the BFB fails, inspect the instrument for malfunction and perform maintenance as necessary. A second BFB tune verification may then be performed. If the second run fails, it may be necessary to retune the system.

11.4.2 After the tuning criteria have been verified, the initial calibration must be checked and verified by analyzing a midrange calibration standard. The 10 ppb level for waters and 50 ppb level for soils is recommended. For water, CCVs are prepared by adding 10µl of the 50 ppm 8260 working standard and 5µl of the 2000 ppm ketone mix into 50 mL reagent water and a 10 mL aliquot is purged. For soil, CCVs are prepared by adding 25µl of the 100ppm (nominal) working standard into 50 mL reagent water, and a 5 mL aliquot is purged.

11.4.3 The CCV result is evaluated for each target compound using the following criteria:

11.4.3.1 If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid.

11.4.3.2 Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet the ≤ 20% criteria. If no more than 20% of the compounds, included in the initial calibration, differ from their true concentration by 40%, the initial calibration is valid and no corrective action is necessary.

Note: The “80/20” criteria allowed under section 11.3.3.2 only applies when the full target compound list is being reported. Individual compounds that are a subset of the entire target analyte list and have ≤ 20% may still be reported (e.g. dilutions, reruns, abbreviated reporting list).

11.4.4 In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit.

11.4.5 Non-detected analytes can be reported from analyses when a CCV exhibit a positive bias (i.e., outside the upper control limit), no further documentation is required.

11.4.6 For situations when the CCV fails to meet the criterion in section 11.3.3, and a confirmed detection exceed the MRL, the sample must be reanalyzed to ensure accurate quantification. If it is not possible to reanalyze the sample, the result must be reported as an estimated value.

11.4.7 If the tune criteria and the continuing calibration criteria are met, then the retention times of all compounds, surrogates, and internal standards are checked against the initial calibration. If the retention time for any internal standard changes by more than 10 seconds from the retention time from the mid-point standard of the most recent initial calibration, the system must be inspected for malfunctions and corrections must be made, as required.

11.4.8 If the area for any of the internal standards changes by a factor of 2 (-50% to +100%) from the area from the mid-point standard of the most recent initial calibration, corrections must be made to the system.

11.4.9 Quantitation of all compounds will be based on the initial calibration.

11.5 GC/MS Analysis

11.5.1 Perform GC/MS screening analysis.

11.5.1.1 Samples are typically diluted 50X for liquid matrices and 500X for solid matrices.

11.5.1.2 Quantify chromatographs from the screening analysis and evaluate based on peaks of interest and the high point of the associated analytical instrument calibration.

11.5.1.3 If required, dilutions are typically performed with the intent to bring the high range analytes of interest into the mid-range of the instrument calibration as well as a base run that dilutes the highest peak to approximately three times the highest point of the instrument calibration.

11.5.1.4 Note the requirement of a dilution in the comment section of the analytical instrument injection log.

11.5.2 Prepare samples as described in section 11. Use the same operating conditions as were used for initial calibration.

11.5.3 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place.

11.6 Identification of Analytes

11.6.1 The MSD data system software identifies a sample component by first finding and identifying the surrogate and internal standards. After they have been integrated, the extracted ion chromatogram is searched for all calibrated analytes.

11.6.2 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum is generated from analysis of a calibration standard and is updated with each initial calibration.

11.6.3 The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

11.6.3.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

11.6.3.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

11.6.3.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

11.6.4 Table 3 lists characteristic ions as given in Method 8260C. If there is no peak found for an analyte in the expected retention time window and the mass spectrum does not match according to the method criteria, then the analyte is "not found". Print out spectra for all confirmed hits.

11.7 The analyst reviews all analyses to confirm (or correct) all data system qualitative interpretations.

11.8 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the SOP for Total Solids.

12) Quality Assurance/Quality Control Requirements

12.1 Initial Precision and Recovery Validation

12.1.1 The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made or when an analyst is new to the procedure. To do this, analyze four water sample spikes, calculate the average recovery and standard deviation, and evaluate as described in EPA SW-846. The concentration of the analytes to be spiked should be in the working calibration range. Initial Demonstration of Capability studies must be performed as part of analyst training. Copies of the studies are maintained in the lab and in the analyst's training file.

12.2 Method Detection Limits/Lower Limit of Quantitation/LOD/LOQ

12.2.1 For projects that require reporting to the method detection limit (MDL), a method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the procedure specified in the corporate QA SOP *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011). The MDL studies should be done for each matrix and include data from all instruments on which the test is analyzed.

12.2.2 Calculate the average concentration found (x) in the sample concentration, and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. The MDL study must be verified as specified in CE-QA011.

12.2.3 The Limits of Detection (LOD) and Limits of Quantitation (LOQ) must be established and verified following the procedure in the SOP *Performing Method Detection Limit Studies and Establishing Limits of Detection and* Quantification (CE-QA011).

12.2.4 The Method Reporting Limits (MRLs) used at ALS are the routinely reported Lower Limits of Quantitation (LLOQ) which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.3 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches* (ADM-BATCH). In general, these include:

12.3.1 Method blank - A method blank is extracted and analyzed with every batch of 20 or fewer samples to demonstrate that there are no method interferences. The method blank must demonstrate that interferences from the analytical and preparation steps minimized. No target analytes should be detected above the MRL in the method blank. For some project specific needs, additional requirements or exceptions may be given.

Note: For DoD projects – The Method Blank will be considered contaminated if:

- The concentration of any target analyte in the blank exceeds ½ the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).
- The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).
- The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

12.3.2 A lab control sample (LCS) must be prepared and analyzed with every batch, not to exceed 20 samples. The LCS is prepared by spiking a blank with the matrix spike solution, and going through the entire preparation and analysis. Calculate percent recovery (%R) as follows:

$$\%R = X/TV \times 100$$

Where:
X = Concentration of the analyte recovered
TV = True value of amount spiked

Compare the %R to LCS acceptance criteria, located in the current ALS-Kelso DQO tables. The accuracy of the analysis is controlled on a subset of target analytes. If the project analyte list is fewer than 20 analytes, all are considered control analytes. For DoD projects all project target analytes are considered control analytes. Analytes which are used for control analytes are listed in Table 4. Project-specific acceptance limits may supersede those listed in this SOP. If the lab control sample (LCS) fails acceptance limits for any of the control compounds, any associated sample data is rejected and corrective action must be taken. This may include evaluation of the sample preparation, analytical system, and calibration; and may require re-extraction, re-analysis, and/or recalibration and re-analysis.

12.3.3 A matrix spike/duplicate matrix spike (MS/DMS) must be prepared and analyzed with every batch of 20 or fewer samples if adequate sample volume is received (4 or more vials are needed). If insufficient sample is received, an LCS/DLCS pair will be analyzed to establish batch precision. In the event a dilution analysis is necessary on a sample chosen for MS/DMS, the sample will be spiked at the base level.

The MS is prepared by spiking a sample aliquot with the matrix spike solution, and going through the entire preparation and analysis. Calculate percent recovery (%R) as follows:

$$\%R = \frac{X - X1}{TV} x\ 100$$

Where:
X = Measured concentration of the spiked sample aliquot
X1 = Measured concentration of the unspiked sample aliquot
TV = True value (theoretical concentration) of the amount spiked

Calculate Relative Percent Difference (RPD) as:

$$RPD = \frac{|R1 - R2|}{(R1 + R2)/2} x\ 100$$

Where:
R1 = Measured concentration of the first sample aliquot
R2 = Measured concentration of the second sample aliquot

Compare the %R and RPD to MS/DMS acceptance criteria located in the ALS-Kelso DQO tables. If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken.

Note: For DoD projects, recovery limits for the MS are the same as the LCS limits specified in the QSM.

12.3.4 The acceptance limits for the surrogates are given in the ALS-Kelso DQO tables. If any surrogate recovery is outside acceptance criteria, the sample data must be closely evaluated for possible matrix interferences. If none are present, then corrective action must be taken. The sample should be re-analyzed if instrument factors (calibration, poor purge, etc.) are suspected.

12.4 Acceptance criteria and corrective action requirements have been outlined above in the Procedure section and in Table 6.

12.5 Additional QA/QC measures include trend analysis by means of control charts or other means.

13) Data Reduction and Reporting (or Documentation and Records)

13.1 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the midpoint concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported.

13.2 Calculations

13.2.1 The GC/MS data stations, in current use, all use the H-P RTE Integrator to generate the raw data used to calculate the standards $\overline{RF}_x$ values, the sample amounts, and the spike values. The software does three passes through each data file. The first two identify and integrate each internal standard and surrogate. The third pass uses the time-drift information from the first two passes to search for all method analytes in the proper retention times and with the proper characteristic quantitation ions. The results for a sample are calculated as follows when $\overline{RF}_x$ is used:

$$A_x = \frac{(Resp_x)(Amt_{ISTD})}{(Resp_{ISTD})(\overline{RF}_x)}$$

Where: A_x = the amount, in ppb, of the analytes in the sample;

$Resp_x$ = the peak area of the analytes of interest;

$Resp_{ISTD}$ = the peak area of the associated internal standard;

Amt_{ISTD} = the amount, in ppb, of internal standard added

$\overline{RF}_x$ = the average response from the five-point for the analytes of interest.

13.2.2 The results for low concentration soil work are calculated by taking the normal print out, in ppb, (see the water results outlined above) and correcting for the total, dry soil sample actually purged:

$$(A_x) = \frac{(5\ grams)}{(ASW_t\ gr)(\%\ Solids)} = A_x\ Low\text{-}Level\ Soil$$

Where: A_X = Amount, in ppb, from the data system

$5\ g$ = Nominal amount of soil that is headed and purged.

ASW_t = Actual soil wet weight, in grams, that is purged

$\%\ Solids$ = Correction factor for dry weight.

13.2.3 Results for a high concentration soil samples (methanol extracts) are calculated as follows:

$$(A_x) = \frac{(Dilution)(V_{EXTR})}{(ASW_t)(\%\ Solids)} = A_x\ High\text{-}Level\ Soil\ Amt.$$

Where: A_X = Amount reported from the data station, in ppb
Dilution = Dilution factor of the extract
% Solids = Correction factor for dry weight
V_{EXTR} = Methanol extract volume (mL)*

* The water contained in the native sample is accounted for when determining the final extract volume. The final volume of the methanol extract is the total volume of the methanol/water mixture. Calculate the final volume as follows:

$$FinalVolume\ Methanol/Water = mL\ of\ solvent + \left(\frac{\%Moisture\ \ x\ Sample\ Wt.(g)}{100} \right)$$

13.3 Data Review

13.3.1 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the *SOP for Laboratory Data Review Process* (ADM-DREV) for details.

13.4 Reporting

13.4.1 Reports are generated in STEALTH or the ALS LIMS which compiles the SMO login, sample prep database, instrument, date, and client-specified report requirements (when specified). This compilation is then transferred to a file which the Stealth reporting system uses to generate a report. The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

14) Method Performance

14.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

14.2 The method detection limit (MDL) is established using the procedure described in *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound, feasibly possible, and within method requirements. Standards are prepared in volumes consistent with laboratory use in order to minimize the volume of expired standards to be disposed of. The threat to the environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Kelso Environmental Lab Waste Management Plan.

15.3 This method uses non-halogenated solvents and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Nonconformity and Corrective Action* (CE-QA008) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected. Table 5 list specific corrective actions that must be made based off method criteria.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

16.2.2 Some examples when documentation of nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision,
- Method blanks or continuing calibration blanks (CCBs) with target analytes above the acceptance limits,
- Sample holding time missed due to laboratory error or operations,
- Deviations from SOPs or project requirements,
- Laboratory analysis errors impacting sample or QC results,
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.),
- Sample preservation or handling discrepancies due to laboratory or operations error.

17) Training

17.1 Training Outline

17.1.1 Review literature by reading references. Review the EPA methodology and any applicable state-specific methods. Review the SOP. Also review the SDS for methanol.

17.1.2 Observe the procedure performed by an experienced analyst at least three times.

17.1.3 Assist in the procedure under the guidance of an experienced analyst for a period of three months. During this training process, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.4 Following the three-month training period the analyst is expected to complete an initial demonstration of capability study (IDC) for solid samples by direct, solid samples by extraction, and water samples. Summaries of the IDC are reviewed and signed by the technical director and forwarded to the employee's training file.

17.1.4.1 Perform IDC studies by preparing and analyzing four replicate laboratory control samples spiked at a level of 10-20 times the MRL. Calculate average percent recovery and relative standard deviation for the four replicate analyses. Refer to Method 8000C and 8260C for analysis and evaluation guidelines.

17.1.4.2 For applicable tests, IDC studies are be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.2 Training is documented following the procedures defined in *ALS-Kelso Training Procedure* (ADM-TRAIN).

17.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 For water samples, a purge volume of 10mL is used, whereas the method (section 7.5.5) states 5mL or 25mL. The use of a 10mL volume ensures sensitivity for "5mL" type analyses *and,* on the analytical systems in use, meets the sensitivity goals of a 25mL purge volume analysis. Also, the use of 10mL rather than 25mL decreases the negative effects of water being introduced into the P/T-GC-MS system.

18.2 11.2.3.1 Reference method recommends recalculation of low point only and that should be ± 30%. This SOP states each point is refit and each point should be with ± 30% but may not exceed ± 50%.

18.3 11.3.3 No limit defined in reference method, so lab assigned a limit of 40% based on CLP protocols.

19) References and Related Documents

19.1 VOC-5030, Purge and Trap for Aqueous Samples.

19.2 VOC-5035, Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples, Closed System.

19.3 Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, *U.S. EPA, SW-846, Method 8260C, Revision 3, August 2006.*

19.4 Purge and Trap, U.S. EPA, SW-846, Final Updates I and III, Methods 5030A Rev. 1, July 1992, 5030B Rev. 2, December 1996, and 5030C Rev. 3, May 2003.

19.5 Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste, U.S. EPA, SW-846, Final Update III, Method 5035, Rev. 0, December 1996; and Method 5035A Rev. 1, July 2002.

20) Summary of Changes since Last Revision

20.1 Signature page updated.
20.2 Typographical, grammatical and formatting revisions.
20.3 Section 8: Various changes to reflect current practice as requested, dated 2/1/17.
20.4 Section 9.11 – Corrected internal standard name.
20.5 Section 11.2 - Added typical instrument operating conditions.
20.6 Section 11.3.2.2 – Added formulas and parameters for clarification.
20.7 Section 11.3.3.2 - Revised NOTE, Change Request dated 12/6/16.
20.8 Section 11.5.1 – New section addressing screens.
20.9 Section 12 - Sentence deletion.
20.10 Section 13.4.1 – Included ALS LIMS reporting.
20.11 Section 13.4.2 – Removed section on Excel reporting.
20.12 Section 19 – Updated references.
20.13 Updated Safety documentation changes to reflect current practice.

21) Attachments/Appendices

21.1 Table 1 – Standard Expiration Date Guidelines

21.2 Table 2 – 4-Bromofluorobenzene Characteristic Ion Abundance Criteria

21.3 Table 3 – Characteristic Masses (m/z) for Purgeable Organic Compounds

21.4 Table 4 – Control Analytes for Non-DoD Projects

21.5 Table 5 – Recommended Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification

21.6 Table 6 – Summary of Corrective Actions.

TABLE 1

Standard Expiration Date Guidelines

Standard	Expiration time
Neat Chemicals supplier's	Expiration date 5 years from date opened, or assigned date.
Stock Standards (unopened ampules, commercially prepared or lab prepared) 1 preparation if no expiration date provided.	Supplier's assigned date, or year from
Opened ampules and working standards	
• concentration $\geq$ 5000 ppm	6 month expiration date.
• concentration 1000 - <5000 ppm	2 month expiration date.
• concentration 200 - <1000 ppm	1 month expiration date.
• concentration < 200 ppm	7 day expiration date.
Internal Standard Solutions	One month expiration date.

Note: The analyst performing specific analytical procedures should use judgment and take into consideration the solution reactivity, volatility, and concentration when using standards to prepare calibration curves. Certain standards, depending on use and storage, may have shorter usable life than described in these guidelines.

TABLE 2

4-Bromofluorobenzene Characteristic Ion Abundance Criteria

Mass	Ion Abundance Criteria *
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5-9% of mass 174
176	95 -101% of mass 174
177	5-9% of mass 176
Reference:	EPA 8260C

* Manufacturer specified ion abundance criteria may be used

TABLE 3

Characteristic Masses (m/z) for Purgeable Organic Compounds

Analyte	1º Ion	2º, 3º, etc. Ion
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64	66
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50	52
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174
1,2-Dichlorobenzene	146	111, 148
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148

TABLE 3 (cont.)

Characteristic Masses (m/z) for Purgeable Organic Compounds

Analyte	1° Ion	2°, 3°, etc. Ion
cis-1,4-Dichloro-2-butene	75	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	43, 42
Ethyl methacrylate	69	41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	127, 141
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-

TABLE 3 (cont.)

Characteristic Masses (m/z) for Purgeable Organic Compounds

Analyte	1º Ion	2º, 3º, etc. Ion
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	66, 92, 78
Pentachloroethane	167	130, 132, 165, 169
Propargyl alcohol	55	39, 38, 53
b-Propiolactone	42	43, 44
Propionitrile (ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Surrogates:		
1,2-Dichloroethane-d4	65	67, 51
4-Bromofluorobenzene	95	174, 176
Dibromofluoromethane	113	111, 192
Toluene-d8	98	99, 70
Internal Standards:		
1,4-Difluorobenzene	114	63, 88
Fluorobenzene	96	77, 70, 50
1,4-Dichlorobenzene-d4	152	115, 150
Chlorobenzene-d5	117	119, 82

TABLE 4

Control Analytes for Non-DoD Projects

1,1-Dichloroethene
Benzene
Trichloroethene
Toluene
Chlorobenzene
1,2-Dichlorobenzene
Naphthalene
1,1,2-Trichloroethane
2-Chlorotoluene
2-Hexanone
Carbon Tetrachloride
Vinyl Chloride
Ethylbenzene
Chloroform
Bromodichloromethane
1,2,3-Trichloropropane

TABLE 5

Recommended Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification

Analyte	Response Factor (RF)
Dichlorodifluoromethane	0.100
Chloromethane	0.100
Vinyl chloride	0.100
Bromomethane	0.100
Chloroethane	0.100
Trichlorofluoromethane	0.100
1,1-Dichloroethene	0.100
1,1,2-Trichloro-1,2,2-trifluoroethane	0.100
Acetone	0.010*
Carbon disulfide	0.100
Methyl Acetate	0.100
Methylene chloride	0.100
trans-1,2-Dichloroethene	0.100
cis-1,2-Dichloroethene	0.100
Methyl tert-Butyl Ether	0.100
1,1-Dichloroethane	0.200
2-Butanone	0.010*
Chloroform	0.200
1,1,1-Trichloroethane	0.100
Cyclohexane	0.100
Carbon tetrachloride	0.100
Benzene	0.500
1,2-Dichloroethane	0.100
Trichloroethene	0.200
Methylcyclohexane	0.100
1,2-Dichloropropane	0.100
Bromodichloromethane	0.200
cis-1,3-Dichloropropene	0.200
trans-1,3-Dichloropropene	0.100
4-Methyl-2-pentanone	0.010*
Toluene	0.400
1,1,2-Trichloroethane	0.100
Tetrachloroethene	0.200
2-Hexanone	0.015*

TABLE 5 (cont.)

Recommended Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification

Analyte	Response Factor (RF)
Dibromochloromethane	0.100
1,2-Dibromoethane	0.100
Chlorobenzene	0.500
Ethylbenzene	0.100
m-/p-Xylene	0.100
o-Xylene	0.300
Styrene	0.300
Bromoform	0.100
Isopropylbenzene	0.100
1,1,2,2-Tetrachloroethane	0.300
1,3-Dichlorobenzene	0.600
1,4-Dichlorobenzene	0.500
1,2-Dichlorobenzene	0.400
1,2-Dibromo-3-chloropropane	0.025*
1,2,4-Trichlorobenzene	0.200
Any other analyte not included in this table	0.010

* These analytes have poor purging efficiencies. Response factors based upon USEPA CLP guidance and laboratory performance after system maintenance.

TABLE 6

Summary of Corrective Actions

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
EPA 8000C EPA 8260C	ICAL	Prior to sample analysis	% RSD ≤ 20 R2 ≥ 0.995 COD ≥ 0.990	Correct problem then repeat ICAL
EPA 8260C	ICV	After ICAL	± 30% Diff	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 8260C	CCV	Prior to sample analysis	See Sec. 11.3.3	Correct problem then repeat CCV or repeat ICAL
EPA 8260C	Method Blank	Include with each analysis batch (up to 20 samples)	< MRL DOD <1/2 MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminant, unless samples contain > 20x amount in blank.
EPA 8260C	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO Tables	If exceeds limits on control compounds, perform corrective actions, re-extract and re-analyze
EPA 8260C	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO Tables	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 8260C	Matrix Spike Duplicates	Include with each analysis batch (up to 20 samples)	Water: RPD ≤ 30 Soil, L: RPD ≤ 40 Soil, M: RPD ≤ 40	Re-analyze if result is > 5 X the MRL

SEMIVOLATILE ORGANIC COMPOUNDS BY GC/MS – METHOD 8270D

ALS-KELSO

SOP ID:	SVM-8270D	Rev. Number:	5	Effective Date:	05/29/2016

Approved By: Jon James Date: 5/16/16
Department Manager/Technical Director – Jon James

Approved By: Date: 5/16/16
QA Manager – Carl Degner

Approved By: Date: 5/16/16
Laboratory Director – Jeff Grindstaff

Issue Date: ___________ Doc Control ID#: ___________ Issued To: ___________

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

ALS-Kelso SOP Annual Review Statement

SOP Code: SVM-8270D
Revision: 5

An annual review of the SOP listed was completed on (date): 3/8/19

☒ The SOP reflects current practices and requires no procedural changes.

Supervisor: cjw   Date: 3/8/19

☐ Revision of the SOP is needed to reflect current practices. Draft revisions are listed below.

SOP Section Number	**Description of Revision Needed**	**Date Procedure Change Implemented**	**Supervisor Initials** Indicating Approval of Revision

ALS-Kelso SOP Annual Review Statement

SOP Code: SVM-8270D

Revision: 5

Attach additional pages or information if necessary

ALS Kelso Annual Review, Reviewed by Carl Degner 1/22/18

ALS-Kelso SOP Annual Review Statement

SOP Code: SVM-8270D
Revision: 5

An annual review of the SOP listed was completed on (date): **6/15/17**

☒ The SOP reflects current practices and requires no procedural changes.

Supervisor: Jon James Date: 6/15/17

☐ Revision of the SOP is needed to reflect current practices. Draft revisions are listed below.

SOP Section Number	**Description of Revision Needed**	**Date Procedure Change Implemented**	**Supervisor Initials** Indicating Approval of Revision

TABLE OF CONTENTS

SEMIVOLATILE ORGANIC COMPOUNDS BY GC/MS – METHOD 8270D

1. SCOPE AND APPLICATION

1.1. This procedure is used to determine the concentrations of Semi-Volatile Organic Compounds in water and soil using EPA Method 8270D. This procedure may also be applicable to various miscellaneous waste samples. Tables 1A and 1B indicate compounds that may be determined by this method and lists their method reporting limits (MRLs) in water and soil. The reported MRL may be adjusted if required for specific project requirements; however, the capability of achieving other reported MRLs must be demonstrated. The Method Detection Limits (MDLs) will vary depending on the instrument used and preparation method.

1.2. This procedure can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivitization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone phase. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. Other compounds than those listed in Tables 1 may be analyzed. Refer to Section 1 of method 8270D.

1.3. In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD) may supersede the requirements defined in this SOP.

2. METHOD SUMMARY

2.1. This method provides Gas Chromatography/Mass Spectrometry (GC/MS) conditions for the detection of Semi-volatile Organic Compounds. Prior to the use of this method, an appropriate sample preparation method must be used to recover the analytes of interest. An aliquot of the extract is injected into the gas chromatograph (GC). The compounds are separated on a fused silica capillary column. Compounds of interest are detected by a mass selective detector. Identification of the analytes of interest is performed by comparing the retention times of the analytes with the respective retention times of an authentic standard, and by comparing mass spectra of analytes with mass spectra of reference materials. Quantitative analysis is performed by using the authentic standard to produce a response factor and calibration curve, and using the calibration data to determine the concentration of an analyte in the extract. The concentration in the sample is calculated using the sample weight or volume and the extract volume.

2.2. The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration and the chromatography for this compound is poor. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, to a chemical reaction in acetone, and can undergo photochemical decomposition. N-Nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-Dinitrophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Chloroaniline, and Benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

3. DEFINITIONS

3.1. **Batch** - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1. Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2. Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2. **Sample**

3.2.1. Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client’s sample.

3.2.2. Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3. **Quality System Matrix** - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1. Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2. Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3. Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4. Nonaqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5. Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6. Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7. Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.3.1 through 3.3.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8. Miscellaneous matrices – Samples of any composition not listed in 3.3.1 – 3.3.7. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.5. Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6. Surrogate - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. The purpose of the surrogates is to evaluate the preparation and analysis of samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to extraction and analysis. Percent recoveries are calculated for each surrogate.

3.7. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.8. Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.9. Independent Verification Standard (ICV) - A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.10. Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.11. Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis.

The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

3.12. Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.13. Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4. INTERFERENCES

4.1. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation of the samples. Corrective action should be taken to eliminate the interferences.

4.2. Accurate determination of phthalate esters can pose difficulties when using this methodology. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware may occur when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

4.3. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in MSDSs where available. Refer to the ALS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3. This method uses Methylene Chloride, a known human carcinogen. Viton brand gloves should be used while rinsing, pouring or transferring the solvent.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Containers used to collect samples should be purchased pre-cleaned containers. Alternatively, containers used to collect samples for the determination of semivolatile organic compounds may be soap and water washed followed by methanol (or isopropanol) rinsing. The sample containers should be of glass or Teflon and have screw-top covers with Teflon liners. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. Highly acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may not be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

6.2. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g., if an automatic sampler is used), run reagent water through the sampler and use the rinseate as a field blank.

6.3. Water and soil samples must be iced or refrigerated at 4 ± 2°C from time of collection until extraction.

6.4. Water samples must be extracted within 7 days and the extracts analyzed within 40 days following extraction. Soil samples must be extracted within 14 days and the extract analyzed within 40 days following extraction. Extracts are stored at <-10°C.

7. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

7.1. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements.

7.2. Solvents: Acetone, methylene chloride, methanol, and other appropriate solvents. Solvents must be of sufficient purity to permit usage without lessening the accuracy of the determination or introducing interferences.

7.3. Stock Standard Solutions (See Table 3)

7.3.1. Stock standard solutions may be purchased from a number of vendors. All reference standards, where possible, must be traceable to SI units or NIST certified reference materials. Commercially prepared stock standards are typically used when available at a concentration of 1000 µg/ml or more. Standard concentrations can be verified by comparison versus an independently prepared standard. Alternatively, prepare stock standard solutions at a concentration of 1000 µg/ml by dissolving 0.0100 g of reference material in methylene chloride or other suitable solvent and diluting to volume in a 10mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Store according to the vendors recommendations.

7.3.2. Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 ± 2°C or per manufacturer's recommendation and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.3.3. Stock standard solutions must be replaced after one year, or sooner, if comparison with check standards or samples indicates a problem.

7.4. Internal Standard Solutions (See Table 3) - The internal standards are 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12} (See Table 4 for corresponding compounds). The nominal concentration of the standard is 4000 ng/µL. Each 1 ml of sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 40 ng/µL of each internal standard. Store at room temperature when not being used. When using premixed certified solutions, store according to the manufacturer's recommendations.

7.5. GC/MS Tuning Standard (See Table 3) - A methylene chloride solution containing 50 ng/µL of Decafluorotriphenylphosphine (DFTPP). The standard should also contain 50 ng/µL each of Benzidine, DDT, and Pentachlorophenol, to verify injection port inertness and GC column performance. Store at 4˚C ±2˚C when not being used, or store according to the manufacturer's recommendations.

7.6. Calibration Standards (See Table 3)

7.6.1. A minimum of five initial calibration standards should be prepared from stock solutions. One of the calibration standards should be at a concentration at or below the method reporting limit; the others should correspond to the range of concentrations found in real samples, but should not exceed the working range of the GC/MS system. At least one calibration standard must be at a concentration corresponding to a sample concentration meeting project-specific data quality objectives. Each standard should contain each analyte for detection by this method. Each 1 ml aliquot of calibration standards should be spiked with 10 µL of the internal standard solution prior to analysis. All calibration standards should be stored at <-10˚C or less and should be freshly prepared once a year, or sooner if check standards indicate a problem.

7.6.2. The daily calibration standard (CCV) is prepared at a nominal 80 ng/µL concentration from stock solutions. The CCV is prepared weekly and can be stored at 4˚C ± 2˚C. The DFTPP standard may be combined with this standard (maintaining 50 ng/µL) providing tuning verification and calibration verification can be done without interferences.

7.7. QC Standards (See Table 4)

7.7.1. Surrogates: Prepare a working solution in methanol containing 2-Fluorophenol, Phenol-d_6, and 2,4,6-Tribromophenol at 150 ng/µL and Nitrobenzene-d_5, 2-Fluorobiphenyl, and Terphenyl-d_{14} at 100 ng/µL. Aliquots of the solution are spiked into all extracted samples, blanks, and QC samples according to the extraction SOP used.

7.7.2. Matrix Spike Standards: Prepare a working solution in methanol containing all analytes of interest ("full list spike") from the standard analyte list (Table1) at 100 ng/µL. Aliquots of the solution are spiked into the selected QC aliquots according to the extraction SOP used.

Note: The spiking level of surrogate and spike may need to be adjusted according to project requirements, if dilutions are expected due to high levels of extracted components, or if a lower calibration range is used.

8. APPARATUS AND EQUIPMENT

8.1. Gas Chromatograph/Mass Spectrometer System

8.1.1. Gas Chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source. Agilent 5890, 6890 or equivalent.

8.1.2. Column: ZB-5MS Guardian- 30 m x 0.25 mm ID x 0.25 µm film thickness silicone-coated fused-silica capillary column. Recommended: Phenomenex with guard.

8.1.3. Mass Spectrometer - Capable of scanning from 35 to 500 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 2 when 1.0 µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

8.1.4. GC/MS Interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

8.1.5. Data System - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. NIST98 Mass Spectral Library is used for spectral comparisons.

8.2. Appropriate analytical balance (0.0001 g), volumetric flasks, syringes, vials, and bottles for standards preparation.

9. PREVENTIVE MAINTENANCE

9.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

9.2. Carrier gas - Inline purifiers or scrubbers should be in place for all sources of carrier gas. These are selected to remove water, oxygen, and hydrocarbons. Purifiers should be changed as recommended by the supplier.

9.3. Gas Chromatograph

9.3.1. Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column. Injection port maintenance includes changing the injection port liner, seal, washer, o-ring, septum, column ferrule, and autosampler syringe as needed. Liners and seals should be changed when recent sample analyses predict a problem with chromatographic performance. In some cases liners and seals may be cleaned and re-used.

9.3.2. Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column cutting tool.

9.3.3. Over time, the column will exhibit poorer overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

9.4. Mass Spectrometer

9.4.1. Tune the MS as needed to result in consistent and acceptable performance while meeting the required ion abundance criteria given in section 11.

9.4.2. For units under service contract, certain maintenance is performed by instrument service staff, including pump oil changed, vacuuming boards, etc., as recommended by the manufacturer.

9.4.3. MS source cleaning should be performed as needed, depending on the performance of the unit. This may be done by the analyst or by instrument service staff.

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the ADM-TRAIN, ALS-Kelso Training Procedure is also the responsibility of the department supervisor/manager.

11. PROCEDURE

11.1. Sample Preparation

11.1.1. Water samples

11.1.1.1. Water samples are prepared using continuous liquid-liquid extraction, EPA method 3520C. Refer to the ALS SOP EXT-3520. In some circumstances, such as rush samples or for TCLP leachates, samples may be prepared using separatory funnel procedures (EPA 3510C). Refer to the ALS SOP EXT-3510.

11.1.1.2. Perform the extraction on a 1000mL aliquot of sample. For TCLP leachates, use 100mL of sample.

11.1.2. Soil, sediment, and solid samples are prepared using automated soxhlet extraction (SOP EXT-3541). The nominal sample size is 30g. Sample amounts may be decreased in the case of high-concentration waste samples.

11.1.3. Product samples are prepared using EPA method 3580A.

11.1.4. Extracts may be screened by GC/FID (SOP SOC-SCR). Cleanup by GPC is performed on solid and waste samples and is optional on water samples.

11.1.5. Following sample preparation, sample extracts are then transferred to the extract storage freezer in the instrument lab. Extracts must be analyzed within 40 days of extraction.

11.2. The recommended GC/MS operating conditions are listed below. The GC conditions may be modified to accommodate specific instrument models and configurations.

Mass range:	35-500 amu
Scan Time:	1 sec/scan
Initial temperature:	40˚C, hold for 3.5 minutes
Temperature program:	40-50˚C at 6˚C/min, 50-270˚C at 15˚C/min, hold for 1.0 min.
Final temperature:	270-320˚C at 6.0 6˚C/min, hold for 3 minutes after Benzo[g,h,i]perylene has eluted
Injector temperature:	150˚C ramp to 300˚C
Detector interface temp:	320˚C
Injector:	split, electronic pressure control with pulse
Sample volume:	1.0 µL
Carrier gas:	Helium at 35 cm/sec

11.3. Initial Calibration

NOTE: The calibration procedure(s) and options chosen must follow the ALS protocols. Any exceptions to the calibration procedures detailed in the ALS SOP for *Calibration of Instruments for Organics Chromatographic Analyses* (SOC-CAL) are described as follows:

11.3.1. Prior to calibration, analyze the GC/MS tuning standard using instrument conditions used for calibration. Obtain the spectrum for evaluation using one of the following options:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.

- Use one scan at the apex of the peak. Background subtraction is required and must be performed using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be used only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.

- Use one scan either directly preceding or following the apex of the peak. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed of instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.

- Use the average across the entire peak up to a total of 5 scans. Peak integration must be consistent with standard operating procedure. If the peak is wider than 5 scans, the tune will consist of the peak apex scan and the two scans immediately preceding and following the apex. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.

11.3.2. Evaluate the spectrum obtained for DFTPP against the tuning criteria in Table 2 (see 8270D, Section 11.3.1 for guidance). The GC/MS must meet the DFTPP ion abundance criteria prior to further analyses.

11.3.3. The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2. See 8270D, Figure 1 for tailing factor calculation. If excessive tailing, poor chromatography, or degradation of >20% is noted, the injection port may require cleaning. It may also be necessary to remove the first 15-30 cm of the GC column. If hardware tuning criteria cannot be met, the source may need cleaning, filaments replaced or other maintenance.

11.3.4. The internal standards should permit most of the components of interest in the chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Refer to Table 5 for internal standards and corresponding analytes assigned for quantitation (other analytes may be added as needed). Use the base peak ion from the specific internal standard as the primary ion for quantitation (See Table 1 of EPA 8270D). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-Dichlorobenzene-d_4, use 152 m/z for quantitation).

11.3.5. Analyze 1.0 µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1 of EPA 8270D). Calculate response factors (RFs) for each compound relative to one of the internal standards as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for compound being measured.

A_{is} = Area of the characteristic ion for specific internal standard.

C_{is} = Concentration of the specific internal standard (ng/µL).

C_x = Concentration of the compound being measured (ng/µL).

11.3.6. The percent relative standard deviation (%RSD) should be less than or equal to 20% for each compound. It is also recommended that a minimum response factor for the most common target analytes, as noted in Table 6, be demonstrated as a means to ensure that these compounds are performing as expected.

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

where:
RSD = relative standard deviation.
$\overline{RF}$ = mean of initial RFs for a compound.
SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - RF)^2}{N - 1}}$$

where:

RF_i = RF for each of the calibration levels
N = Number of RF values (e.g., 6)

11.3.7. The relative retention times (RRT) of each compound in each calibration run should agree within 0.06 relative retention time units.

$$RRT = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

11.3.8. Linearity - If the % RSD of any compound is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

11.3.9. If the %RSD for a compound is >20%, then alternative calibration models should be used. Refer to the SOP for *Calibration of Instruments for Organics Chromatographic Analysis* (SOC-CAL) for alternative fit guidance.

11.3.10. If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.

11.3.11. When calculating the calibration curves using the alternative curve fits, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (see Method 8000C for additional details). It is not necessary to re-analyze a low concentration standard; rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration.

NOTE: Certain project plans (DoD QSM) contain additional initial calibration acceptance criteria (e.g. CCC, SPCC). In these cases, the QAPP-specified criteria are used.

NOTE: Certain state or program protocols have specific procedures for calibration. This may include all or part of Method 8000C. The analyst must ensure that the correct procedures are used. Known uses of 8000C are as follows:

- The use of quadratic regression calibration is not allowed for projects (samples) originating from South Carolina and under the SC DHEC lab certification where historically that analyte responds in a linear manner.

11.4. Initial Calibration Verification

11.4.1. Following initial calibration, analyze an ICV standard. The ICV solution must contain all analytes in the calibration standards at a concentration in the middle of the range of the initial calibration. Calculate the concentration using the typical procedure used for quantitation. Calculate the percent difference (%D) from the ICV true value. The maximum allowed % Difference or % Drift is ±30%.

NOTE: DoD ELAP projects may use the acceptance criteria of ± 20%.

11.5. Continuing Calibration

11.5.1. Following an acceptable tune, a calibration standard, or standards, at mid-concentration containing all semivolatile analytes, and all required surrogates, must be analyzed every 12 hours during analysis.

Note: When analyzing samples subject to Wisconsin DNR regulations, a second CCV must be analyzed when second order (quadratic) calibrations are used. One will be analyzed at the lower end of the calibration range and one at a point where the curve can no longer be characterized as first order.

11.5.2. If the percent difference or percent drift for each compound is less than or equal to 20%, the initial calibration is assumed to be valid and the analysis of samples may begin.

Calculate the percent drift using:

$$\% \, Drift = \frac{C_1 - C_c}{C_1} \times 100$$

where:

C_1 = Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

11.5.3. If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet the ≤ 20% criteria. If no more than 20% of the compounds, included in the initial calibration, differ from their true concentration by 40%, the initial calibration is valid and no corrective action is necessary.

11.5.4. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit.

11.5.5. Non-detected analytes can be reported from analyses when a CCV exhibit a positive bias (i.e., outside the upper control limit), no further documentation is required.

11.5.6. For situations when the CCV fails to meet the criterion in section 11.5.3, and a confirmed detection exceeds the MRL, the sample must be reanalyzed to ensure accurate quantification. If it is not possible to reanalyze the sample, the result must be reported as an estimated value.

11.5.7. The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the midpoint standard of the most recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrective action identified, as required. If the EICP area for any of the internal standards changes by a factor of two (50% to 200%) from that in the midpoint standard of the most recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrective action identified, as appropriate. When corrective action is taken, reanalysis of samples analyzed while the system was malfunctioning is required. Update the reference spectra and retention times in the quantitation database for the instrument method or ID file. The initial calibration average RF or calibration curve is then used in the quantitation of subsequent analyses.

11.5.8. A blank (method blank, GPC blank, or solvent blank) should be analyzed after the CCV, or at any other time during the analytical shift, to prove the system is free of contaminants. If contaminants are found in a method blank or GPC blank, then a solvent blank should be analyzed to help isolate the source of contamination.

11.5.9. Each of the most common target analytes in the calibration verification standard should meet the minimum response factors noted in Table 6.

11.5.10. If the minimum response factors are not met, the system should be evaluated, and corrective action should be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination of the front end of the analytical column, and active sites in the column or chromatographic system.

11.6. GC/MS Analysis

11.6.1. Evaluate FID screens if performed and make proper dilution (See FID screening SOP).

11.6.2. Spike the 1 ml extract obtained from sample preparation with 10 µL of the internal standard solution just prior to analysis. Use the same operating conditions as were used for initial calibration.

11.6.3. If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/µL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

11.6.4. Store the extracts at <-10°C or less, protected from light in vials equipped with un-pierced Teflon lined septa. Archive extracts in freezer for 3 months after analysis in the instrument/date specific storage boxes.

NOTE: Client specific QAPPs may require extracts to be kept for a longer period of time.

12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation

12.1.1. The accuracy and precision of the procedure must be validated before analyses of samples begin, or whenever significant changes to the procedures have been made. To do this, four clean matrix samples (water or solids) are spiked with the LCS spike solution, then prepared and analyzed.

12.2. Method Detection Limits and Method Reporting Limits

12.2.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike seven blank matrix (water or soil) samples with MDL spiking solution at a level below the MRL. Follow the analysis procedures in Section 11 to analyze the samples.

12.2.2. Calculate the average concentration found (x) in µg/L or mg/Kg, and the standard deviation of the concentrations (s) in µg/L or mg/Kg for each analyte. Calculate the MDL for each analyte. Refer to *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011). The MDL study must be verified annually (or quarterly, if used for DOD work).

12.2.3. Limits of Quantification (LOQ)

12.2.3.1. The laboratory establishes a LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within the LCS acceptance limits to verify the data reporting limit. Refer to *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011).

12.2.4. The Method Reporting Limits (MRLs) used at ALS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit. Current MDLs and LODs can be found in the laboratory Data Quality Objectives.

12.3. Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches* (ADM-BATCH). In general, these include:

12.3.1. Method blank - A method blank is extracted and analyzed with every batch of 20 or fewer samples to demonstrate that there are no method interferences. The method blank must demonstrate that interferences from the analytical and preparation steps minimized. No target analytes should be detected above the MRL in the method blank. For some project specific needs, exceptions may be noted and method blank results above the MRL may be reported for common lab contaminants (phthalate esters, etc.).

Note: DoD requires no analytes detected at > ½ the RL or 1/10 the regulatory limit, whichever is greater. For common laboratory contaminates there should be no detection > the RL.

12.3.2. A lab control sample (LCS) must be extracted and analyzed with every batch of 20 or fewer samples. The LCS will routinely contain the entire target analyte list. The LCS is prepared by spiking a blank with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

Acceptance criteria for lab control samples are listed in the laboratory Data Quality Objectives (DQO) tables. The accuracy of the analysis is controlled on a subset of target analytes. If the project analyte list is fewer than 20 analytes, all are considered control analytes. Analytes which are used for control analytes are listed in Table 7. For DoD projects all project target analytes are considered control analytes. If the LCS recovery for any control analyte fails acceptance limits, corrective action is required. If instrument corrective action is not applicable or ineffective, re-extraction of the associated samples is required. If any other analyte fails the advisory acceptance limits, the analyst must evaluate the impact on data quality and take any necessary corrective action, which may include re-extraction of the associated samples. Project-specific requirements may require all compounds to be treated as control analytes, or dictate use of project acceptance criteria.

12.3.3. A matrix spike/duplicate matrix spike (MS/DMS) must be extracted and analyzed with every batch of 20 or fewer samples. The MS is prepared by spiking a sample aliquot with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{R1 - R2}{(R1 + R2)/2} \times 100$$

Where R1 = recovered concentration in the higher result
R2 = recovered concentration in the lower result

The acceptance limits for the MS/DMS recovery are listed in the laboratory Data Quality Objectives (DQO) tables. If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken. The RPD acceptance limits are 30% for water and 40% for soils, sediments, and solids. Project-specific requirements may dictate the use of project acceptance criteria.

12.3.4. The acceptance limits for the surrogates are listed in the laboratory Data Quality Objectives (DQO) Tables. If any surrogate recovery is outside acceptance criteria, the sample data must be closely evaluated for possible matrix interferences. If none are present, then corrective action must be taken. The sample should be re-analyzed if instrument factors (calibration, injection port) are suspected. If not, re-extraction and re-analysis is required, except in cases of high recovery and no positive hits in the sample for the analyte class represented by the particular surrogate.

12.4. Additional QA/QC measures include control charting of QC sample results.

13. DATA REDUCTION AND REPORTING

13.1. Qualitative Analysis - The qualitative identification of compounds determined by this procedure is based on retention time, and comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the instrument and conditions used for the sample analysis. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

13.1.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

13.1.2. The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

13.1.3. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. Use professional judgment in interpretation where interferences are observed.

13.1.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is <50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13.1.5. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks appear to represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification. When analytes co-elute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

13.2. For samples containing components not associated with the calibration standards, a library search may be made of the purpose of tentative identification. Refer to method 8270D for guidance on tentatively identified compound (TIC) identification and quantification.

13.3. Quantitation and Calculations

13.3.1. The GC/MS data stations, in current use, all use the H-P RTE Integrator to generate the raw data used to calculate the standards $\overline{RF_x}$ values, the sample amounts, and the spike values. The software does three passes through each data file. The first two identify and integrate each internal standard and surrogate. The third pass uses the time-drift information from the first two passes to search for all method analytes in the proper retention times and with the proper characteristic quantitation ions.

When $\overline{RF_x}$ is used, calculate the extract concentration as follows:

$$C_{ex} = \frac{(Resp_x)(Amt_{ISTD})}{(Resp_{ISTD})(\overline{RF_x})}$$

Where:
C_{ex} = the concentration in the sample extract (ppm);
$Resp_x$ = the peak area of the analytes of interest;
$Resp_{ISTD}$ = the peak area of the associated internal standard;
Amt_{ISTD} = the amount, in ppm, of internal standard added
$\overline{RF_x}$ = the average response from the initial calibration.

13.3.2. The concentration of analytes in the original sample is computed using the following equations:

Aqueous Samples: $$Concentration\ (\mu g / L) = \frac{(Cex)\ (Vf)\ (D)}{(Vs)}$$

Where
Cex = Concentration in extract in µg/mL
Vf = Final volume of extract in mL
D = Dilution factor
Vs = Volume of sample extracted, liters

Non-aqueous Samples: $$Concentration\ (mg / Kg) = \frac{(Cex)\ (Vf)\ (D)}{(W)}$$

Where
Cex = Concentration in extract in µg/mL
Vf = Final volume of extract in mL
D = Dilution factor
W = Weight of sample extracted in grams.

13.4. Tentative identification of compounds (TIC)

13.4.1. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The current library is NIST98.

13.4.2. After a visual comparison of sample spectra with the nearest library searches the analyst assigns a tentative identification. Guidelines for tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 30%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

13.5. Data Review

Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the SOP for *Laboratory Data Review Process* (ADM-DREV) for details.

13.6. Reporting

13.6.1. Reports are generated in the ALS LIMS by compiling the SMO login, sample prep database, instrument, date, and client-specified report requirements (when specified). This compilation is then transferred to a file that the Stealth reporting system uses to generate a report. The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.6.2. As an alternative, reports are generated using Excel© templates located in R:\SVM\forms. The analyst should choose the appropriate form and QC pages to correspond to required tier level and deliverables requirements. The detected analytes, surrogates and matrix spikes are then transferred, by hand or electronically, to the templates.

13.6.3. Sample concentrations are reported when all QC criteria for the analysis have been met or the results are qualified with an appropriate footnote.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Nonconformity and Corrective Action* (CE-QA008) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

15.1. This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

15.2. The method detection limit (MDL) is established using the procedure described in the SOP *Performing Method Detection Limit Studies and Limits of Detection and Quantification* (CE-QA011). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Environmental Health and Safety Manual.

16.3. This method uses Methylene Chloride and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and recycled off site.

16.4. This method uses non-halogenated solvents and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations.

17. TRAINING

17.1. Training outline

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of 3 months. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.2. Training is documented following *ALS-Kelso Training Procedure* (ADM-TRAIN).

When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. METHOD MODIFICATIONS

18.1. Section 11.5.3, no limit defined in reference method, so lab assigned a limit of 40% based on CLP protocols.

19. REFERENCES

19.1. *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry*, Method 8270D, EPA Test Methods for Evaluating Solid Waste, SW-846, Final Update IV, February 2007.

19.2. *Determinative Chromatographic Separations*, Method 8000C, EPA Test Methods for Evaluating Solid Waste, SW-846, On-Line March 2003.

19.3. *Determinative Chromatographic Separations*, Method 8000B, EPA Test Methods for Evaluating Solid Waste, SW-846, Update III, December 1996.

20. CHANGES SINCE THE LAST REVISION

20.1. Updated QA Manager.
20.2. Minor grammatical and formatting revisions to improve readability.
20.3. Deleted duplicates in Tables 1A and 1B.

Table 1A – Routine Analytes and MRL/LOQ

ANALYTE	WATER MATRIX		SOIL/SOLID MATRIX	
	MRL/LOQ	Units	MRL/LOQ	Units
1,2,4-Trichlorobenzene	10	µg/L	0.33	mg/Kg
1,2-Dichlorobenzene	10	µg/L	0.33	mg/Kg
1,2-Diphenylhydrazine	10	µg/L	0.33	mg/Kg
1,3-Dichlorobenzene	10	µg/L	0.33	mg/Kg
1,4-Dichlorobenzene	10	µg/L	0.33	mg/Kg
2,3,4,6-Tetrachlorophenol	10	µg/L	0.33	mg/Kg
2,4,5-Trichlorophenol	10	µg/L	0.33	mg/Kg
2,4,6-Trichlorophenol	10	µg/L	0.33	mg/Kg
2,4-Dichlorophenol	10	µg/L	0.33	mg/Kg
2,4-Dimethylphenol	10	µg/L	0.33	mg/Kg
2,4-Dinitrophenol	25	µg/L	2	mg/Kg
2,4-Dinitrotoluene	10	µg/L	0.33	mg/Kg
2,6-Dinitrotoluene	10	µg/L	0.33	mg/Kg
2-Chloronaphthalene	10	µg/L	0.33	mg/Kg
2-Chlorophenol	10	µg/L	0.33	mg/Kg
2-Methyl-4,6-dinitrophenol	25	µg/L	2	mg/Kg
2-Methylnaphthalene	10	µg/L	0.33	mg/Kg
2-Methylphenol	10	µg/L	0.33	mg/Kg
2-Nitroaniline	25	µg/L	0.33	mg/Kg
2-Nitrophenol	10	µg/L	0.33	mg/Kg
3,3'-Dichlorobenzidine	25	µg/L	0.33	mg/Kg
3-Nitroaniline	25	µg/L	0.33	mg/Kg
4-Bromophenyl Phenyl Ether	10	µg/L	0.33	mg/Kg
4-Chloro-3-methylphenol	10	µg/L	0.33	mg/Kg
4-Chloroaniline	10	µg/L	0.33	mg/Kg
4-Chlorophenyl Phenyl Ether	10	µg/L	0.33	mg/Kg
4-Methylphenol	10	µg/L	0.33	mg/Kg
4-Nitroaniline	25	µg/L	2	mg/Kg
4-Nitrophenol	25	µg/L	2	mg/Kg
Acenaphthene	10	µg/L	0.33	mg/Kg
Acenaphthylene	10	µg/L	0.33	mg/Kg
Acetophenone	10	µg/L	0.33	mg/Kg
Aniline	25	µg/L	1	mg/Kg
Anthracene	10	µg/L	0.33	mg/Kg
Atrazine	10	µg/L	0.33	mg/Kg
Benz(a)anthracene	10	µg/L	0.33	mg/Kg
Benzo(a)pyrene	10	µg/L	0.33	mg/Kg
Benzo(b)fluoranthene	10	µg/L	0.33	mg/Kg
Benzo(g,h,i)perylene	10	µg/L	0.33	mg/Kg
Benzo(k)fluoranthene	10	µg/L	0.33	mg/Kg
Benzaldehyde	10	µg/L	0.33	mg/Kg
Benzoic Acid	25	µg/L	2	mg/Kg
Benzyl Alcohol	10	µg/L	0.33	mg/Kg
Biphenyl	10	µg/L	0.33	mg/Kg
Bis(2-chloroethoxy)methane	10	µg/L	0.33	mg/Kg
Bis(2-chloroethyl) Ether	10	µg/L	0.33	mg/Kg
Bis(2-chloroisopropyl) Ether	10	µg/L	0.33	mg/Kg

Table 1A - continued

Bis(2-ethylhexyl) Phthalate	10	µg/L	0.33	mg/Kg
Butyl Benzyl Phthalate	10	µg/L	0.33	mg/Kg
Caprolactam	10	µg/L	0.33	mg/Kg
Carbazole	10	µg/L	0.33	mg/Kg
Chrysene	10	µg/L	0.33	mg/Kg
Dibenz(a,h)anthracene	10	µg/L	0.33	mg/Kg
Dibenzofuran	10	µg/L	0.33	mg/Kg
Diethyl Phthalate	10	µg/L	0.33	mg/Kg
Dimethyl Phthalate	10	µg/L	0.33	mg/Kg
Di-n-butyl Phthalate	10	µg/L	0.33	mg/Kg
Di-n-octyl Phthalate	10	µg/L	0.33	mg/Kg
Fluoranthene	10	µg/L	0.33	mg/Kg
Fluorene	10	µg/L	0.33	mg/Kg
Hexachlorobenzene	10	µg/L	0.33	mg/Kg
Hexachlorobutadiene	10	µg/L	0.33	mg/Kg
Hexachlorocyclopentadiene	10	µg/L	0.33	mg/Kg
Hexachloroethane	10	µg/L	0.33	mg/Kg
Indeno(1,2,3-cd)pyrene	10	µg/L	0.33	mg/Kg
Isophorone	10	µg/L	0.33	mg/Kg
Naphthalene	10	µg/L	0.33	mg/Kg
Nitrobenzene	10	µg/L	0.33	mg/Kg
N-Nitrosodimethylamine	25	µg/L	2	mg/Kg
N-Nitrosodi-n-propylamine	10	µg/L	0.33	mg/Kg
N-Nitrosodiphenylamine	10	µg/L	0.33	mg/Kg
Pentachlorophenol	25	µg/L	2	mg/Kg
Phenanthrene	10	µg/L	0.33	mg/Kg
Phenol	10	µg/L	0.33	mg/Kg
Pyrene	10	µg/L	0.33	mg/Kg
Pyridine	25	µg/L	0.33	mg/Kg

Table 1B – Non-Routine Analytes and MRL/LOQ

ANALYTE	WATER		SOIL/SOLID	
	MRL/LOQ	Units	MRL/LOQ	Units
2-Picoline	10	µg/L	0.6	mg/Kg
N-Nitrosodiethylamine	10	µg/L	0.3	mg/Kg
Methyl Methanesulfonate	10	µg/L	0.3	mg/Kg
Pentachloroethane	10	µg/L	1	mg/Kg
N-Nitrosopyrrolidine	10	µg/L	0.3	mg/Kg
N-Nitrosomorpholine	10	µg/L	0.3	mg/Kg
N-Nitrosopiperidine	10	µg/L	0.3	mg/Kg
O,O,O-Triethyl Phosphorothioate	10	µg/L	0.3	mg/Kg
2,6-Dichlorophenol	10	µg/L	0.3	mg/Kg
Hexachloropropene	10	µg/L	0.3	mg/Kg
N-Nitrosodi-n-butylamine	10	µg/L	0.3	mg/Kg
p-Phenylenediamine	10	µg/L	0.3	mg/Kg
Safrole	10	µg/L	0.3	mg/Kg
1,2,4,5-Tetrachlorobenzene	10	µg/L	0.3	mg/Kg
Isosafrole	10	µg/L	2	mg/Kg
1,3-Dinitrobenzene	10	µg/L	0.3	mg/Kg
Pentachlorobenzene	10	µg/L	0.3	mg/Kg
1-Naphthylamine	10	µg/L	0.3	mg/Kg
2-Naphthylamine	10	µg/L	0.3	mg/Kg
2,3,4,6-Tetrachlorophenol	10	µg/L	0.3	mg/Kg
Diphenylamine	10	µg/L	0.3	mg/Kg
1,3,5-Trinitrobenzene	25	µg/L	2	mg/Kg
Phenacetin	50	µg/L	2	mg/Kg
4-Aminobiphenyl	10	µg/L	0.3	mg/Kg
4-Nitroquinoline N-Oxide	10	µg/L	2	mg/Kg
Total Aramite	50	µg/L	3	mg/Kg
3,3'-Dimethylbenzidine	25	µg/L	2	mg/Kg
7,12-Dimethylbenz(a)anthracene	10	µg/L	0.3	mg/Kg
Hexachlorophene	150	µg/L	5	mg/Kg
3-Methylcholanthrene	10	µg/L	0.3	mg/Kg
N,N-Dimethyl-1-phenethylamine	10	µg/L	20	mg/Kg
2-Acetylaminofluorene	10	µg/L	0.3	mg/Kg
o-Toluidine	10	µg/L	0.3	mg/Kg
Ethyl Methanesulfonate	10	µg/L	0.3	mg/Kg
1,4-Naphthoquinone	10	µg/L	0.3	mg/Kg
5-Nitro-o-toluidine	10	µg/L	0.3	mg/Kg
p-Dimethylaminoazobenzene	10	µg/L	0.3	mg/Kg
Pentachloronitrobenzene	50	µg/L	2	mg/Kg
Methapyrilene	100	µg/L	4	mg/Kg
Chlorobenzilate	10	µg/L	0.3	mg/Kg
2-sec-Butyl-4,6-Dinitrophenol (Dinoseb)	25	µg/L	1	mg/Kg
Diallate	10	µg/L	0.3	mg/Kg
Dimethoate	10	µg/L	0.3	mg/Kg
Disulfoton	10	µg/L	0.3	mg/Kg
Famphur	10	µg/L	0.3	mg/Kg
Isodrin	10	µg/L	0.3	mg/Kg
Kepone	100	µg/L	4	mg/Kg
Methyl Parathion	10	µg/L	0.3	mg/Kg

Table 1B - continued

Parathion	10	µg/L	0.3	mg/Kg
Phorate	10	µg/L	0.3	mg/Kg
Pronamide	10	µg/L	0.3	mg/Kg
Thionazine	25	µg/L	2	mg/Kg

TABLE 2
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	10-80% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-60% of mass 198
365	> 1% of mass 198
441	Present but <24 % of mass 442
442	Base peak, or > 50% of mass 198
443	15-24% of mass 442

Alternate tuning criteria (from Method 625, CLP OLM03.1, or manufacturer's specified criteria) may be used provided that method performance is not adversely affected and that method performance criterion is met. The criteria used must be the same for **all** ion abundance criteria checks associated with a given analysis. For example, initial calibration, continuing calibration(s), QC, and sample analyses for a given sample must all use the same criteria.

TABLE 3
8270 STANDARDS

CALIBRATION
Recommended: Supelco stock standards (or equivalent from other vendors*):

Supelco EPA CLP Semivolatile Calibration Mix
Supelco EPA 8270 Calibration Mix 4
Supelco EPA 8270 Benzidine Mix
Supelco n-Nitrosodiphenylamine
Absolute 2,3,4,6-Tetrachlorophenol
AccuStandard Method 8270 surrogate standard

Prepare 1 ml of each calibration point from purchased stock standards.
Calibration curve: 1 ppm, 5 ppm, 10 ppm, 20 ppm, 50 ppm, 80 ppm, 100 ppm, 120 ppm, 160 ppm, and 200 ppm.
Add 10 µl internal standard (Z-014J) for each 1 ml calibration standard when curve is prepared. Store all calibration standards in 1 ml amber autosampler vials at -10ºC. Expiration is set at 1 year from date prepared or expiration date of the parent standard(s), whichever is earliest.

ICV
Recommended: AccuStandard catalog # (or equivalent from other vendors*):

CLP-HC-BN-R, 1ml x 2, 2000 ppm BN mix
Z-014E-R3, 1ml x 2, 2000 ppm Composite3 mix
Z-014F, 1ml x 2, 2000ppm Benzidines mix
CLP-HC-AR, 1ml x 2, 2000ppm Acid mix
M-8270-SS-PAK, 1ml x 5, 4000ppm Surrogates mix

Add 10 µl internal standard (Z-014J) for each 1 ml of ICV prepared.
Place in 1 ml amber autosampler vial, recap, and store at -10ºC.
Expiration is set at 1 year from date prepared or expiration date of the parent standard(s), whichever is earliest.

CCV & TUNE
Use the same solutions that were used for the calibration curve

Z-014J, 1ml x 5, 4000ppm Internal Standards mix
M-625C, 1ml x 3, 25000ppm DFTPP (added to CCV)
M-625-TS-20x, 1000ppm (separate tuning standard)

Prepare 1 ml of 80 ppm 8270 CCV standard, place in autosampler vial and cap with a crimp top seal. 80ppm is the nominal concentration. CCV concentrations must be varied periodically.
CCV expiration is set at 1 week from date prepared or expiration date of the parent standard(s), whichever is earliest. Tune standard expiration is set at 1 year from date prepared or expiration date of the parent standard(s), whichever is earliest.

RECAP AND STORE IMMEDIATELY AFTER INJECTING
Store remaining stock solutions in 1 ml amber vials and store.
Expiration date is one year after ampoule is opened.
Order when down to one unopened ampoule.

* Vendor must be A2LA and/or ISO9000 certified.

TABLE 4
QC Standards

Supelco Parent	Initial Concentration	Dilution (mixed)*	Final Conc.
8270 Surrogate			
B/N Surrogate Mix (Absolute cat no. 23016)	5000 µg/mL	20mL to 1000mL in MeOH	100 µg/mL
Acid Surrogate Mix (cat no 86-1376)	10000 µg/mL	15mL to 1000mL in MeOH	150 µg/mL
PAH Surrogate Mix (cat no S8522)	5000 µg/ml	20 ml to 1000ml in MeOH	100 µg/ml
8270 Matrix Spike (mixed solution)			
CLP Semivolatile Mix (cat no. 5-06508)	1000 µg/mL	10mL to 100mL in MeOH	100 µg/mL
Benzidines Mix (cat no. 4-8467)	2000 µg/mL	5mL to 100mL in MeOH	100 µg/mL
N-Nitrosodiphenylamine (cat no. 46702-U)	5000 µg/mL	2mL to 100mL in MeOH	100 µg/mL
8270 Cal Mix 4 (cat no. 86-1148)	2000 µg/mL	5mL to 100mL in MeOH	100 µg/mL, 200 µg/mL Pyridine
2,3,4,6-Tetrachlorophenol (cat no. 79131)	1000 µg/mL	10mL to 100mL in MeOH	100 µg/mL
1-Methylnaphthalene (cat no. 4-8162)	2000 µg/mL	5mL to 100mL in MeOH	100 µg/mL
Pyridine (cat. no. App-9-186-20x)	2000 µg/mL	5mL to 100mL in MeOH	200 µg/mL

* For surrogate solution, split the total volume made into 4 bottles for storage and use. To avoid waste, the quantity made can be varied as anticipated for workload.

Standards Expiration: 6 months from preparation date. Purchased standards may be retained past the expiration date for internal R&D, but must be physically separated from standards in active use by placing in a separate, labeled area. Prepared spiking solutions must not be retained past the expiration date. Sequester expired or concentrated spiking solutions in labeled drawers awaiting disposal.

TABLE 5
INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d4 Internal Standard		
N-Nitrosodimethylamine	1,2-Dichlorobenzene	2-Methylphenol
Aniline	1,3-Dichlorobenzene	3- and 4-Methylphenol (co-eluting)
2-Fluorophenol (surrogate)	1,4-Dichlorobenzene	2-Picoline
Bis(2-chloroethyl) Ether	N-Nitrosodi-n-propylamine	Bis(2-chloroisopropyl) Ether
Phenol-d6 (surrogate)	Hexachloroethane	N-Nitrosopyrrolidine
Phenol	Methyl Methanesulfonate	N-Nitrosomorpholine
2-Chlorophenol	N-Nitrosomethylethylamine	*o*-Toluidine
Benzyl Alcohol	Acetophenone	Ethyl Methanesulfonate
Nitrobenzene	N-Nitrosodiethylamine	Pentachloroethane
Pyridine	Nitrobenzene-d5 (surr.)	
Naphthalene-d8 Internal Standard		
	Hexachlorobutadiene	N-Nitrosodi-*n*-butylamine
	2-Methylnaphthalene	N-Nitrosopiperidine
Isophorone	2-Nitrophenol	N,N-Dimethyl-1-phenethylamine
Bis(2-chloroethoxy)methane	2,4-Dimethylphenol	O,O,O-Triethyl Phosphorothioate
1,2,4-Trichlorobenzene	Benzoic Acid	Hexachloropropene
Naphthalene	2,4-Dichlorophenol	*p*-Phenylenediamine
4-Chloroaniline	4-Chloro-3-methylphenol	Safrole
α,α-Dimethylphenethylamine	2,6-Dichlorophenol	1,2,4,5-Tetrachlorobenzene
Acenaphthene-d10 Internal Standard		
2-Fluorobiphenyl (surrogate)	2,4-Dinitrotoluene	1-Naphthylamine
Hexachlorocyclopentadiene	2,6-Dinitrotoluene	2-Naphthylamine
2-Chloronaphthalene	Diethyl Phthalate	2,3,4,6-Tetrachlorophenol
2-Nitroaniline	4-Chlorophenyl Phenyl Ether	Pentachlorobenzene
3-Nitroaniline	Fluorene	1,3-Dinitrobenzene
4-Nitroaniline	4-Nitrophenol	1,4-Naphthoquinone
Dimethyl Phthalate	2,4,6-Trichlorophenol	5-Nitro-*o*-toluidine
Acenaphthylene	2,4,5-Trichlorophenol	Thionazine
Acenaphthene	2,4-Dinitrophenol	Diphenylamine
Dibenzofuran	Isosafrole	2-Methyl-4,6-dinitrophenol
1,2-Diphenylhydrazine	N-Nitrosodiphenylamine	

TABLE 5 – continued

Phenanthrene-d10 Internal Standard		
4-Bromophenyl Phenyl Ether	Pentachlorophenol	Pentachloronitrobenzene
Hexachlorobenzene	1,3,5-Trinitrobenzene	Disulfoton
Phenanthrene	Phorate	2-sec-Butyl-4,6-Dinitrophenol (Dinoseb)
Anthracene	Phenacetin	Methyl Parathion
Di-n-butyl Phthalate	Diallate	4-Nitroquinoline N-Oxide
Fluoranthene	Dimethoate	Parathion
Carbazole	4-Aminobiphenyl	Methapyrilene
Sulfotep	Pronamide	Isodrin
2,4,6-Tribromophenol (surrogate)		
Chrysene-d12 Internal Standard		
Pyrene	Bis(2-ethylhexyl) Phthalate	Chlorobenzilate
Butyl benzyl Phthalate	Chrysene	Kepone
Benzidine	Terphenyl-d14 (surrogate)	3,3'-Dimethylbenzidine
3,3'-Dichlorobenzidine	Total Aramite	Famphur
Benz(a)anthracene	*p*-Dimethylaminoazobenzene	2-Acetylaminofluorene
Perylene-d12 Internal Standard		
Di-n-octyl Phthalate	Indeno(1,2,3-c,d)pyrene	Hexachlorophene
Benzo(b)fluoranthene	Dibenz(a,h)anthracene	3-Methylcholanthrene
Benzo(k)fluoranthene	Benzo(g,h,i)perylene	
Benzo(a)pyrene	7,12-Dimethylbenz(a)anthracene	

TABLE 6
Recommended Minimum Response Factor Criteria

Compound	**Minimum Response Factor (RF)**
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl) Ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2’-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitrosodi-n-propylamine	0.500
Hexachloroethane	0.300
Isophorone	0.400
Nitrobenzene	0.200
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1’-Biphenyl	0.010
2-Chloronaphthalene	0.800
2,-Nitroaniline	0.010
Dimethyl Phthalate	0.010
2,6-Dinitrotoluene	0.200

TABLE 6 (continued)

Compound	**Minimum Response Factor (RF)**
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3’-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800

TABLE 6 (continued)

Compound	**Minimum Response Factor (RF)**
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

TABLE 7
Control Analytes for Non-DoD Projects

1,2,4-Trichlorobenzene
1,4-Dichlorobenzene
2,4-Dinitrotoluene
2-Chloronaphthalene
2-Chlorophenol
4-Bromophenyl Phenyl Ether
4-Chloro-3-methylphenol
4-Nitrophenol
Acenaphthene
Benzo(a)pyrene
Diethyl Phthalate
Hexachloroethane
N-Nitrosodi-n-propylamine
Pentachlorophenol
Phenol
Pyrene

TABLE 8

Summary of Corrective Actions

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
EPA 8000C, EPA 8270D	ICAL	Prior to sample analysis	% RSD ≤ 20 COD ≥ 0.990	Correct problem then repeat ICAL
EPA 8000C, EPA 8270D	ICV	After ICAL	± 30% Diff	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 8000C, EPA 8270D	CCV	Prior to sample analysis	± 20% Diff	Correct problem then repeat CCV or repeat ICAL
EPA 8000C, EPA 8270D	Method Blank	Include with each analysis batch (up to 20 samples)	<MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminate, unless samples contain > 20x amount in blank.
EPA 8000C, EPA 8270D	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO Table	If exceeds limits, re-extract and re-analyze
EPA 8000C, EPA 8270D	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO Table	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 8000C, EPA 8270D	Matrix Spike Duplicates	Include with each analysis batch (up to 20 samples)	W: RPD ≤ 30 S: RPD ≤ 40	Re-homogenize and re-analyze if result is > 5 X the MRL

SPECIFIC GRAVITY

SM 2710 F-2004, ASTM D854-83

ALS-KELSO

SOP ID:	GEN-SPGRAV	Rev. Number:	2	Effective Date:	8/01/2016

Approved By: ______________________ Date: 7/25/16
Department Manager/Technical Director – Harvey Jacky

Approved By: ______________________ Date: 7/25/16
QA Manager – Carl Degner

Approved By: ______________________ Date: 7/26/16
Laboratory Director – Jeff Grindstaff

Issue Date: ___________ Doc Control ID#: ____________ Issued To: ____________

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date
Signature	Title	Date
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Signature	Title	Date

ALS-Kelso SOP Annual Review Statement

SOP Code: GEN-SPGRAV
Revision: 2

An annual review of the SOP listed was completed on (date): _____

☒ The SOP reflects current practices and requires no procedural changes.

Supervisor: HLJ Date: 8/7/17

☐ Revision of the SOP is needed to reflect current practices. Draft revisions are listed below.

SOP Section Number	**Description of Revision Needed**	**Date Procedure Change Implemented**	**Supervisor Initials** Indicating Approval of Revision

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SPECIFIC GRAVITY

1. SCOPE AND APPLICATION

1.1. This Standard Operating Procedure (SOP) is used to determine the specific gravity of liquids, aqueous sludge, non-aqueous sludge, and solid material (including sediment and soil). The nature of the sample will usually determine which method is to be followed.

1.2. The two methods used in this SOP are Standard Methods method 2710F for liquid and aqueous sludge, and ASTM D854-83 for non-aqueous sludge and solid material.

2. METHOD SUMMARY

2.1. In both methods, the specific gravity is determined by comparing the mass of a known volume of homogeneous sample at a specific temperature to the mass of the same volume of de-ionized water.

3. DEFINITIONS

3.1. Specific Gravity: The ratio of the mass of a unit volume of a material at a stated temperature to the mass in air of the same volume of gas-free de-ionized water at a stated temperature

3.2. Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.2.1. Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.3. Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.4. Sample

3.4.1. Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client’s sample.

3.4.2. Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.5. Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.5.1. Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.5.2. Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.5.3. Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.5.4. Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.5.5. Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.5.6. Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.5.7. Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.5.8. Miscellaneous matrices – Samples of any composition not listed. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.6. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7. Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8. Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

4. INTERFERENCES

4.1. There are no interferences associated with these methods, however large particles present in the sample will require a much larger container and a larger volume of sample to be used.

5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in MSDSs where available. Refer to the ALS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Liquid and aqueous sludge can be collected in either plastic bottles or glass jars. Non-aqueous sludge and solids should be collected in glass jars.

7. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

7.1. Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination.

7.2. Reagents and Standards must comply with the traceability, labeling and documentation practices specified in the SOP for *Making Entries in Logbooks and Onto Benchsheets,* and the SOP for *Reagents and Standards Login and Tracking,* ADM-RLT*.*

7.3. All stocks, working solutions and sample dilutions should be prepared using deionized water (DI) conforming to ASTM Type I or ASTM Type II reagent water. For more information on reagent water generation, refer to the related SOP, Operation and Maintenance of Laboratory Reagent Water Systems.

8. APPARATUS AND EQUIPMENT

8.1. Container: A beaker or vial that can be marked and hold the known sludge volume during weighing.

8.2. Pycnometer.

8.3. Analytical Balance: 0.1mg accuracy. Alternately, for larger sample size, up to 2 Kg capacity.

8.4. Volumetric pipette 10 mL or 20 mL.

9. PREVENTIVE MAINTENANCE

9.1. Multi-point balance calibration verifications are required for each day the balance is used. The NELAC Quality System Standards and DoD Quality System Manual require that the balance verifications be performed *prior to use* on each day of use. The calibration verification weights must bracket the range of use. For additional information, refer to the SOP *Documenting Laboratory Balance and Temperature Checks* (ADM-BAL).

9.2. A bound logbook is used to record all balance measurements. Format the logbook such that the date, initials, balance I.D., weight set ID, measurements, and specifications for the check weights are listed for each balance. Record each calibration verification measurement in the logbook. Entries into logbooks are to be performed in accordance with the SOP for *Making Entries Onto Analytical Records* (CE-QA007).

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the ADM-TRAIN, ALS-Kelso Training Procedure is also the responsibility of the department supervisor/manager.

11. PROCEDURE

11.1. SM 2710 F (Liquid and Aqueous Sludge)

11.1.1. Allow samples and an aliquot of de-ionized water to warm to room temperature.

11.1.2. Tare a 20 mL scintillation vial and volumetrically pipette 10 mL de-ionized water. Record the weight, W.

11.1.3. Mark the vial at the bottom of the meniscus of the water.

11.1.4. Empty and dry the vial.

11.1.5. Tare the vial and add homogenized sample to the mark and record the weight, S.

11.1.6. Calculate the specific gravity, G, and report to three significant figures using the following equation:

$$G = S / W$$

11.2. ASTM D854-83 (Non-aqueous Sludge, Soils, Sediments and other Solids)

11.2.1. It is intended that the following procedure be used for samples passing a No. 4 (4.75mm) sieve. For particle sizes larger than a No, 4 sieve, refer to GEN-E1109 SOP, Bulk Density of Solid Waste Fractions.

11.2.2. Allow samples and an Aliquot of de-ionized water to warm to room temperature.

11.2.3. Record the tare weight of the clean, dry pycnometer with the stoppered thermometer inserted into the opening and the glass cover on the vent hole.

11.2.4. Fill the pycnometer to about half way up the neck with de-ionized water. Insert the stoppered thermometer into the neck slowly allowing all air and excess water to escape through the neck and the vent hole. Dry the outside of the pycnometer and place the glass cover over the vent hole. Record the weight of the water, Wa.

11.2.5. Empty the water out of the pycnometer and tare on the balance. Add approximately 2.0 g of homogenized sample to the pycnometer and record the weight of the wet sample, Wo.

11.2.6. Add deionized water to about halfway up the neck of the pycnometer. Insert the stoppered thermometer into the neck slowly allowing all air and excess water to escape through the neck and the vent hole. Dry the outside of the pycnometer and place the glass cover over the vent hole. Tare the balance and record the weight of the pycnometer, sample, and water. Subtract the tare weight of the pycnometer and record the weight of the sample and water, Wb.

11.2.7. Record the temperature of the sample and water.

11.2.8. Calculate the Specific Gravity G, and report the results to three significant figures using the following equation:

$$G = \frac{\underline{Wo}}{[Wo + (Wa-Wb)]}$$

12. QA/QC REQUIREMENTS

12.1. This method shall operate under the formal Quality Assurance Program established at ALS and must maintain records that define the quality of data that is generated. Data shall be compared to established criteria in order to determine if the results of the analyses meet the performance characteristics of the method.

12.2. Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches.* Additional QC Samples may be required in project specific quality assurance plans (QAPP). General QC Samples are:

12.3. QC samples required

12.3.1. Method Blank

12.3.1.1. A method blank is extracted and analyzed with every batch of 20 (or fewer) samples to demonstrate that there are no method interferences. If the method blank shows any hits above the reporting limit, corrective action must be taken. Corrective action includes recalculation, reanalysis, system cleaning, or re-extraction and reanalysis. For some project specific needs, exceptions may be noted and method blank results above the MRL may be reported for common lab contaminants.

12.3.2. Sample Duplicate

12.3.2.1. Run one duplicate sample for every sample batch of 20 or per Service Request Tier II or higher, whichever is more frequent.

12.3.2.2. The Relative Percent Difference (RPD) between duplicate sample analyses must be ≤ 20.

Calculate Relative Percent Difference (RPD) as:

$$\% RPD = \frac{|R1 - R2|}{(R1 + R2) / 2} \times 100$$

Where R1= Higher Result
R2= Lower Result

13. DATA REDUCTION AND REPORTING

13.1.1. Reports are generated in the ALS LIMS by compiling the SMO login, sample prep database, instrument date, and client-specified report requirements (when specified). This compilation is then transferred to a file which Excel© uses to generate a report. The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.1.2. As an alternative, reports are generated using Excel© templates located in R:\WET. The analyst should choose the appropriate form and QC pages to correspond to required tier level and deliverables requirements. The results are then transferred, by hand or electronically, to the templates.

13.2. Data Review and Assessment

13.2.1. Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to ADM-DREV, *Laboratory Data Review Process* for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Manager to inclusion in the report narrative.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Nonconformity and Corrective Action* (CE-QA008) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations.
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).
- Sample preservation or handling discrepancies due to laboratory or operations error.

15. METHOD PERFORMANCE

15.1. This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Environmental Health and Safety Manual.

17. TRAINING

17.1. Training outlines - Refer to ADM-TRAIN, *ALS-Kelso Training Procedure* for the required Training Plan format.

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst. Documentation of this step by step training is maintained using the appropriate training plan for this SOP.

17.1.3. Independently perform QC Analyses. For Initial Demonstration of Capability the analyst shall perform 4 consecutive CCV (color standard) analyses with the results within the acceptance limits and RSD < 20%. The data must be reviewed by a supervisor and the supervisor must document that the analyst is trained.

17.2. Training is documented following ADM-TRAIN, *ALS-Kelso Training Procedure*.

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. METHOD MODIFICATIONS

18.1. There are no known modifications in this laboratory standard operating procedure from the reference method.

19. REFERENCES

19.1. M 2710 F-2004, Standard Methods for the Examination of Water and Wastewater, 20th Ed., 1998.

19.2. ASTM Method D854, November 1983

19.3. Analytical Worksheet: R:\WET\ANALYSES\SpecGrav\templates\PICNOMETER TEMPLATE.xls.

20. CHANGES SINCE THE LAST REVISION

20.1. Updated document to the current ALS format.
20.2. Updated SOP references and standardization throughout the document.
20.3. Signature Page: Updated Quality Assurance Manager.
20.4. Section 9: Added balance calibration verification and records requirement.

Dissolved Gas Analysis in Aqueous Samples using a Headspace Equilibration Technique

DOCUMENT ID: VOA-DISGAS, REV 17

Approved By: Kate Kaneko Date: 1/30/19
Laboratory Director - Kate Kaneko

Approved By: Chaney Arend Date: 1/31/19
Quality Assurance Manager - Chaney Arend

Approved By: Date: 1/23/19
Technical Manager (Volatiles GC) - Wade Henton

Doc Control ID: UNCONTROLLED
Archived Date:

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1) Scope and Applicability

1.1 This gas chromatographic method is used for the analysis of dissolved carbon dioxide, methane, ethane, ethene (ethylene), propylene (propene), and propane in groundwater and other aqueous samples. This method is appropriate for quantifying target-dissolved gases from approximately 1.0μg/L to high mg/L values. It is easily adaptable for the analysis of other dissolved gases in water matrix samples. The approximate number of analyses (including sample preparation) which can be performed in one eight hour day is twenty.

1.2 The reported MDL and MRL are listed in Attachment D of this document and may be adjusted if required for specific project requirements; however, the capability of achieving other MRLs must be demonstrated.

2) Summary of Procedure

2.1 An aqueous sample is collected with zero headspace and delivered to the laboratory usually in a 40mL VOA vial. A headspace is generated by displacing twenty percent (20%) of the sample volume with either nitrogen or helium gas. The sample is sonicated in a water bath at ~20°C for fifteen (15) minutes and then equilibrated at ~20°C for two to four hours, depending on the analytes of interest. An aliquot of equilibrated headspace usually 100μL is drawn using a gastight syringe and directly injected onto a capillary chromatographic column where the analytes are separated and detected using a flame ionization detector (FID) and/or thermal conductivity detector (TCD). The concentration of the dissolved gas in the original sample is calculated by using Henry's Law Constant for each analyte, the determined concentration of the gas in the headspace, the submitted sample container volume, and the sample temperature.

3) Definitions

3.1 May This action, activity, or procedural step is neither required nor prohibited.

3.2 Must Not This action, activity, or procedural step is prohibited.

3.3 Must This action, activity, or procedural step is required.

3.4 Shall This action, activity, or procedural step is required.

3.5 Should This action, activity, or procedural step is suggested, but not required.

3.6 Analytical Sequence The analytical sequence describes exactly how the field and QC samples in an analytical batch are to be analyzed.

3.7 Field Sample A sample collected and delivered to the laboratory for analysis.

3.8 Batch QC Batch QC refers to the QC samples that are analyzed in an analytical batch of field samples and includes the Method Control Sample (MCS), Laboratory Control Sample (LCS), Matrix Spike (MS), Duplicate Matrix Spike (DMS) or Laboratory Duplicate (LD), etc.

3.9 Calibration Standard (Initial Calibration – ICAL) A calibration standard is an analyte at a known concentration prepared from a primary standard, which is, in turn, prepared from a stock standard material. A calibration standard is analyzed at specific concentrations and used to calibrate the response of the measurement system with respect to analyte concentration.

3.10 Initial (or Independent) Calibration Verification (ICV) Standard An ICV is a standard that is prepared from materials obtained from a source other than the source for the calibration standards and is analyzed after the measurement system is calibrated, but prior to sample analysis in order to verify the calibration of the measurement system.

3.11 Method Control Sample (MCS) An analyte-free (except carbon dioxide) matrix to which either nitrogen or helium gas is added in the same quantities or proportions as used in field sample processing and carried through the entire analytical process. It is used to evaluate the process for contamination from the laboratory with the exception of carbon dioxide.

3.12 Laboratory Control Sample (LCS) A laboratory control sample is an analyte-free matrix to which a known quantity of analyte(s) is (are) added. The LCS is subjected to the same processing as field samples and is carried through the entire analytical process. The percent recovery of the analyte(s) in the LCS is used to assess method performance with respect to the particular matrix in question.

3.13 External Standard Calibration External standard calibration involves comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards.

3.14 Analytical Batch A group of samples which behave similarly with respect to the sampling or the test procedures being employed and are processed as a unit using the sample lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. In an analytical batch of samples, the time period is 24 hours or up to twenty sample injections, whichever comes first of continuous operation without interruption.

3.15 Reagent Blank (RB) A reagent blank for this method is analyte-free helium that is analyzed to verify the zero point of the analytical system and to verify freedom from carryover.

3.16 Continuing Calibration Verification (CCV) Standard A continuing calibration verification standard is a calibration standard that is analyzed periodically to verify the continuing calibration of the measurement system.

3.17 Precision Precision of a method is how close results are to one another.

3.18 Bias The bias of a method is an expression of how close the result(s) (produced by the method) is(are) to the true value.

3.19 Manual Integration This term applies to a data file in which setpoints have been changed and reintegration has occurred under the changed setpoints; baselines have been adjusted; peak integration start and stop "ticks" have been changed; and peak area or peak height has been adjusted. In addition, these are changed after the time of data collection and data file generation.

3.20 Laboratory Duplicate Separate aliquots (two) of a sample taken from the same container under laboratory conditions and processed and analyzed independently. Since a submitted sample must not be opened, laboratory duplicates, for the purpose of this analysis, shall be duplicate manual injections.

3.21 Duplicate Field Sample Replicate containers of a sample submitted to the laboratory for analysis.

3.22 Limit of Detection (LOD) The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%. (DoD Clarification). For consistency purposes, the LOD may be referred to as the MDL once it is reported; however, full verification will be on file in the laboratory per the procedures detailed in this document.

3.23 Limit of Quantitation (LOQ) The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. (DoD Clarification). For consistency purposes and since the LOQ and MRL are equivalent with regards to laboratory procedure, the LOQ will be referred to as the MRL in this document and once it is reported. Full verification will be on file in the laboratory per the procedures detailed in the document.

3.24 Detection Limit (DL) / Method Detection Limit (MDL) The smallest analyte concentration that can be demonstrated to be different from zero or a blank concentration at the 99% level of confidence. At the DL, the false positive rate (Type 1 error) is 1%. (DoD Clarification). For consistency purposes, the DL may be referred to as MDL. Also, as far as reporting is concerned the MDL will be raised up (where necessary) to the verified LOD per the procedures defined in this document and reported accordingly.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review and reporting per the corresponding standard operating procedures. Laboratory personnel that have successfully demonstrated the ability to generate acceptable results according to this SOP are approved to perform sample analysis and interpretation of the results.

4.2 The department supervisor/manager or designee shall perform final review and sign-off on the data.

5) Interferences

5.1 Sample Contamination Care must be taken to prevent ambient air intrusion into the sample container during headspace generation and laboratory analysis. The sampling syringe should be flushed a minimum of 2-3 times with the gas being used to create the headspace (i.e. helium or nitrogen) in order to remove residual ambient air. An aliquot of the headspace gas, greater than needed is drawn, and the syringe plunger is adjusted to the appropriate volume *immediately* before injection.

5.2 Sample Preservation If the sample is to be analyzed for carbon dioxide it must not be preserved with hydrochloric acid at the time of collection. The addition of acid changes Henry's Law Constant for carbon dioxide and may artificially elevate the CO_2 result. The lower pH [increased (H+)] converts HCO_3^- in solution to CO_2.

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$

$$K_A = \frac{[HCO_3^-][H^+]}{[CO_2][H_2O]}$$

5.3 Sample Temperature Since the sample temperature is used in the final calculation, excessive handling of the sample should be avoided. The samples are considered ambient at the time of analysis. Henry's law constants are only available for certain analytes at certain temperatures, therefore, 20°C is used as it most closely approximates the actual ambient temperature of the laboratory. See Section 13.10.3 for the available Henry's Law Constant values.

5.4 Carbon Dioxide Concentrations in Water Carbon dioxide is found naturally dissolved in water, therefore, the method control sample may contain this analyte.

5.5 Methane Interference There is an interference that elutes at the same time as methane. This interference may be due to septa bleed. The concentration does tend to be consistently at or a little above the calculated method detection limit. Therefore, the reportable method detection limit for methane has been evaluated and raised to prevent false positives for clients who request the use of reporting estimated results below the method reporting limit.

6) Safety

6.1 Each compound, mixture of compounds, standards, as well as samples, should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest level possible through the use of hoods (to minimize inhalation). For proper handing, use and disposal refer to the laboratory's Environmental, Health and Safety Manual, SDS (located in the safety cubicle in the front office), as well as the *Simi Valley Lab Waste Management Plan*.

6.2 Safety Data Sheets Safety data sheets (SDS) are available and should be reviewed as part of employee training. Care should be taken when handling standard material in neat or highly concentrated form.

6.3 Protective Clothing At a minimum, personal protective clothing such as safety glasses and gloves should be worn when utilizing procedures detailed in this document.

6.4 Pressurized Gases The use of pressurized gases is required for this procedure. Care must be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. The regulator should never remain on small cylinders following use. Sources of flammable gases (i.e. pressurized hydrogen) shall be clearly labeled.

6.5 Syringes Care should be taken to avoid personal injury as a result or improper handling techniques.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Sample pH should be adjusted by the client at the time of collection to <2 with 1:1 HCl unless carbon dioxide concentration is to be evaluated. In addition, the laboratory shall receive samples in airtight borosilicate glass bottles or vials with Teflon-lined septa, at a temperature of ≤ 4°C with zero headspace (both evaluated by Sample Management upon receipt). The sample must be stored in the laboratory at 4°C ± 2°C and analyzed within 14 days (except carbon dioxide; no criteria) after sample collection, unless otherwise specified by the client. If the analysis is for carbon dioxide, it is recommended whenever possible, that the sample preparation take place within approximately 5 days from date of collection.

7.2 The analyst shall take the pH of the exact vial that was analyzed (especially if reporting CO2) using pH paper or strips. This reading must follow completion of the analysis and after review of all the QC results associated with the samples in order to prevent a loss of sample integrity. The analyst must record the information per vial including any comments on the Sample Acceptance Check Form accompanying the sample. The information that is to be included is the sample pH, method of analysis, and date and initials of the analyst that performed the pH evaluation.

7.3 Since there is no specific requirement for pH preservation (with the exception of carbon dioxide), the Project Manager (PM) in charge need not be contacted if the submitted samples were not preserved. However, if the client has specified instructions for pH preservation and there is a deviation, the PM must be notified and the PM shall decide whether the client should be contacted. All documentation must be retained regarding the outcome of the PM's decision as well as the client's reply. The pH should be noted (or must be included on the Sample Acceptance Check Form) on the final report.

7.4 When cross-contamination is a possibility, samples suspected of containing high concentrations of target analytes shall be isolated from other samples in a separate refrigerator designated for high concentration RSK175 samples. In the event that the client informs the project manager of potentially high concentration samples prior to sample receipt, the project manager must notify SMO so that the samples can be stored appropriately.

8) Apparatus and Equipment

8.1 Gas Chromatograph The analysis is performed using a Hewlett-Packard Model 5890 Series II Gas Chromatograph or equivalent equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD), using a split injection.

8.2 Column The analytical columns used to separate the gases are as follows:

Thermal Conductivity Detector .... Carboxen 1010, 0.53mm x 30m
Flame Ionization Detector .... J&W MXT-QPlot, 0.53mm x 30m

Gas Chromatograph Column Conditioning Initial conditioning of the chromatographic column is required prior to use of the system. The column should be conditioned with a continuous flow of laboratory helium (UHP/ZERO 99.999% purity or better) and temperature programmed from 35 degrees Celsius to 225 degrees Celsius at a rate of five degrees per minute. The column should then be held at 225 degrees Celsius overnight.

8.3 Sample Preparation and Analysis

8.3.1 Headspace Generation Kit

- A 10mL gas-tight syringe equipped with a 2 inch sidehole needle (gauge 22)
- 1/8 inch outer diameter Teflon tubing
- 100mL graduated cylinder
- Rubber stopper with two 1/8 inch holes
- Sonicator

8.3.2 Syringes

- 250µL
- 500µL
- 1.0mL
- 10mL

8.3.3 pH Paper

Range: 0-14

9) Standards, Reagents, and Consumable Materials

9.1 All standards and reagents, must be prepared, handled and labeled in accordance with the *SOP for Handling Consumable Materials*. For purchased standards, a unique standard identification number, all concentrations, received date, expiration date, and balance gas, as well as analyst's initials must be identified on the label. Each prepared standard, must include a unique standard identification number, the exact concentration of each analyte, expiration date, and balance gas, as well as analyst's initials (the date prepared shall be included in the laboratory standard identification number).

9.2 Certificates of analysis (CofA) must be maintained for all purchased standards, nitrogen, helium, hydrogen and zero air cylinders. All of the information listed above must be included on the CofA and turned in to the Quality Assurance Department for traceability purposes.

9.3 Purchased Stock Standards

The exact concentration specified in this section may change with each cylinder received; refer to the most recent Certificate of Analysis.

9.3.1 Matheson or Equivalent

Methane ....~4%
Oxygen..................~5%
Carbon dioxide ....~5%
Hydrogen...............~4%
Carbon monoxide ...~5%
Helium...................Balance

Methane..................~1%
Oxygen ....~1%
Carbon dioxide ....~1%
Hydrogen ....~1%
Carbon monoxide ....~1%
Helium ....Balance

Note: 1% = 10,000ppm

9.3.2 Scotty Mix 48 or Equivalent

Compound	Approximate Concentration (ppm by vol.)
Methane	15
Ethylene	15
Ethane	15
Propane	15
Acetylene	15
Propylene	15
Propyne	15
n-Butane	15
Balance: Nitrogen	

These stock standards contain compounds that are not reported. The actual concentrations of these standards may change with each purchase.

9.3.3 Neat Standards

Compound	Approximate Concentration (ppm)
Carbon dioxide	990,000
Ethylene (Ethene)	990,000
Methane	990,000
Propylene	990,000
Propane	990,000
Ethane	990,000

The specific concentrations of these standards may change with each purchase. If utilizing an ultra-high purity (UHP) gas cylinder, the certificate must be on file and it shall meet all of the minimum UHP requirements with respect to impurity content.

9.4 Calibration Standards

9.4.1 Initial Calibration (ICAL) and Continuing Calibration Verification (CCV) Standards

Working standards shall be prepared from higher concentration stock standards purchased from commercial vendors.

9.4.1.1 Procedure Aliquots of the stock standards are spiked into a cleaned and evacuated 6 liter canister (*SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters)* by using gastight syringes. The canister is then balanced with helium or nitrogen per the *SOP for Evaluation and Pressurization of Specially Prepared Canisters*.

Step 1: Determine the actual pressurized volume of the 6L canister by the use of the following equation.

$$PV = PDF(V) \qquad \text{(Equation 1)}$$

Where:

PV	Pressurized canister volume (L)
PDF	Pressure Dilution Factor, where PDF = $\frac{p_{atm} + p_f}{p_{atm} - p_i}$
P_f	Final Canister Pressure
P_i	Initial Canister Pressure
V	Volume of canister at 1atm
p_{atm}	Pressure at 1atm = 14.7

Example:

$$\frac{14.7 + 65}{14.7 - 0}(6L) = 32.53L$$

Step 2: Determine the amount required to achieve the desired concentration(s) by utilizing the following equation.

$$S = \frac{(C_1)(PV)}{(C_2)} x \frac{1000mL}{1L} \qquad \text{(Equation 2)}$$

Where:

S	Spike amount required in order to obtain the desired concentration (mL)
C_1	Desired concentration (ppm)
C_2	Concentration of source (ppm)
PV	Pressurized volume of canister determined in Step 1 (L)

The concentrations listed in this table are based on the purchased neat standards and may change with each purchased standard. However, the nominal concentration values should remain close to that listed below.

Compound	Source Conc. (ppm)	Introduce (mL)	Nominal Conc. (ppm)
Carbon dioxide	998,000	326	10,000
Methane	990,000	82.15	2500
Ethene	10,000	1626.5	500
Ethane	990,000	16.43	500
Propane	990,000	16.43	500
Propene	10,000	1626.5	500

Note: The exact volumes injected, to make a working standard, must be used to determine the final concentration of the standard.

In order to achieve all of the desired concentrations for each analyte in the ICAL or CCV, additional standard dilutions may be required. These dilutions may be prepared in glass dilution bombs (i.e., 125mL) or Tedlar bags and are achieved by following step 3 below.

Step 3: Determine the correct injection amount based on the desired final concentration for a target analyte by utilizing the following equation.

Using $C_1V_1 = C_2V_2$

Where:

C_1=Initial concentration (i.e., 2500ppm methane stock solution)
C_2=Final desired concentration (i.e., 2.5ppm)
V_2=Final volume (125mL or 125000uL – glass dilution bomb)
V_1=Solve for V_1 (uL)

Step 4: To perform the ICAL or to analyze a CCV, determine the correct instrument injection volume for an analyte by utilizing the following equation.

$$I = \frac{C_2}{C_1}$$

where:

I	required injection (mL)
C_1	Source (initial) concentration (ppm)
C_2	Desired concentration (ppm)

9.4.2 Initial Calibration Verification (ICV) Standard This standard must be from a second source and used as a verification of the initial calibration. Prepare the same as an ICAL standard.

DoD compliance: Second source standards must be obtained from a second manufacturer or must be from a second lot obtained from the same manufacturer (independently prepared from different source materials).

9.4.3 Laboratory Control Sample Spike The same standard as the ICV may be used to spike the LCS and LCSD.

9.4.4 Matrix Spike The standard as detailed in Section 9.4.1 is used to spike the MS and MSD.

9.5 Gases

9.5.1	Helium	99.999%, carrier gas, sample preparation displacement gas
9.5.2	Hydrogen	99.999%, fuel source for FID
9.5.3	Nitrogen	99.999%, makeup gas
9.5.4	Zero Air	Ultra

9.6 Reagent Water

Boiled Deionized Water or Equivalent

9.7 Storage and Expiration Dates

9.7.1 Neat Standards

Neat standards are purchased in gas cylinders and are stored at ambient temperature for a period of five years or as recommended by the manufacturer.

9.7.2 Stock Standards

Stock standards are purchased in gas cylinders and are stored at an ambient temperature for a period of two years or as recommended by the manufacturer.

9.7.3 Calibration Standards (ICAL, ICV and CCV)

Store each standard at an ambient temperature for a period detailed below, depending on the container.

Specially Prepared Canister - two years
Tedlar Bag - 3 days
Glass dilution bomb - 3 days

10) Preventive Maintenance

10.1 A maintenance log must be kept documenting maintenance performed on each analytical system. The serial number(s) of each instrument must be noted in the front of the logbook, which must be kept current. An entry shall be made in the appropriate log every time maintenance is performed (no matter the extent). The entry in the log must include:

(a) The date of maintenance
(b) Who did the maintenance
(c) Description of the maintenance
(d) Proof that the maintenance activity was successful

The extent of the maintenance is not important, however, it is important that a notation be included for each maintenance activity such as changing a column or cleaning the detector. A notation of a successful continuing calibration or initial calibration that accompanies the data shall serve as proof that the maintenance is complete and the instrument is in working order.

10.2 Gas Chromatograph

10.2.1 Column Over time, the column will exhibit a poor overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. This is especially evident in calibration difficulties. Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column.

Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column-cutting tool.

Poor performance can also be due to ineffective column ferrules, which should be replaced when a tight seal around the column is no longer possible. This can be detected with the use of a leak detector.

10.2.2 Injection Port Injection port maintenance includes changing the injection port liner, and column ferrule as needed. Liners should be changed when recent sample analyses predict a problem with chromatographic performance.

10.2.3 In-Line Purifiers shall be changed and maintained as recommended by the supplier.

10.2.4 Injector Septa Septa should be changed periodically, whenever there is a noticeable change in peak definition.

10.2.5 Detectors Clean detectors when needed or whenever there is a noticeable change in the background interference and peak definition.

11) Procedure

11.1 Data System and Analytical Sequence

11.1.1 Data System Load the appropriate method for the GC temperature program. Also, load the appropriate analytical sequence (example: J:\GC10\Sequence\rskboth.s) and enter the analytical sequence information in the table window, including sample/standard name, volume and method file. Load the appropriate analytical method (J:\GC10\Methods\“current ICAL file”). Run the sequence and inject the standards and samples in the appropriate order detailed in Section 11.1.2.

11.1.2 Analytical Sequence The number of samples in an analytical batch shall not exceed 20. Matrix spikes (MS), duplicate matrix spikes (DMS), laboratory duplicates (LD), and sample dilutions are not considered separate samples. Matrix spikes, matrix spike duplicates and duplicate field samples must be analyzed at the request of the client. Whenever possible, the analysis of the laboratory duplicate (LD), matrix spike (MS) and duplicate matrix spike (DMS) shall be rotated among clients. A client may request to have one or more of these batch QC samples run at each sample submission.

Batch QC samples may be analyzed anywhere in the analytical sequence; i.e., it is not necessary to analyze the batch QC samples in the exact order or position shown in this section. This analysis shall be run as a “closed” batch (beginning and ending with a CCV).

Analytical Sequence Guidelines

Sequence Position	*Sample Type*	*Sample Description / Detector*[1]
1	QC	CCV (FID &/or TCD)[7]
2	QC	ICV (FID &/or TCD)[2]
3	QC	RB (Helium – FID &/or TCD)[3]
4	Batch QC	MCS (FID &/or TCD)[4]
5	Batch QC	LCS (FID &/or TCD)[5]
6	Batch QC	LCS Duplicate (FID &/or TCD)[6]
7-15	Field	Samples 1-8 (FID &/or TCD)
16	Batch QC	MS (FID &/or TCD)[9]
17	Batch QC	LD (FID &/or TCD)[8]
18	QC	CCV (FID &/or TCD)[7]
19-28	Field	Samples 9-18 (FID &/or TCD)

29	QC	CCV (FID &/or TCD)[7]

[1] The reportable analytes associated with the FID (or TCD) need only be evaluated if one or more field samples are to be reported for those analytes. In addition, only a single injection is necessary for analysis on both detectors.

[2] The ICV is an optional daily standard.

[3] The reagent blank (RB) should be analyzed daily as a system check.

[4] The method control sample (MCS) must be prepared and analyzed with each batch of 20 or fewer samples. Refer to Section 3.11 for the complete definition.

[5] An LCS must be prepared and analyzed at a frequency of 1 in 20 or fewer samples.

[6] The LCSD must be analyzed as a check of method precision (including preparation) and is especially necessary since the LD is only a duplicate manual injection.

[7] An acceptable CCV must be analyzed initially, every ten sample injections (or every 12 hours, whichever is more frequent) and at the completion of the analytical sequence. Refer to Section 11.7 for additional information.

[8] A laboratory duplicate (LD) should be analyzed at a frequency of 1 in 20 or fewer samples.

[9] A matrix spike (MS) must be prepared and analyzed as requested by the client.

11.2 Sample Submission

A minimum of one 40mL VOA vial will be held as a “back up” for every sample submission if provided. Whenever required, other vials may be used as LD, MS and DMS.

11.3 Chromatographic Conditions

The settings and system parameters are as follows:

HP 5890 GC Instrument Control Parameters

Sample Inlet: GC
Injection Source: Manual
Injection Location: Front
Run Time: ~10.0 min (refer to Section 11.12.2, #3)

OVEN

Initial Temperature: 55°C
Initial Time: 2.0min
Maximum Temperature: 250°C
Equilibration Time: 0.0min

Ramps: Rate: 20°/min
Final Temp.: 205°C
Final Time: 0.5min

INJECTOR

Mode: Packed
Temp.: 100°C
Pressure: 20psi at 55°C oven temperature

COLUMN 1

Model No.: Supelco Carboxen 1010 PLOT
Max. Temp.: 250°C
Nominal Length: 30.0m
Nominal Diameter: 0.53mm ID
Initial Flow: 10 mL/min

COLUMN 2

Model No.: Restek MXT-QPLOT
Max. Temperature: 250°C
Nominal Length: 30.0m
Nominal Diameter: 0.53mm ID
Initial Flow: 10 mL/min

DETECTORS

FID		TCD	
Temperature:	280˚C	*Temperature*:	250˚C
H_2 Flow:	30 mL/min	*Reference Flow*:	45 mL/min
Air:	350 mL/min	*He Make up*:	20 mL/min
N2 Make up:	30 mL/min		

11.4 Initial Calibration

Introduce each initial calibration concentration by direct injection using a gastight syringe. The ICAL concentrations may change as long as the low standard analyzed is at or below the reporting limit for each analyte. Refer to Section 13.2 for calculations and Section 12.3 for the acceptance criteria. If an initial calibration is not used (did not pass criteria), it must be noted in the run logbook.

11.4.1 Initial Calibration Analysis Requirements These requirements apply to both detectors/columns for this method.

1. An initial calibration (ICAL) can be used as long as the continuing calibration verification standard (CCV) analysis at the beginning of and throughout the analytical sequence meets the analysis' criteria. Once a set of ICAL standards is analyzed and found to be acceptable, the previous ICAL can no longer be used to analyze new samples and it is to be archived. The only time an archived ICAL can be used thereafter is to review or re-evaluate sample(s) previously processed using that ICAL. *The practice of evaluating a CCV versus historical ICALs is not permitted.*
2. If a CCV analysis at the beginning of an analytical sequence fails to meet the analysis' criteria, a second CCV may be analyzed. If the second CCV meets the analysis' criteria, the analysis may continue. If the second CCV fails to meet the analysis' criteria, the analysis is to be stopped, corrective action is to be taken and documented (for example, in the maintenance logbook). *Analysis of more than two CCVs in succession without documented corrective action is not permitted.* Refer to Section 12.5.2 for DoD QSM CCV requirements.

    - Initial calibration requirements

        a. A minimum of five concentrations
        b. The concentration of the lowest calibration standard must be at or below the MRL for each reportable analyte.
        c. The highest concentration, together with the lowest concentration, defines the calibration range.
        d. An instrument blank should be analyzed prior to beginning the analysis of the calibration standards and each analyte concentration in it should be <MRL.
        e. All the ICAL analyses must be completed within 48 hours.
        f. The initial calibration event must not be interrupted by maintenance.
        g. Only one value per concentration is to be used.
        h. Multiple analyses of a calibration standard and use of all the analyses in the ICAL or picking-and-choosing responses from one analysis or the other to use in the analyte's ICAL is not permitted. Once the ICAL has been used on a sample, it is not to be changed.
        i. One ICAL standard may be re-analyzed as long as the requirements of the point dropping policy are met.
        j. The ICAL must be verified by analysis of an ICV standard (i.e., a second-source standard) prior to the analysis of samples.
        k. Point dropping policy:

- Minimum of five consecutive concentrations is required.
- Lowest concentration must be at or below the MRL and is not to be dropped unless the MRL is changed to the concentration of the remaining lowest standard.
- Points may be dropped from the high end, but doing so lowers the calibration range.
- Points must not be dropped from the “interior” of a curve unless there is an assignable cause* for doing so that affects many (if not all) the analytes in the calibration standard. If a calibration standard is to be dropped from the interior of the curve, all the analytes in the calibration standard must be dropped from all the analytes’ calibration curves.
- If a point or a calibration standard is dropped, the reason must be documented.
- One calibration standard may be re-analyzed if the first analysis of the standard has been dropped and the other requirements in this policy are met (e.g., still within 48 hours). The replacement standard must be analyzed within 24 hours of the original calibration standard analysis for the particular calibration level.

* Assignable causes include

- Standard preparation error
- Instrument malfunction (e.g., acquisition halts during the analysis)
- Bad injection or purge
- If ≥25% of the analytes in a multi-analyte calibration standard have a response that is <50% of the expected response based on the other calibration standards

11.4.2 ICAL Update Procedure

1. Open most recent method.
2. Save to new ICAL method ID. The date used in method ID is the date files were analyzed.
3. Clear all responses prior to update initiation and/or clear levels if different concentrations are to be used (Initial Calibration → Clear All Calibration Responses; Initial Calibration → Clear All Calibration Levels).
4. Quantitate standard
5. Review all peaks for retention time, integration, etc.
6. Update responses for standard
7. Repeat for all standards
8. If necessary load midpoint standard and update retention times.
9. Save method.
10. Verify Calibration Files listed on Response Factor Report are correct (Both Primary and Secondary Reviewer).
11. Verify responses of Page 3 of Edit Compounds are correct (Both Primary and Secondary Reviewer).
12. Verify file ID, acquisition time, quant time, update time, and last update information is correct on the Calibration Status Report (Both Primary and Secondary Reviewer).
13. Save Method. Confirm that no other copies of the method are open on other computer workstations.

Note: It is also acceptable to quantitate all standards and review all peaks before updating responses but steps 1-2 still must be completed initially. Step 3 also must be done prior to beginning ICAL update.

11.4.3 Initial Calibration File

An ICAL file is to be created for each initial calibration performed per instrument into which is placed the following ICAL documents. The file shall remain in the laboratory and be filed by instrument and date.

- Injection log (optional)
- ICAL Checklist filled out, reviewed and approved
- Blank analysis quantitation report
- Calibration status report (aka Calibration History)
- Relative Response Factor Report / Percent Relative Standard Deviation
- Quantitation report for each calibration standard (including manual integration documentation – before and after manual integration)
- ICV quantitation report and evaluate continuing calibration report (aka Percent Difference Report-either automated or through manual calculations)

11.4.4 Initial Calibration Review

Analyst's calculation and assessment along with a peer review of all ICAL data and documentation is required before the ICAL may be used to analyze samples. Sample results may only be reported if the ICAL is reviewed and found to be acceptable. The ICAL checklist in Attachment B must be properly completed to document the review and approval process and filed with the ICAL raw data.

11.4.5 Directions for ICAL

Inject the ICAL standard (Section 9.4.1) at a minimum of five levels (refer to Section 11.4.1). The following are the analytes and their associated detectors from which the results are reported.

Carbon dioxide	TCD
Methane	FID
Ethylene (Ethene)	FID
Ethane	FID
Propylene (Propene)	FID
Propane	FID

1. Purge standard cylinder valve at least three times using a 10mL syringe.
2. Take an appropriate size syringe and purge the standard cylinder valve with the standard gas a minimum of three times to prevent contamination.
3. Fill the syringe with greater than the amount to inject and adjust to the appropriate volume immediately before injection into the GC.
4. Allow chromatogram to run until all of the analytes have eluted.
5. Repeat steps 1-4 for each of the remaining standard volumes using the appropriate size syringe and dilution of the standard.

11.5 Initial Calibration Verification (ICV)

When an ICAL is performed it must always be followed by an ICV standard (second source standard) prior to the analysis of submitted samples. Refer to Section 12.4 for the acceptance criteria.

Directions for ICV Determination (FID)

1. Purge cylinder valve at least three times using a 10mL syringe.
2. Take a 500µL syringe and purge the cylinder valve with the standard gas a minimum of three times to prevent contamination.
3. Fill the syringe with >100µL and adjust to 100µL immediately before injection into the GC.
4. Allow chromatogram to run until all of the analytes have eluted.

The actual syringe listed and the injection volume may change with the desired concentration to be analyzed.

Directions for ICV Determination (TCD)

1. Purge cylinder valve at least three times using a 10mL syringe.
2. Take a 500µL syringe and purge the cylinder valve with the standard gas a minimum of three times to prevent contamination.
3. Fill the syringe with >100µL and adjust to 100µL immediately before injection into the GC.
4. Allow chromatogram to run until all of the analytes have eluted.

The actual syringe listed and the injection volume may change with the desired concentration to be analyzed.

11.6 LOQ Establishment, Verification, and Acceptance Criteria

1. The LOQ must be set within the calibration range (≥ low std. of the current passing ICAL) prior to sample analysis.
2. The LOQ for each analyte must be ≥ the analyte's LOD.
3. Initially a passing demonstration of precision and bias must be performed at the LOQ
4. Run CCV 2 times at LOQ and:
   - Evaluate the LOQ for precision and bias using current control chart limits or fixed limits of 70-130% until enough points have been generated.
   - Check the signal to noise ratio (S/N) using the software. The S/N ratio must be at least 3:1 for each analyte.
   - If anything fails, verify at higher level and notify reporting. Also, make a note in the ICAL documentation.
   - Turn in all LOQ verification data (quant reports and software reports/checks) to QA (regardless of pass/fail).
5. Verify the LOQ on each instrument quarterly by running the CCV at the LOQ and verifying that ongoing precision and bias requirements are met.

11.7 Continuing Calibration Verification (CCV)

Reportable results must be bracketed by CCV results that meet the QC requirements for the verification of the calibration. Also, sample concentrations must be quantitated from the current initial multi-point calibration and may not be quantitated from any continuing calibration verification standard. A continuing calibration check is performed at the beginning and end of every sequence and after every ten sample injections or every 12 hours, whichever is more frequent. The concentrations of the CCV should be varied within the established calibration range.

Directions for CCV Determination

The continuing calibration check shall be performed with the injection of a known amount of the ICAL/CCV standard (Section 9.4.1).

1. Purge cylinder valve at least three times using a 10mL syringe.
2. Take an appropriate size syringe and purge the cylinder valve with the standard gas a minimum of three times to prevent contamination.
3. Fill the syringe with a volume greater than the required amount and adjust to the proposed volume immediately before injection.
4. Allow chromatogram to run until all of the analytes have eluted.

The actual syringe listed and the injection volume may change with the desired concentration to be analyzed.

11.8 Reagent Blank (RB)

A RB is to be analyzed daily and follow the CCV standard or ICV standard (if analyzed).

Directions for RB Determination

The RB check is performed with the injection of 100µL of high purity helium.

1. Purge cylinder valve at least three times using a 10mL syringe.
2. Take a 500µL syringe and purge the cylinder valve with the standard gas a minimum of three times to prevent contamination.
3. Fill the syringe with >100µL and adjust to 100µL immediately before injection into the GC.
4. Allow chromatogram to run until all of the analytes have eluted.

The actual syringe listed and the injection volume may change with the desired concentration to be analyzed.

11.9 Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD)

The LCS and LCSD must be both prepared and analyzed with the corresponding field samples. The purpose of these batch QC samples is to evaluate analyst specific precision and bias or to assess the performance of all or a portion of the procedure (preparation and analysis). A LCS and LCSD are prepared with either the ICV or ICAL standard and are analyzed for each detector during the analytical sequence. The standard used must be noted on the run log for both the LCS and LCSD.

1. Fill a 40mL VOA vial with Sparkletts crystal water or equivalent and cap it with a Teflon-lined septum producing zero headspace.
2. LCS headspace generation inject 8mL of the LCS (FID) standard (Section 9.4.2) into the vial by following step 3 Section 11.12.1.
3. Complete steps 4-9 of Section 11.12.1.
4. Analyze sample per steps 1-3 of Section 11.12.2.
5. Repeat steps 1-4 of this section for the LCSD (FID), LCS (TCD) and LCSD (TCD)

11.10 Matrix Spike (MS)/Matrix Spike Duplicate (MSD) Analysis

Matrix spikes and matrix spike duplicates should be analyzed whenever possible. The MS and MSD must be both prepared and analyzed with the corresponding field samples. The purpose of these batch QC samples is to evaluate the effect of the matrix on a method's recovery efficiency and the precision of the recovery for each analyte.

Matrix spiking should only be performed on samples received in four (one for a back-up) separate vials, or at the specific request of the client. Matrix spikes shall be prepared and analyzed as outlined in Section 11.12 except the CCV standard is used in place of the helium.

11.11 Method Control Sample (MCS)

The MCS must be prepared and analyzed with the corresponding field and batch QC samples.

1. Fill a 40mL VOA vial with Sparkletts crystal water or equivalent and cap it with a teflon-lined septum producing zero headspace.
2. MCS headspace generation - inject 8mL of helium into the vial by following step 3 of Section 11.12.1.
3. Complete steps 4-9 of Section 11.12.1.
4. Analyze sample per steps 1-3 of Section 11.12.2.
5. Refer to Section 12.9 for quality control requirements including acceptance and rejection of the MCS.

11.12 Sample Preparation and Analysis

All samples must be prepared and analyzed with the MCS and LCS and LCSD for each detector. In addition, the time between sample preparation completion (after sonication) and the beginning of the associated analytical sequence should not exceed five hours but all samples (including standards and batch QC) must be analyzed the same day they are prepped.

Note: It is unacceptable to prepare batch QC samples at a separate time than the field samples.

11.12.1 Instructions for Headspace Generation

1. Remove the sample from storage (refrigerator).
2. Purge the headspace gas through a 10mL gastight syringe equipped with a sidehole needle (gauge 22) for approximately 30 seconds prior to beginning sample preparation.
3. Place the end of the waste sample overflow line into a graduated cylinder and insert the needle of the waste sample overflow through the Teflon faced septum of the sample.
4. Flush the 10mL gastight syringe with the headspace gas a minimum of 2-3 times to eliminate ambient air. Draw an aliquot of the headspace gas greater than what is needed, and adjust the syringe plunger to the appropriate volume *immediately* before injecting. Fill with a volume aliquot of gas equivalent to 20 % of the sample volume. For example, if the sample is taken in a 40mL VOA vial then 8.0mL of the headspace gas is added.
5. Introduce the headspace gas by slowly pushing the plunger of the gas tight syringe into the sample container. Once the desired volume of headspace gas is injected, remove the syringe quickly.
6. Allow approximately 2 minutes for the sample overflow to complete and quickly remove the waste sample overflow needle.
7. Verify that the volume in the graduated cylinder is equal to the volume of displaced gas introduced to the sample prior to proceeding to the next step.
8. Place the sample container in a sonication bath for at a minimum of 10 minutes at ~20°C.
9. Allow the sample to equilibrate at ~20°C for 2-4 hours (see Section 11.12.2 below).

11.12.2 Sample Analysis is performed by a direct injection technique using a gastight syringe. The samples are allowed to equilibrate according to the analytes requested by the client. Refer to the table below for the correct equilibration time for each sample type.

Reporting Compounds	Equilibration Time
Methane, Propane, Ethane, Ethene, Propene	2 hours minimum
Carbon Dioxide	4 hours minimum
Methane, Propane, Ethane, Ethene, Propene, and Carbon Dioxide	4 hours minimum

A sample volume of 100µL is used unless the detector response requires a smaller sample volume. The sample concentration of any identified analyte must be calculated from the current initial multi-point calibration. The response for the analyte must be within the range of responses of that analyte from the lowest to the highest initial calibration standards. If the response is greater than the highest standard, it must be reanalyzed (see Section 11.12.3).

Note: All samples, including batch QC, must be analyzed together the same day they are prepared. This is required in order to minimize the loss of sample integrity. The preparation and analysis of the LCS and LCSD with the corresponding field samples adds to this evaluation of sample integrity.

1. Take a 500µL syringe and puncture the Teflon septa and pump the syringe within the sample headspace a minimum of three times to get a representative sample.
2. Fill the syringe with greater than the amount to inject and adjust to the appropriate volume *immediately* before injection into the GC.
3. If methane, ethene and/or ethane concentrations are being evaluated, the run may be cut short after the ethane peak has eluted. However, after every third or fourth sample, the chromatogram must be run to the end in order to evaluate carry-over. In addition, if carbon dioxide is being evaluated, allow the chromatogram to run until all of the analytes have eluted.

Identification of peaks: Retention time windows are generated in accordance with the procedure described in Section 11.17. The retention time for each sample peak (from each column) shall be compared to the retention times in the continuing calibration verification standard in order to confirm qualitative analysis.

Refer to Section 13.10 for calculations.

11.12.3 Sample Dilution Samples require dilution if peak saturation occurs or if the quantified concentration is above the upper calibration range. Dilute the sample by injecting a smaller volume. Make sure that the correct injection volumes are recorded on the run log as well as the quantitation report. Guidance in performing dilutions and exceptions to this requirement are given below.

1. Use results from the original analysis to determine the approximate dilution factor required and get the largest analyte peak within the calibration range.
2. The dilution factor chosen should keep the response of the analyte peak for a reported target compound in the upper half of the calibration range of the instrument. Additional compounds may be reported as long as they are within the calibration range.

Refer to Section 13.10 for calculations.

11.13 Laboratory Duplicate

Analyze two separate aliquots from the same sample vial. Refer to Section 13.8 for the required calculations.

11.14 Duplicate Field Samples

Duplicate field samples may be analyzed when they are submitted and shall be reported as separate samples. Replicate samples must be analyzed following all the field sample guidelines detailed in this SOP.

11.15 Manual Integration

If manual integration is necessary the guidelines described in the *SOP for Manual Integration Policy* shall be followed. This includes the criteria for performing a manual integration; defining unacceptable data file manipulation, required documentation and review, as well as guidelines to follow when performing a manual integration.

11.16 Method Detection and Reporting Limits

The detection limit for this method is determined by following the guidelines in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.* Detection limits must be determined each time there is a change in the test method that affects how the test is performed, or when a change in instrumentation is such that it affects the sensitivity of the analysis. The method detection limit (MDL) must be verified at a minimum annually. Quarterly verifications as detailed below are required for DoD accredited analytes. All sample processing steps shall be included in the determination of the detection limit and all supporting data retained.

Method reporting limits (MRL) are the minimum quantities of a target analyte, for a given method, which are reported to the client. The low standard concentration for each analyte must be at or below the set MRL. The quantitation (reporting) limit for each analyte is defined as greater than the MDL to meet laboratory requirements. Refer to Section 5.5 for information on the MRL for methane.

The MDL should be verified with a standard analyzed at 1-4x the previously determined MDL. If each peak has a signal to noise ratio of at least 3:1, the MDL is considered verified. Otherwise, analyze at a higher concentration until the sensitivity is determined and raise the MDLs and method reporting limits (MRLs) as specified in this section.

The detection limit shall be used to determine the LOD for each analyte. Once determined on each instrument, the highest LOD (for each analyte from all instrument determinations) shall be used as the uniform LOD.

11.16.1 Performance and Acceptance Criteria

1. Perform Limit of Detection (LOD) verification on all instruments (performing this method) immediately following the MDL study. Spike the LOD at 2-4x the MDL; the spike level establishes the LOD.
2. LOD Acceptance
   - Analyte must be detected reliably and identified by the method-specific criteria and produce a signal that is at least 3 times the instrument's noise level (3:1 signal to noise ratio).
   - It is specific to each combination of analyte, matrix, method and instrument configuration.
   - The LOD must be verified quarterly on each instrument (spiked at LOD) using the criteria listed above.
3. If the LOD verification fails (per #2), repeat the detection limit determination and LOD verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.
4. The laboratory shall maintain documentation for all detection limit determinations and LOD verifications (regardless of pass or fail).

11.17 Retention Time Windows

Retention time windows for each target analyte must be generated whenever there is a major change in instrument conditions including flow rates or when standard analyses result in analyte retention times outside the established windows. The procedure for determining the retention time windows for this method is as follows. However, other approaches may be employed, providing that the analyst can demonstrate that they provide performance appropriate for the intended application. For example, the analyst may use the corresponding retention times from the initial calibration as they may show shifts in RTs due to the volume injected (higher concentrations lead to wider peaks).

1. Make sure that the system is operating reliably and that the system conditions have been optimized for the target analytes in the sample matrix to be analyzed.
2. Make four injections of all applicable standard mixes over a 72-hour period. Make the injections cover the entire 72-hour period or the end result could be windows, which are too tight.
3. Record the retention time for each single component analyte to three decimal places. Calculate the mean and standard deviation of the four absolute retention times for each single component analyte.
4. If the standard deviation of the retention times for the target compound is 0.000, then additional injections may be included or the use of a default standard deviation of 0.01 minutes.

5. The width of the retention time window for each analyte is defined as ±3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation of 0.01 is used, the width of the window will be 0.03 minutes.
6. Establish the center of the retention time window for each analyte by using the absolute retention time for each analyte in the continuing calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.
7. Retention time windows must be calculated for each analyte on each column and instrument. New retention time windows must be established when a new column is installed or if analysis parameters are changed.

12) Quality Control Requirements and Corrective Action

12.1 This section of the standard operating procedure contains technical acceptance criteria and preferred corrective actions to data nonconformities. Corrective actions shall follow the procedures outlined in the *SOP for Nonconformance and Corrective Action*, where appropriate.

12.2 To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.3 Initial Calibration

The Instrument must be recalibrated initially, whenever the laboratory takes corrective action (i.e. maintenance, which may change or affect the initial calibration criteria), or if the continuing calibration acceptance criteria have not been met.

12.3.1 Acceptance Criteria

- The percent relative standard deviation (% RSD) of the analytes of each of the levels must be less than 20% for the calibration to be considered acceptable.
- All initial instrument calibrations must be verified with a standard obtained from a second manufacturer or lot (see Section 9.4.2).
- The retention time for each analyte (at each calibration level) must within 0.10 minutes of the mean RT over the ICAL range. However it must be noted that higher injection volumes and/or higher concentrations of any analyte may not meet this criteria, which is acceptable.

12.3.2 Corrective Action

If the initial calibration technical acceptance criteria are not met, inspect the system for possible sources. It may be necessary to replace the syringe needle, column, Teflon tip on the syringe plunger or take other corrective actions such as clean or replace the detector to meet the initial calibration technical acceptance criteria. A demonstration of an in-control system is required before proceeding with the analysis. Refer to Section 11.4 for the initial calibration requirements as it includes information on dropping points. Also, check standards for a bad injection and re-analyze standard. If a bad injection is not evident, perform maintenance and attempt another initial calibration (make notation in maintenance logbook regarding any steps taken). Note in the run log that the initial ICAL was not used. Upon the completion of another unacceptable ICAL, the expiration date of the standards will be evaluated and new standards prepared if necessary.

12.4 Initial Calibration Verification (ICV) Standard

12.4.1 Acceptance Criteria

The percent difference of each calculated analyte concentration (per detector) must be within ±15% of the actual concentration of the standard.

12.4.2 Corrective Action If the initial calibration verification fails to meet the acceptance criteria, it must be reanalyzed. A second failed ICV must initiate corrective action and two consecutive standards must pass in order for the ICAL to be deemed acceptable. It may be necessary to prepare either new ICAL or ICV standards, perform maintenance or reanalyze the initial calibration. A demonstration of an in-control system is required before proceeding with the analysis.

12.5 Continuing Calibration Verification (CCV) Standard

12.5.1 Acceptance Criteria

All continuing calibration verification standards within an analytical sequence must be evaluated against the following acceptance criteria.

- The percent difference (%D) for each calculated target analyte must be within ≤15%.
- The RT of each analyte in the CCV must fall within 0.33 minutes of the mean RT from the ICAL.

12.5.2 Corrective Action

If the criteria are not met a second continuing calibration standard shall be analyzed. If the result is still unacceptable per this SOP, then the analyst must demonstrate performance after corrective action with a successful calibration verification or initial calibration. If there has not been evidence of acceptable performance then samples may not be analyzed until a successful ICAL is established and verified. However, sample data associated with unacceptable calibration verification may be reported as qualified data under the following special conditions:

1. When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then any non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.
2. When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a known maximum regulatory limit. Otherwise the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

Note: No greater than two consecutive CCV standards may be analyzed before corrective action is initiated.

DoD QSM Requirement: If a CCV fails, the laboratory must immediately analyze two additional consecutive CCVs (immediately is defined as within one hour).

- Both of these CCVs must meet acceptance criteria in order for samples to be reported without reanalysis.

- If either of these two CCVs fail or if the laboratory cannot immediately analyze two CCVs, the associated samples cannot be reported and must be reanalyzed.
- Corrective action(s) and recalibration must occur if the above scenario fails. All affected samples since the last acceptable CCV must be reanalyzed.
- Flagging data for a failed CCV is only appropriate when the affected samples cannot be reanalyzed. The laboratory must notify the client prior to reporting data associated with a failed CCV.

12.6 Reagent Blank (RB)

12.6.1 Acceptance Criteria

The main purpose for analyzing the reagent blank is to verify the zero point of the analytical system and to evaluate carryover. Review Section 5.5 for information on methane interference. The analyte concentrations (in ppm) for the RB (He) must not be greater than the reporting limit. Typically, the only analyte with a concentration close to the criteria is the methane interference peak. It is not necessary to run the integrated concentrations through the worksheet to evaluate the acceptance criteria. The action limit for this peak is considered to be approximately 0.15ppm (without putting it through the worksheet calculations) and it must be reanalyzed.

12.6.2 Corrective Action

If the analyte results in the RB do not meet the acceptance criteria determine whether the cause is instrumentation problems or the result of a poor injection. If the problem is with the injection, re-analyze the RB. However, if the cause is due to an instrumentation problem, maintenance must be performed, along with the proper logbook documentation, and the RB re-analyzed.

12.7 Laboratory Control/Laboratory Control Sample Duplicate (LCS/LCSD) Analysis

12.7.1 Acceptance Criteria

- The LCS and LCSD percent recovery must fall within the laboratory generated limits where available. If limits are not available the percent recovery must fall within 70% to 130% for all analytes except CO2. The LCS/LCSD percent recovery for CO2 shall be 50-150%.
- The reproducibility of the LCS/LCSD are considered acceptable when the results agree within the laboratory generated limits where available. If limits are not available, the RPD must be ±15% for all analytes except CO2 which shall be ±30%.
- DoD Requirement: Refer to Attachment 4 for DoD QSM acceptance criteria.

12.7.2 Corrective Action

An out of control LCS may be an indication of a problem with the sample preparation or analysis portions of the procedure. It is important to evaluate the cause to determine if the samples have been affected in the same or similar manner and therefore, will be reported either bias high or bias low depending on the percent recovery of the LCS/LCSD. If the LCS criteria are not met, determine whether the cause is instrumentation problems, result of poor injection or a problem with sample preparation. If necessary, perform maintenance and if the problem is with the injection re-analyze the sample. All samples processed with an out of control LCS will require to be re-prepared/analyzed if sufficient backup samples are available or have data qualifiers attached to the analytical results.

12.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Analysis

12.8.1 Acceptance Criteria

- The percent recovery must fall within fixed control limits of 50%-150%.
- Analytes must have a RPD of ±30%.
- DoD Requirement: Refer to Attachment 4 for DoD QSM Acceptance Criteria.

12.8.2 Corrective Action

If the criteria are not met, determine if there was an injection problem. If this is the case then reanalyze one or both of the samples. If they are still unacceptable and there is an assignable cause such as matrix interferences the results should be qualified.

12.9 Method Control Sample

12.9.1 Acceptance Criteria

Due to the nature of water, there is no true blank for carbon dioxide. Therefore, results for the MCS are reported to the client. However, any other detected analytes must not exceed the method reporting limit.

For DoD samples, the method control sample will be considered to be contaminated if:

1. The concentration of any target analyte in the blank exceeds 1/2 the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);
2. The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
3. The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

The laboratory shall evaluate whether reprocessing of the samples is necessary based on the above criteria.

12.9.2 Corrective Action

If the analyte results in the MCS do not meet the acceptance criteria the source of the problem must be investigated and measures taken to eliminate the source. Determine whether the contamination is from the instrument or due to contamination in the helium, nitrogen, syringe, or other source. Regardless, appropriate corrective measures must be taken and documented. If the result in the MCS has been determined to originate from the previous sample the MCS may be reanalyzed. If the results are the same, the MCS along with all associated samples must be reported to the client with the appropriate qualifiers.

12.10 Sample Analysis

Sample results must be quantitated from the current instrument initial calibration and may not be quantitated from any continuing calibration verification standard.

12.10.1 Acceptance Criteria

- The field samples must be analyzed along with a laboratory method control sample that met the MCS criteria in Section 12.9.
- All target analyte peaks must be within the initial calibration range.
- All analytes must be within the retention time windows, utilizing the CCV (or midpoint concentration, if analyzing samples during the same sequence as the ICAL) as the absolute RT.
- All analytes must be within 0.33 minutes of the mean RT of the ICAL.

- Once the samples have been prepared they must be analyzed the same day in order to prevent loss of sample integrity.
- All batch QC samples must be prepared and analyzed with submitted samples so that sample integrity may be further evaluated and the results reported accordingly.

12.10.2 Corrective Action

To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s). When corrective actions are made, samples analyzed while the system was not functioning properly must be reanalyzed.

- Results not bracketed by initial instrument calibration standards (within calibration range) must be analyzed with a smaller injection volume or reported as having less certainty, e.g., defined qualifiers or flags.
- The retention time of the analyte must meet the criteria to be considered a reportable result.
- If the pH reading indicated that the sample was preserved and CO_2 is to be reported the result must be reported as estimated.
- Field and batch QC samples exceeding the same day hold time requirement between preparation and analysis must be re-prepared and analyzed.

12.11 Laboratory Duplicate

12.11.1 Acceptance Criteria

The results must meet all of the criteria stated in Section 12.10 and be within the laboratory generated limits where available. If these limits are not available for a particular analyte the RPD must be ±15%. This is required provided that the analytes are at least 10 times the method reporting limit.

12.11.2 Corrective Action

If the replicate results do not fall within the technical acceptance window, the sample should be re-analyzed. If the results are still unacceptable and there does not appear to be any matrix effects, interfering peaks, or instrument problems, the results for both injections shall be reported to the client.

12.12 Replicate Field Sample

Due to the variation in analyte concentrations (this is especially true for methane and carbon dioxide) for replicate sample submissions, results will be reported to the client as separate samples.

13) Data Reduction and Reporting

13.1 Quantitation

The headspace result for each analyte (in ppm) from the Hewlett Packard Chemstation data system shall be entered into a Microsoft Excel worksheet. The worksheet calculates the final concentration of dissolved gas in the liquid sample for each target analyte based on the calculations specified in this section.

Each chromatogram must be carefully scrutinized for errors in integration performed by the Enviroquant Chromatography Data Processing Program (CDPP). If it is determined that an analyte peak was incorrectly integrated or if a peak was misidentified the peak must be manually integrated in accordance with the *SOP for Manual Integration Policy.*

13.2 Initial Calibration

The initial calibration curve must be saved with a two letter identification followed by the date of the analysis (mm,dd,yy). No curve may be overwritten at any time to ensure a complete and accurate audit trail.

- Tabulate the peak area along with standard concentration injected to determine the response factor (RF) for each analyte at each concentration using equation number 10.
- Calculate the percent relative standard deviation (%RSD) of the mean RF (equation number 11) for each analyte using equation numbers 7 and 8.
- Determine the mean retention time of each analyte spanning the initial calibration range using equation number 5.

13.3 Initial Calibration Verification

- Calculate the concentration for each analyte using equation numbers 1-4.
- Calculate the % difference between calculated concentration (see above) and the actual concentration using equation number 9.
- Determine the retention time difference for each analyte between the initial calibration and the ICV using equation number 6.

13.4 Continuing Calibration Verification

- Calculate the concentration for each analyte using equation numbers 1-4 for each standard analyzed within a given analytical sequence.
- Calculate the % difference between the calculated concentration (for each CCV in a sequence, see above) and the actual concentration using equation number 9.
- Determine the retention time difference for each analyte between the initial calibration and the each CCV in the sequence using equation number 6.

13.5 Laboratory Control Sample / Duplicate Laboratory Control Sample

- Calculate the concentration for each analyte using equation numbers 1-4.
- Calculate the percent recovery (%R) for all analytes in both the LCS and LCSD (for both detectors, if applicable) using equation number 12.
- Calculate the relative percent difference in the LCS and LCSD, for each detector (if applicable) for each of the target analytes using equation number 13.

13.6 Matrix Spike / Matrix Spike Duplicate (if applicable)

- Calculate the concentration for each analyte using equation numbers 1-4.
- Calculate the relative percent difference in the MS and MSD for each of the target analytes using equation number 13, if applicable.
- Calculate the percent recovery (%R) for all analytes in both the MS and MSD (if applicable) using equation number 12.

13.7 Sample Analysis

Quantitative Analysis - Calculate the concentration for each analyte using equation numbers 1-4.

13.8 Laboratory Duplicate

- Calculate the concentration for each analyte using equation numbers 1-4.
- Determine the relative percent difference calculated using equation number 13.

13.9 Duplicate Field Samples

- Calculate the concentration for each analyte using equation numbers 1-4.

13.10 Calculations

13.10.1 Equation Number 1

Headspace Concentration (ppm)

$H_p = [(D)(1)/V_i]DF$

where:

D is the concentration in ppm from the HP Chemstation data system
1 is the default injection volume (1 ml) as required by the data system
V_i is the actual headspace injection volume in milliliters
DF is any applicable dilution factor
H_p is the concentration in ppm in the headspace

13.10.2 Equation Number 2

Headspace Concentration (µg/L)

$H_m = H_p(1/10^6)(\text{mole}/24.06\text{L})(MW_{(g)}/\text{mole})(10^6\ \mu g/g)$

where:

MW is the molecular weight in grams of the analyte in question
24.06 is the gas constant at 1 atm pressure and 20°C
$(1/10^6)$ coverts ppm to a decimal (ppm to Atm)
H_m is the concentration in µg/L in the headspace

13.10.3 Equation Number 3

Equilibrated Water Concentration (µg /L)

$$E_w = \frac{(H_p)(M_w)(MW)(1 \times 10^3)(1 \times 10^3)}{(1 \times 10^6)(C)}$$

the units in the above equation cancel as follows:

$$\mu g/L = \frac{(\text{ppm})(\text{moles}/L)(g/\text{mole})(mg/g)(\mu g/mg)}{(\text{ppm}/\text{atm})(\text{atm}/\text{mole fraction})}$$

where:

E_w is the concentration of dissolved gas in mg/L in the equilibrated water (liquid phase)
H_p is the concentration in ppm in the headspace
M_w is the number of moles of water in one liter (55.51 moles/liter)
MW is the molecular weight of the analyte of interest in g/mole
1×10^3 mg/g is the factor used to convert from grams to milligrams
1×10^3 µg/mg is the factor used to convert from milligrams to micrograms

1×10^6 ppm/atm is the factor used to convert from ppm to partial pressure

C is the Henry's law constant* for the analyte in question in atm/mole fraction

Henry's Law Constants at 20°C (atm/mole fraction)

Methane	3.76×10^4
Ethane	2.63×10^4
Ethylene (Ethene)	1.02×10^4
Propylene (Propene)	6.00×10^3
Propane	7.06×10^4
Carbon dioxide	1.42×10^3

13.10.4 Equation Number 4

Dissolved Gas Concentration (µg/L)

$$W = \frac{(H_m)(V_h)}{(V_s)} + E_w$$

where:

W is the concentration of dissolved gas in mg/L in the zero headspace sample;

H_m is the concentration in mg/m^3 in the headspace;

V_h is the volume of headspace in milliliters added to the sample;

V_s is the volume of sample in milliliters remaining after displacement.

13.10.5 Equation Number 5

Mean Retention Times ($\overline{RT}$)

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

Where:

$\overline{RT}$	Mean retention time, minutes
RT_i	Retention time for the analyte in the standard, minutes
n	number of standards

13.10.6 Equation Number 6

Retention Time Difference (RTD)

$$\left| RT_c - RT_s \right|$$

where:

RT_C	Retention time of the target compound in the CCV, minutes.
RT_S	Retention time of the compound in the standard, minutes.

13.10.7 Equation Number 7

Standard Deviation, SD

$$SD = \sqrt{\sum_{i=1}^{N} \frac{\left(RF_i - \overline{RF}\right)^2}{N-1}}$$

where:

RF_i	are the individual RFs from each concentration level in the initial calibration curve
$\overline{RF}$	Average (or Mean) RF of all concentration levels in the initial calibration curve
N	total number of calibration concentration levels

13.10.8 Equation Number 8

Percent Relative Standard Deviation, %RSD

$$\%RSD = \frac{SD}{\overline{RF}}(100)$$

where:

SD	Standard Deviation calculated in equation number 3
$\overline{RF}$	Average or Mean RF

13.10.9 Equation Number 9

Percent Difference, %D

The %D is used for evaluating ICV and CCV vs. the initial calibration

$$\%D = \frac{C_{CCVorICV} - C_{std}}{C_{std}}(100)$$

where, for any given analyte:

$C_{CCVorICV}$	is the concentration being evaluated.
C_{std}	is the concentration from the current calibration curve;
C_{std}	actual concentration x injection volume.

13.10.10 Equation Number 10

Response Factor (RF)

The response factor, for analyte *x* is given by:

$$RF = \frac{A_x}{C_x}$$

where:

A_x = Area of the analyte in the standard
C_x = Concentration of the analyte in the standard, in ppm

13.10.11 Equation Number 11

Average (or Mean) RF

$$\overline{RF} = \frac{\sum_{i=1}^{N} RF_i}{N}$$

where:

RF_i are the individual RFs from each concentration level in the initial calibration curve.
N is the number of calibration concentration levels.

13.10.12 Equation Number 12

Percent Recovery (%R)

$$\%R = \frac{C}{S} x100$$

where:

C = Concentration of the analyte recovered
S = Spiked amount

13.10.13 Equation Number 13

Relative Percent Difference (RPD)

$$\frac{|R_1 - R_2|}{\left(\frac{R_1 + R_2}{2}\right)} x100$$

where:

R_1 First measurement value
R_2 Second measurement value

13.11 Data Review

The analyst must review data on a real time basis for all calibration and QC data. Any samples, QC samples or batch QC found to be unacceptable will require to be handled according to the guidelines described in this procedure. Also, the results must not be reported until they are appropriately reviewed and approved according to this SOP. The QC data must be evaluated by analytical sequence following the data review checklist in

Attachment C. In order to access batch precision, the laboratory duplicate must be checked against the acceptance criteria detailed in this document for all reported samples. Since matrices differ, matrix spikes or matrix spike duplicates are not used to evaluate batch performance. They are utilized to access the ability of the method to produce acceptable results for particular sample matrices.

The data shall be reviewed and the sample results calculated and assessed by one analyst and reviewed by a second qualified analyst. The data review checklist must be used to document the reviews and once it has been completed, initialed and dated it is to be filed with each job file. In addition, the data review process shall be conducted in accordance with both the *SOP for Data Review and Reporting* and the *SOP for Laboratory Ethics and Data Integrity*.

Initial calibrations must be reviewed with all ICAL documentation retained in a separate file organized by instrument and date. Refer to the initial calibration checklist in Attachment B for the review guideline. The ICAL file must contain all the pertinent information stated in Section 11.4.3.

13.12 Reporting

The results of each test shall be reported clearly, unambiguously and objectively, and shall include all the information necessary for the interpretation of the test results and all information required by this SOP and the *SOP for Data Review and Reporting.*

If reporting carbon dioxide, and the pH reading indicated that the sample was acid preserved, the report shall include a qualifier (refer to Section 16.8.3).

If the laboratory recommended hold time of 14 days is exceeded for propane, propene, or carbon dioxide a notation in the case narrative is required (no data flags are required).

13.13 Sample Preparation and Analysis Observations / Case Narrative Summary Form

This form, which is included in the *SOP for Laboratory Storage, Analysis and Tracking*, must be generated when there are specific sample composition information or analysis issues and/or observations. In addition, during the analysis, specific identification information or problems, interferences, calibration issues, flags, and additional/expanded explanation of flags should be added to the form. This form may be modified as long as the sections and basic concepts are reserved.

This form is necessary as a means for documentation. This form, among other information, will be reviewed when compiling the final report and case narrative. All information regarding the job shall remain in the file, in order that sufficient documentation is available to recreate the job from sample receipt through analysis, data reduction, and reporting.

13.14 Sufficient raw data records must be retained of the analysis (field samples, calibration standards and batch QC), instrument calibrations and method detection limit studies. This includes analysis/calibration date, test method, instrument, sample identification, each analyte name, analyst's initials, concentration and response, and standards used for the analysis and calibrations as well as any manual integrations. All information entered and reported on the quantitation reports must be complete and accurate.

13.15 The essential information to be associated with analysis, such as computer data files, run logs, etc. shall include: Sample ID code, date and time of analysis, instrument operating conditions/parameters (or reference to such data), analysis type, all manual calculations including dilutions and manual integrations, analyst's initials, sample preparation, standard and reagent origin, receipt, preparation, and use; calibration criteria, frequency and acceptance criteria, data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions.

14) Method Performance

14.1 An on-going assessment of method performance is conducted in order to ensure that the laboratory is capable of reporting results which are acceptable for its intended use. Validation of the method is confirmed by the examination and provision of objective evidence that these requirements are met.

14.2 Method Detection Limit (MDL)

The procedure used to determine the method detection limits are as stated in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as defined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.* The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero or blank concentration. MDLs can be obtained using standards at a concentration of about 0.3ug/L to 0.9ug/L and making at least seven replicate measurements of the compounds of interest, computing the standard deviation, and multiplying this value by the appropriate Student’s t value for 99 percent confidence.

The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. Refer to Section 11.16.1 for the LOD verification criteria.

14.3 Accuracy and Precision

Refer to Section 12.11 for information on replicate precision criteria for method performance. Single laboratory accuracy is presented as the second source initial calibration verification standard, which meets the method performance criteria of 15%. Additionally, laboratory generated control limit data for LCSs are presented for the analytes of interest and may be referenced in Attachment D. Refer to Section 11.6 for the accuracy and precision LOQ requirements.

14.4 Demonstration of Capability

This laboratory has continuously performed this method since before July 1999. Ongoing demonstration of capability shall be performed and documented; however, the initial demonstration of method capability is not required.

14.5 Proficiency Testing (PT) Program

Proficiency testing samples are not available from a third party for this method. Repeatability studies will be performed biannually to meet the DoD QSM proficiency testing requirements. A minimum of eight QC analyses performed over multiple days or on the same day will be compiled. Statistical validity will be assessed by evaluating results against LCS control limits and an RSD of 15%.

15) Pollution Prevention and Waste Management

15.1 The following wastes are generated during the analysis of groundwater samples by RSK 175 method: liquid samples (neutral or pH 2), displaced sample volume (8 mL), intermediate gaseous standards and purchased intermediate and stock gaseous standards. All of the waste shall be disposed of in accordance with the *Simi Valley Lab Waste Management Plan.*

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 All results that are out of control must be qualified on the corresponding final reports. It is important to provide the client with all of the appropriate information regarding the sample analysis, QC and batch QC.

16.2 Initial Calibration/Initial Calibration Verification

No data shall be reported which are associated with an out of control ICAL or ICV.

16.3 Continuing Calibration Verification

Refer to Section 12.5.2 for sample reporting criteria associated with an unacceptable CCV value.

16.4 Reagent Blank

No samples may be analyzed or data reported which are associated with an out of control RB/system.

16.5 Laboratory Control Sample/Laboratory Control Sample Duplicate

All samples processed with an out of control LCS will require to be re-prepared/analyzed if sufficient backup samples are available or have data qualifiers attached to the analytical results.

16.6 Matrix Spike/Matrix Spike Duplicate

If the client requests the MS or MS/MSD results, they must either have a data qualifier or a discussion in the case narrative.

16.7 Method Control Sample

Results for carbon dioxide are not considered a contamination and shall be reported to the client. However, all other sample results associated with a “contaminated” method control sample must be “flagged” in the report and/or discussed in the case narrative.

16.8 Field Samples

When sample quality control results are out-of-control: examine the sample results for matrix interferences and for carry-over. Re-analyze the samples and/or re-analyze the sample(s) at a lower aliquot. If the out-of-control results are due to matrix interferences, report the results with a matrix interference qualifier.

16.8.1 Sample Preparation and Analysis Holding Times

A statement dictating all holding time occurrences (most specifically, the same day requirement between preparation and analysis) must accompany the sample results in the final report. However, if all samples including QC samples are prepared and analyzed together, the LCS/LCSD results may be evaluated in order to determine the estimated loss of sample integrity, especially if this time limit has been exceeded. If the results for the LCS/LCSD do not meet the acceptance criteria all results shall be flagged, noted as being estimated and the reason included in the case narrative.

16.8.2 ICAL Dynamic Range

Results not bracketed by initial instrument calibration standards (within calibration range) must be reported as having less certainty, e.g., defined qualifiers or flags or explained in the case narrative.

16.8.3 pH for Carbon Dioxide

If the pH reading indicated that the sample was preserved and CO_2 is to be reported the result must be reported as estimated.

16.8.4 Thermal Preservation

A comment must be included in the case narrative or a reference to the Sample Acceptance Check form for samples that are received outside of the required temperature.

16.9 Laboratory Duplicate

The appropriate data qualifier or a discussion in the case narrative must be included with an out of control LD result. The LD may be accessed with the LCS/LCSD and reported accordingly.

17) Training

17.1 Demonstration of Capability

Training demonstrations shall be conducted in accordance with the *SOP for Training Policy,* DoD QSM, and TNI requirements. An initial demonstration of proficiency must be performed prior to independent analyses of samples. In addition, ongoing demonstration must be performed annually.

Once performance is found to be acceptable, a required certification statement must be completed by the QA Manager and either the immediate supervisor or Laboratory Director and retained on file as a demonstration of compliance.

17.1.1 Quarterly Demonstration A demonstration of method sensitivity must be performed *quarterly on each instrument* performing this method.

1) A spike at the current LOD must be analyzed.
2) Verification of precision and bias at the LOQ must be performed.

Refer to Section 11.6 (LOQ) and 11.16.1 (LOD) for additional information on how these demonstrations are to be performed as well as the acceptance criteria.

17.1.2 Annual Demonstration Each analyst must perform this demonstration both initially and annually. Analyze four LCS standards at 1-4x the MRL (LOQ) either concurrently or over a period of days as a verification of precision and bias of the quantitation range. The standard deviation (n-1) and average percent recovery of the four replicates are compared against current laboratory control limits for precision and bias. See Attachment E.

17.1.3 Change in Personnel, Instruments, Method and/or Matrix The requirements in Sections 17.1.1 and 17.1.2 must be performed per the schedule noted and when there is a change in personnel, instruments, method or matrix. “Change” refers to any change in personnel, instrument, test method, or sample matrix that potentially affects the precision and bias, sensitivity, or selectivity of the output (e.g., a change in the detector, column type, matrix, or other components of the sample analytical system, or a method revision).

All attempts at this demonstration must be completed and turned into the QA department for retention.

18) Summary of Changes

Table 18.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
17.0	02/02/2019	C. Arend	Applied updated SOP formatting style to first two pages and header/footer. Sections renamed and reorganized to align with *SOP for Preparing Standard Operating Procedures.* Section references updated throughout.
			6.1 – updated reference
			9.4.1.1 – removed “Summa”
			9.7.3 – removed “Summa”

			11.1.2 – Revised to state MS, DMS, LD and Dilutions are not considered separate samples. Edited Analytical Sequence Guidelines to reflect change. Revised footnote 7 to clarify 10 sample injections
			11.4 – 2nd sentence – revised to add clarification; removed last sentence with annual ICAL requirement
			11.4.1 - #1 – removed annual ICAL requirement; #2 last sentence – added reference to DoD QSM Requirement; (i) and (k) last bullet – updated ICAL requirements to align with 2016 TNI Standard
			11.7 – 3rd sentence – changed “ten samples” to “ten sample injections”
			12.3 – removed annual ICAL requirement
			12.7.1 – changed “DoD QSM 5.0” to “DoD QSM”
			12.8.1 – changed “DoD QSM 5.0” to “DoD QSM”
			Information previously in section 13 removed – redundant to information covered in section 12.
			14.2 – 2nd sentence – added “or blank concentration”
			15.1 – updated reference
			Information previously in section 17 removed – redundant to information covered in administrative SOPs.
			19 – removed references to internal SOPs
			19.6 – updated reference
			19.7 – added reference
			Attachment 3 - #6 and #7 – changed “DoD QSM 5.0” to “DoD QSM”
			Attachment 4 – changed “DoD QSM 5.0” to “DoD QSM” throughout; updated MDLs/LODs/LOQs and Laboratory Control Limits

19) References and Related Documents

19.1 D. H. Kampbell, J. T. Wilson and S. A. Vandegrift, *Dissolved Oxygen and Methane in Water by GC Headspace Equilibration Technique*, Intern. J. Environ. Anal. Chem., Vol. 36, pp. 249-257, Gordon and Breach, Science Publishers. Inc., 1989.

19.2 *CRC Handbook of Chemistry and Physics*, 66th edition.

19.3 *Hawley’s Condensed Chemical Dictionary*, 11th edition.

19.4 *Wastewater Engineering*, Metcalf and Eddy, Inc. McGraw-Hill, 1972.

19.5 Perry, J. H., *Chemical Engineer’s Handbook*, McGraw-Hill, New York, 1978, 5th ed.

19.6 *Department of Defense (DoD) Quality Systems Manual (QSM) for Environmental Laboratories*, Version 5.1, January 2017; Version 5.1.1, February 2018; Version 5.2, December 2018.

19.7 TNI Standard Volume 1, 2009 and 2016

20) Attachments

20.1 Attachments

Attachment 1 – Training Plan

Attachment 2 – Initial Calibration Checklist

Attachment 3 – Data Review Checklist

Attachment 4 – MDLs, LODs, MRLs, and Control Limits

Attachment 1

Training Plan

Training Plan for Analysis of Dissolved Gases by GC/FID/TCD

Trainee ________________________ Trainer ______________________ Instrument _________

1. Read SOP Trainer ____ Trainee ____ Date _________
2. Read Article: "Dissolved Oxygen and Methane in Water by GC Headspace Equilibration Technique" Trainer ____ Trainee ____ Date _________
3. Demonstrated understanding of the scientific basis of analysis Trainer ____ Trainee ____ Date _________

   Gas chromatography   Thermal Conductivity Detector
   Henry's Constant   Flame Ionization Detector

4. Demonstrated familiarity with related SOPs Trainer ____ Trainee ____ Date _________

   SOP for Batches and Sequences
   SOP for Making Entries onto Analytical Records
   SOP for Manual Integration Policy
   SOP for Significant Figures
   SOP for Nonconformance and Corrective Action
   SOP for Performing MDL Studies and Establishing Limits of Detection and Quantitation

5. Observe performance of SOP Trainer ____ Trainee ____ Date _________

   ___standard preparation
   ___sample preparation
   ___analytical sequence setup
   ___initial calibration and initial calibration verification
   ___continuing calibration verification
   ___batch QC sample setup
   ___sample analysis
   ___EnviroQuant introduction
   ___data reduction and reporting

6. Perform SOP with supervision Trainer ____ Trainee ____ Date _________

   ___standard preparation
   ___sample preparation
   ___analytical sequence setup
   ___initial calibration and initial calibration verification
   ___continuing calibration verification
   ___batch QC sample setup
   ___sample analysis
   ___EnviroQuant use
   ___data reduction and reporting

7. Independent performance of the SOP Trainer ____ Trainee ____ Date _________

   ___standard preparation
   ___sample preparation and sample analysis
   ___analytical sequence setup including batch QA sample preparation
   ___initial calibration, initial calibration verification, and continuing calibration verification
   ___EnviroQuant proficiency
   ___data reduction and reporting
   ___initial demonstration of competency
      ___ Four consecutive laboratory control samples

8. Instrument operation and maintenance Trainer ____ Trainee ____ Date _________

   ___gas chromatograph and capillary column installation
   ___detector (FID) setup and maintenance
   ___detector (TCD) setup and maintenance ____data system

Attachment 2

Initial Calibration Checklist

Initial Calibration Checklist (Dissolved Gases in Water by RSK-175)

Analysis: RSK-175

ICAL Date ____________________ Instrument ☐ GC10 ☐ GC _____

Analyst **Reviewer**

☐ 1. Is the required documentation in the ICAL file? ☐
  ☐ Sequence report
  ☐ Blank analysis Quantitation Report
  ☐ Calibration Status Report (aka Calibration History) – Initial
  ☐ Response Factor Report
  ☐ Quantitation Report for each calibration standard (including manual integration documentation – before and after printouts)
  ☐ ICV Quantitation Report and Evaluate Continuing Calibration Report (aka % Diff. report)

☐ 2. ICAL performed continuously (i.e., not interrupted for maintenance or sample analysis)? ☐

☐ 3. Was the ICAL, including any re-analysis, performed within a 48 hour period? ☐

☐ 4. Were the standards analyzed from low concentration to high concentration? ☐

☐ 5. For each analyte, is the lowest standard's concentration at or below the MRL? ☐

☐ 6. Does each analyte's ICAL include a minimum of 5 consecutive concentrations? ☐

☐ 7. For each analyte, is there only one value used for each calibration level? ☐

☐ 8. If a point is dropped, is information noted in the ICAL explaining the reason? ☐

☐ 9. If a point was dropped from the interior was there a proper assignable cause? ☐

☐ 10. For each analyte, are there no levels skipped? ☐

☐ 11. Are all peak integrations including manual integrations (per *SOP for Manual Integration Policy*) acceptable? *If so, initial and date the appropriate pages.* ☐

Quality Control

☐ 12. The %RSD for each analyte is ≤20%? ☐

☐ 13. For the ICV analysis, is the percent recovery for each analyte 85-115%? ☐

☐ 14. The RT for each target compound at each level within the generated retention time window (using the midpoint as the absolute RT) and within 0.1min of the mean RT? ☐

☐ 15. All analytes in the MB are ≤MRL (as long as low standard from the ICAL is ≤MRL)? ☐

COMMENTS:

____

____

____

____

Analyst ______________________ Secondary Reviewer ______________________

Date ______________________ Date ______________________

Attachment 3

Data Review Checklist

Dissolved Gases in Water by RSK-175
Data Review Checklist

(Note exceptions and include Sample Preparation and Analysis Observations / Case Narrative Summary Form as appropriate)

Analysis Date ____________ Instrument ☐ GC10 ☐ GC ___ Analyst ____________
QC Level ____________ Project # ____________ Due Date ____________

Analyst **Reviewer**

Initial Calibration

☐ 1. Is the referenced ICAL the most recent ICAL performed? .... NA

Continuing Calibration

☐ 2. Does each CCV in the sequence have a %difference of ≤15%? .... ☐
☐ 3. RT for each analyte for each CCV fall within 0.33min of the mean RT from the ICAL? .... ☐

Batch QC

☐ 4. Is the laboratory duplicate within 15% of their average (for all hits 10x the RL)? .... ☐
☐ 5. LCS/LCSD RPD within lab generated limits (where available), RPD±15% others (CO2 30%)? .... ☐
☐ 6. LCS/LCSD recovery within lab generated limits (where available), 70-130% others (CO2 50-150%)? .... ☐
DoD: Must meet DoD QSM LCS/DLCS limits
☐ 7. Is the MS/MSD (RPD) within ±30%?; Is the recovery within 50-150%? .... ☐
DoD: MS/MSD must meet DoD QSM LCS/DLCS limits
☐ 8. Are all the analytes in the Method Control Sample (MCS) < the MDL? .... ☐

Sample Data

☐ 9. All target analyte responses are within calibration range? .... ☐
☐ 10. Are peak integration are acceptable? .... ☐
☐ 11. All manual integrations flagged and documented (before and after)? If so, initial and date. .... ☐
☐ 12. All analyte peaks are within corresponding RT window using the CCV as the absolute RT? .... ☐
☐ 13. All analyte peaks within 0.33min of the mean RT from the ICAL? .... ☐
☐ 14. All calculations correct? .... ☐
☐ 15. First quantitation report initialed and dated by analyst? .... ☐
☐ 16. **DOD:** Are manual integrations notated in the case narrative? .... ☐

Documents Included

☐ 17. Injection Log (optional) .... ☐
☐ 18. Sample raw data .... ☐
☐ 19. CCV Analysis Quantitation Report and Evaluate Continuing Calibration Report (%D report) .... ☐
☐ 20. LCS/LCSD Analysis Quantitation Report .... ☐
☐ 21. MCS Analysis Quantitation Report .... ☐
☐ 22. MS/MSD Analysis Quantitation Report, if applicable .... ☐
☐ 23. Laboratory Duplicate Analysis Quantitation Report, if applicable .... ☐
☐ 24. Quantitation Report for each sample (including manual integration documentation) .... ☐

COMMENTS:

____

____

☐ LIMS Run Approval ☐ LIMS Supervisor Approval
Analyst ____________ Secondary Reviewer ____________
Date ____________ Date ____________

Attachment 4

Method Detection Limits, Limits of Detection, Method Reporting Limits, and Control Limits

Method Detection Limits, Limits of Detection, and Method Reporting Limits

Analyte	MDL	LOD	MRL	Units	Comments
Methane	0.51	1.0	1.3	ug/L	DoD Certified
Ethylene (Ethene)	0.24	0.55	1.0	ug/L	DoD Certified
Ethane	0.16	0.47	0.60	ug/L	DoD Certified
Propane	0.26	-	1.0	ug/L	
Propylene	0.45	-	1.0	ug/L	
Carbon dioxide	370	860	1000	ug/L	DoD Certified

[1] 0.30ug/L is the lowest reportable method detection limit for methane this laboratory will use. Refer to Section 5.5 “Methane Interference”.

The method detection and reporting limits may change with each new MDL study and ICAL performed, check the current documentation for verification.

Laboratory Control Sample / Laboratory Control Sample Duplicate / Relative Percent Difference

Analyte	LCS - LCL (%R)	LCS - UCL (%R)	LD (RPD)
Methane	65	129	26
Ethylene (Ethene)	80	122	11
Ethane	78	119	10
Propane	73	112	10
Propylene	97	151	11
Carbon dioxide	56	105	12

Note 1: These limits are calculated annually and may change when new limits are determined. Therefore, refer to current documentation for verification. DoD Requirement: LCS/DLCS must meet DoD QSM LCS/DLCS limits.

Note 2: All Matrix Spikes and Matrix Spike Duplicates will be fixed at 50-150 with an RPD of 30. DoD Requirement: MS/MSD must meet DoD QSM LCS/DLCS limits.

DoD QSM Requirements

Analyte	LCS - LCL (%R)	LCS - UCL (%R)	MS – LCL (%R)	MS – UCL (%R)
Methane	73	125	73	125
Ethylene (Ethene)	72	133	72	133
Ethane	74	131	74	131
Carbon dioxide	80	122	80	122

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP)

DOCUMENT I.D. MET-ICP

Approved By: ______________________ Date: 11/19/18
Technical Director, Jeff Coronado

Prepared By: ______________________ Date: 11/19/18
Quality Assurance Manager, Carl Degner

Prepared By: ______________________ Date: 11/21/18
General Manager, Ambrose Hughey

Doc Control ID:	________________	Archived Date:	________________

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DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP)

1) Scope & Applicability

1.1 This procedure describes the steps taken for the analysis of soil, sludge surface water and drinking water digestates using EPA methods 6010D and 200.7 for a variety of elements. The digested samples and QC standards are all diluted in a similar acid matrix. A procedure is also given for calculation of hardness by Standard Methods 2340B.

1.2 The Method Reporting Limits (MRLs) for common elements are listed in the lab Data Quality Objective (DQO) tables. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL). Therefore, MRL=EQL. The reported MRL may be adjusted if required for specific project requirements, however, the capability of achieving other reported MRLs must be demonstrated. The Method Detection Limits (MDLs) that have been achieved are listed in the DQO tables. The MDL and MRL may change as annual studies are performed.

1.3 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP or project which require older versions of EPA methods (i.e. 6010B/6010C). QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD5) may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 A representative aliquot of sample is prepared as described in the applicable digestion SOP. The digestate is analyzed for the elements of interest using ICP spectrometry. The instrument measures characteristic emission spectra by optical spectrometry. The intensity of emission lines are monitored.

2.2 Final results are calculated using the digestion information and the results from the ICP analysis. Data is reported using standard ALS procedures and formats, or following project specific reporting specifications.

2.3 Deviations from the reference method(s): This SOP contains no deviations from the reference methods.

3) Definitions

3.1 Batch - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1 Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2 Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Sample

3.2.1 Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2 Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3 Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1 Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2 Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3 Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4 Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5 Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6 Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7 Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.3.1 through 3.3.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8 Miscellaneous matrices – Samples of any composition not listed in 3.3.1 – 3.3.7. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid-point of the calibration range or at levels specified by a project analysis plan.

3.5 Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7 Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8 Independent Verification Standard (ICV) - A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.9 Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. The CCV is used to verify that the initial calibration curve is still valid for quantitative purposes.

3.10 Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.11 Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4) Interferences

4.1 Interferences from contaminated reagents must be eliminated. The purity of acids must be established by the laboratory as being high enough to eliminate the introduction of contamination above the MRL (or above ½ the RL for DoD work).

4.2 Background emission and stray light can be compensated by background correction.

4.3 Spectral overlaps resulting in interelement contributions can be corrected for by using interelement correction factors. Interelement correction factors are established for each instrument and are maintained by the analyst at the workstation.

5) Safety

5.1 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Chemical Hygiene Plan and the appropriate SDS prior to beginning this method.

5.2 Hydrochloric, Nitric and Hydrofluoric Acids are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. Safety glasses, lab coat and gloves should be worn while working with the solutions.

5.3 High Voltage - The power unit supplies high voltage to the RF generator which is used to form the plasma. The unit should never be opened. Exposure to high voltage can cause injury or death.

5.4 UV Light -The plasma when lit is a very intense light, and must not be viewed with the naked eye. Protective lenses are in place on the instrument. Glasses with special protective lenses are available.

6) Sample Collection, Containers, Preservation, and Storage

6.1 Samples are prepared via procedures in SOPs MET-DIG, MET-3010A, MET-3050, MET-3051M, MET-3052M, or MET-TDIG. Samples are received in the ICP lab as completed digestates. Samples are stored in 16 mL plastic test tubes, 50 mL plastic centrifuge tubes, 100 mL digestion vessels or in 100 mL volumetric flasks.

6.2 Water samples analyzed by EPA method 200.7 are preserved after arrival at the laboratory. These samples are held for a minimum of 24 hours and the pH verified to be <2 prior to digestion.

6.3 Soil samples are diluted prior to instrumental analysis by a factor of 2. This allows the method to meet the required 1 g of sample to 200 mL dilution during digestion.

6.4 Following analysis, digestates are stored until two weeks after all results have been reviewed and then brought to 6< pH <9 and disposed of through the sewer system. The neutralization step is considered hazardous waste treatment and must be documented. See the ALS Lab Waste Management Plan for details.

7) Standards, Reagents, and Consumable Materials

7.1 Standards Preparation

7.1.1 Stock standard solutions may be purchased from a number of vendors. All reference standards, where possible, must be traceable to SI units or NIST certified reference materials. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking* (ADM-RTL) for the complete procedure and documentation requirements. Manufacturer's expiration dates are used to determine the viability of standards.

7.1.2 Calibration standards are prepared from commercially purchased single element 1000 ppm or 10,000 ppm stock standards as well as pre-mixed multi element stock standards. All standards are aliquoted using Class A volumetric pipettes, or calibrated fixed and adjustable volume auto-pipettors. All dilutions are made in Class A volumetric glassware.

The standard mixes for each ICP system vary based on the requirements of each instrument. The composition of the ICAP 6500 standards are outlined in Table 2.

7.1.3 Continuing Calibration Verification (CCV) Standards

CCV standards are analyzed at the midpoint of the calibration. These standards are produced by making a two-fold dilution of each calibration standard. The CCV standards are then run in sequence during the analytical run.

7.1.4 Initial Calibration Verification (ICV) Standards

The ICV working standards are produced by direct dilution of two certified mixed stock solutions (QCP-CICV1 and QCP-CICV3 purchased from Inorganic Ventures or another qualified vendor and various single element stock solutions from sources different than the calibration standards. The composition of these standards is outlined in Table 3.

7.1.5 Interference Check Solutions (ICSA & ICSAB)

The ICSA and ICSAB working standards are produced by direct dilution of certified mixed stock solutions (CLPP-ICS-A and CLPP-ICS-B or equivalent.) Antimony is also added to the ICSAB solution from a 1000 ppm single element stock standard. The composition of these standards is outlined in Table 4.

7.1.6 Low Level Calibration Verification

The CRI, Low Level Continuing Calibration Verification (LLCCV), and Low Level Continuing Calibration Verification (LLCCV) are produced by diluting 1000 or 10000ppm single stock standards into a 100X intermediate standard and then diluted 1/100 to obtain the MRL level. Note: The level used is that of the normal MRL used for both instruments.

7.1.7 The solutions and materials used for the LCS and matrix spikes are described in the applicable digestion SOP.

7.1.8 Standard Log

The analyte, source, initial volume, final volume, final concentration and expiration date are recorded in a standard logbook kept in the ICP lab. The operator who prepares the standard must date and initial the entry in the standards logbook. The operator also places his initials and the date prepared on the standard container. In addition to working standards used in calibration, all other standards used in the analytical run such as ICVs, MRL standards, and other project or client specific standards shall be documented in the standard logbook.

7.2 High Purity Argon.

7.3 Capillary, rinse and peristaltic pump tubing.

7.4 17 x 100 mm polypropylene test tubes.

8) Apparatus and Equipment

8.1 Inductively Coupled Plasma Atomic Emission Spectrometer

8.1.1 Thermo Scientific ICAP 6500 (AES-03).
8.1.2 Thermo Scientific ICAP 6500 (AES-04).

8.2 Concentric nebulizers.

8.3 Microflow nebulizer for ICAP 6500.

8.4 Torches and injector tips for each ICP.

8.5 Cyclonic spray chambers for each instrument.

8.6 Water coolers for each ICP.

8.7 ESI SC4 DX Autosampler with Fast System for ICAP 6500.

8.8 Peristaltic Pumps for each Spectrometer.

8.9 RF Generators for each ICP (internal on the ICAP 6500).

9) Preventative Maintenance

9.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

9.2 Torch, nebulizer, and spray chambers are cleaned as required. All instrument filters are vacuumed monthly. Dirty ICP torches and mixing chambers are soaked in aqua regia overnight, rinsed and placed in a clean dry area. Dirty nebulizers are soaked in dilute HF. If still problematic the unit is returned to the manufacturer for repair.

10) Responsibilities

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2 It is the responsibility of the department supervisor/manager to document analyst training. Training and proficiency is documented in accordance with the *ALS Kelso – Training Procedure* (ADM-TRAIN).

11) Procedure

11.1 Operating Parameters

11.1.1 For each Thermo Scientific ICAP 6500, the operating parameters are defined in the Method file. Default operating parameters are given in Tools/Options/New Method Parameters. However, each unique set of operating parameters is saved as a new file and the analyst must select and use the correct Method file for the application. Refer to the method files on the workstation for a listing of parameters for each file. The interelement correction factors to be used are established for the ICAP 6500 and are saved on the workstation also. Since these parameters change with method and correction factor updates, and due to the large amount of hardcopy printout for listing these parameters, it is not practical to include the parameters in this SOP.

11.2 Calibration/Standardization

11.2.1 ICAP 6500

11.2.1.1 Plasma is ignited and instrument is allowed to warm up for at least 30 minutes.

11.2.1.2 An internal standard is used for routine analyses on this instrument. Yttrium and Indium are used as internal standards. The internal standard solution is introduced into the analyzed solutions (standards, blanks, QC, samples, etc.) at 4.0 µg/mL for Y, and 8.0 µg/mL for In.

11.2.1.3 Run a peak check standard and adjust peaks as needed.

11.2.1.4 Standardize by running a Blank and a High Standard for each element in the analytical method. Analyst will initial and date the first page of the standardization.

11.3 Analytical Run

11.3.1 Following standardization, the remainder of the run is determined by what analytical method is being performed; 200.7 or 6010D.

11.3.1.1 For 200.7 the sequence is:

- CCVB (aka. IPC): RSD of 4 replicates must be <3% and recovery must be within ± 5%.
- CCVA (aka IPC): RSD of 4 replicates must be <3% and recovery must be within ± 5%.
- ICB: Result should be < ½ MRL.
- ICVB (aka QCS): Recovery must be within ± 5%.
- ICV (aka QCS): Recovery must be within ± 5%.
- CCB: Result should be less than 3 times the standard deviation of the mean background signal.
- LLICV: Spiked at MRL level with the result > MDL and <2x the MRL.
- ICSA: To check validity of Interelement Correction Factors (IECs).
- ICSAB: Recovery must be within ± 20% for the CLPP-ICS-B elements and Sb.
- 10 samples
- CCV: Recovery must be within ± 10%.
- CCB: Result should be less than 3 times the standard deviation of the mean background signal.
- Repeat CCV/CCB standards every 10 samples as needed.

11.3.1.2 For 6010D the sequence is:

- ICVB: Recovery must be within ± 10%.
- ICV: Recovery must be within ± 10%.
- ICB: Result should be < ½ LLOQ.
- CCVB: Recovery must be within ± 10%.
- CCVA: Recovery must be within ± 10%.
- CCB: Result should be < MRL.
- LLICV: Spiked at MRL level with recovery within ± 20%.
- ICSA: To check validity of Interelement Correction Factors (IECs).
- ICSAB: Recovery must be within ± 20% for the CLPP-ICS-B elements and Sb.
- 10 samples
- CCV: Recovery must be within ± 10%.
- CCB: Result should be less than 3 times the standard deviation of the mean background signal.
- Repeat CCV/CCB standards every 10 samples as needed.

11.3.2 Evaluate the initial QC using the following criteria:

11.3.2.1 For methods 200.7 and 6010D, the following criteria apply:

- The ICB and CCB results are evaluated using method specified requirements. The following guidelines should also be used to determine acceptability:

- For 200.7, the result should be less than 3 times the standard deviation of the mean background signal.

- For method 6010D, the result should be less than 1/2 the Lower Limit of Quantitation (LOQ).

- The CCV immediately following standardization must verify within ± 10% of the true values. For 200.7, the first CCV must verify within ± 5% with a RSD of <3% from 4 replicates. Calculate %RSD as follows:

$$\%RSD = \frac{StdDev_{CCV}}{Average_{CCV}} x\,100$$

Where:

StdDevccv = Standard deviation of the replicate integrations

Averageccv = Average of the replicate CCV integrations

- The LLICV or CRI is a low level standard with concentrations at the RL. For DoD projects, the LLICV standard concentrations will be equal to the project RLs. For method 6010D the CRI results should be within 20% of the true value. For 200.7 LLICV/CRI results should be greater than the MDL and less than 2X the MRL.

- The ICSA is run to check the validity of the Interelement Correction Factors (IECs).

Note: DoD QSM requires this to be run at the beginning of each analytical run.

- The ICSAB must be within 20% of the expected value for the CLPP-ICS-B elements and Sb.

11.3.2.2 The ICV, LLICV, ICB, CCV, CCB, CRI, and ICSAB must meet the criteria listed. Reanalyze any elements that fail.

11.3.3 Continuing Calibration Verification

11.3.3.1 CCVs are analyzed after every 10 samples and at the end of the analytical run. They must verify within ±10% of the expected value with a RSD of <10%.

11.3.3.2 CCBs are analyzed after every 10 samples and at the end of the analytical run. CCBs are evaluated as in section 11.3.2.1.

11.3.4 If the CCV or CCB solutions fail, reanalyze any elements to be reported.

12) Quality Assurance/Quality Control Requirements

12.1 Initial Precision and Recovery Validation

12.1.1 The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four LCS aliquots are prepared and analyzed. The average percent recovery for each analyte must meet LCS criteria and the RSD< 30%.

12.2 Method Detection Limits

12.2.1 A Method Detection Limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates at a level near or below the MRL. Follow the procedures in Section 11 to analyze the samples. Refer to the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (ADM-MDL).

12.2.2 Calculate the average concentration found (x) and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. MDLs must be performed whenever there is a significant change in the background or instrument response.

12.2.3 A Limit of Detection (LOD) check must be performed after establishing the MDL and at least annually (quarterly if DoD) afterward. A blank is spiked with analytes at 2-4X the MDL and carried through the preparation and analytical procedure. The LOD is verified when the signal/noise ratio is > 3 for all analytes.

12.3 Limit of Quantitation Check (LOQ)/Lower Limit of Quantitation Check (LLQC)

12.3.1 For Method 6010D and drinking waters by method 200.7 a Lower Limit of Quantitation Check (LOQ/LLOQ) sample must be analyzed after establishing the MRL and at least annually (quarterly if DoD) afterward to demonstrate the desired detection capability. The LOQ/LLOQ sample is spiked at 1-2X the MRL and must be carried through the entire preparation and analytical procedure. Limits of quantitation are verified when all analytes are detected within 30% of their true value.

12.4 Linear Dynamic Range

12.4.1 The upper limit of the LDR must be established for each wavelength utilized. It must be determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR should be determined by analyzing at least three succeeding higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% above or below the stated concentration of the standard. Determined LDRs must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and re-analyzed. The LDRs are verified every six months or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be re-determined.

Method 6010D requires that the linear range for each wavelength be verified on a daily basis. The linear range verification standard must recover within 10% of the true value and can be analyzed anywhere within a particular run. If a linear range verification is not analyzed for a specific element, the highest calibration standard becomes the linear range. All reported sample measurements must fall within the linear range.

12.5 Instrument Detection Limit

12.5.1 The IDLs should be determined annually or after major instrument maintenance. The IDL is determined as the mean of the blank results plus 3 times the standard deviation of 10 replicate analyses of the reagent blank solution.

12.6 Interelement Correction Factors

12.6.1 Spectral Interference Checks (SIC) are performed when an instrument is initially set up, the every six months. During the course of routine work, other interferences may be found. They are verified by the operator during the analytical run and data is manually corrected. Copies of this data are kept on file. Data can be manually corrected or automatically corrected using iTEVA software.

12.7 Internal Standard

12.7.1 Internal standard values are tracked by the instrument software. Values should remain within 60-125% of the value found in the calibration blank. If a sample is found to have and internal standard outside this value, the sample will be diluted to bring the internal standard into range.

12.8 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches* (ADM-BATCH). Additional QC Samples may be required in project specific quality assurance plans (QAPP). For example projects managed under the DoD ELAP must follow requirements defined in the DoD *Quality Systems Manual for Environmental Laboratories.* General QA requirements for DoD QSM are defined in the laboratory SOP, Department *of Defense Projects – Laboratory Practices and Project Management* (ADM-DOD5). General QC Samples are:

12.8.1 Each sample preparation batch must have a method blank associated with it. The method blank result should be < MRL. If the method blank is found to be contaminated, it may be reported if the concentration in the associated samples is at least 20 times the amount found in the method blank for methods 200.7, otherwise re-digest the batch. For Method 6010D, the method blank may be reported if the concentration in the associated samples is at least 10 times the amount found in the method blank. A contaminated method blank (MB) may also be reported if all of the associated samples are non-detect (ND).

Note: DoD QSM requires contamination in the MB be <1/2 the RL or < 1/10 any sample amount.

12.8.2 A Laboratory Control Sample (LCS) is digested one per batch, or per 20 samples. For soil samples, the recovery must fall within the ranges specified for the reference material. For "blank spike" Laboratory Control Samples recoveries must fall within ± 15% of the true value for 200.7 and ±20% of the true value for 6010D. For specifics on the preparation and composition of LCS samples refer to the appropriate digestion SOP.

12.8.3 A Duplicate sample is digested one per batch, or per 20 samples (i.e. 5%) for 6010D analysis, or per 10 samples (i.e. 10%) for 200.7 analyses. If the RPD is outside acceptance limits, either re-digest the sample batch or flag the data appropriately, depending on the physical nature of the samples (e.g. non-homogenous).

12.8.4 A Laboratory fortified Blank (LFB) at the MRL is digested and analyzed with every batch of drinking water samples (method 200.7). The default acceptance criteria of 50-150% are to be used until sufficient data points are acquired to calculate in-house control limits.

12.8.5 A Matrix Spike sample is digested one per batch, or per 20 samples (i.e. 5%) for 6010D analysis, or per 10 samples (i.e. 10%) for 200.7 analyses. Where specified by project requirements, a matrix spike duplicate may be required. If the recovery is outside acceptance limits, either re-digest the sample batch or flag the data appropriately, depending on the physical nature of the samples (e.g. non-homogenous). If the sample concentration is >4x the spike level, no action is required and data is flagged accordingly. For specifics on the preparation and composition of matrix spike solutions refer to the appropriate digestion SOP.

12.8.6 Acceptance criteria

12.8.6.1 Current ALS control limits and acceptance criteria for ongoing QC analyses are listed in the current ALS-Kelso DQO tables. Criteria are subject to change as statistical data are generated. The default method criteria may be used if statistically generated criteria are broader or insufficient points are available for accurate statistical limits.

12.8.6.2 For all QC analyses, project-specific or program-specific (e.g. DoD) acceptance criteria may supersede ALS criteria.

12.8.7 Matrix Interference

12.8.7.1 When an analyst suspects that there may be any matrix interferences present, a post digestion spike may be performed. The recovery should be ± 20% for method 200.7 and ±25% for 6010D.

12.8.7.2 If the post spike fails, a 1:5 serial dilution test shall be performed. The dilution should be within ± 10% of the original result for 200.7 and ±20% for method 6010D.

12.8.7.3 A 1:5 serial dilution shall be performed for all Tier III or IV deliverables.

12.8.7.4 Post spikes for 6010D shall be performed for Tier III and Tier 1V.

12.9 Additional QC measures include control charting and compiling of QC data for generation of control limits.

12.10 CLP analyses are performed as per the QA/QC guidelines in the most current CLP SOW.

13) Data Reduction and Reporting

13.1 Calculate sample results using the data system printouts and digestion information. The digestion and dilution information is entered into the data system. The data system then uses the calculations below to generate a sample result. The wavelengths used to quantify each metal are summarized in Table 5 for the IRIS and Table 6 for the ICAP6500.

Aqueous samples are reported in µg/L:

$$\mu g/L\ (Sample) = C^{*}\ x\ Digestion\ Dilution\ Factor\ x\ Post\ Digestion\ Dilution\ Factor \times 1000\,\mu g / mg$$

Solid samples are reported in mg/Kg:

$$mg/Kg\ (Sample) = C^{*}\ x\ Post\ Digestion\ Dilution\ Factor\ x\ \frac{Digestion\ Vol.(ml)}{Sample\ wt.(g)}\ x\ \frac{1mg}{1000ug}\ x\ \frac{1L}{1000ml}\ x\ \frac{1000g}{1Kg}$$

C*= Concentration of analyte as measured at the instrument in µg/L (in digestate).

13.2 If total hardness is to be reported, use Calcium and Magnesium results to calculate as follows. For reporting calcium hardness, use only the calcium portion of the equation.

$$Hardness, mg\ equivalent CaCO_3/L = 2.497[Ca, mg / L] + 4.118[Mg, mg / L]$$

13.3 A daily run log of all samples analyzed is maintained. All CLP data should be printed and stored after operator has checked for evenness of burns. A copy of this document will go with each package of Tier III or higher data run that day.

13.4 Data Review and Reporting

13.4.1 It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in section 12. The data is then placed in a work order file until complete. When the work order is complete, a report is generated. A final review is performed and the data is delivered to the project management department.

14) Method Performance

14.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional available method performance data.

14.2 The method detection limit (MDL) is established using the procedure described in the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (ADM-MDL). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

15) Pollution Prevention and Waste Management

15.1 It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

15.3 This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 5-9 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS Lab Waste Management Plan for details.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Refer to the SOP for *Nonconformance and Corrective Action Procedures* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

16.2 Handling out-of-control or unacceptable data

16.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

16.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations.
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.).
- Sample preservation or handling discrepancies due to laboratory or operations error.

17) Training

17.1 Refer to the SOP *ALS-Kelso Training Procedure* (ADM-TRAIN) for standard procedures.

17.2 Training outline

17.2.1 Review literature (see references section). Read and understand the SOP. Also review the applicable SDSs for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.2.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.2.3 Perform initial precision and recovery (IPR) study as described above for water or soil samples. Summaries of the IPRs are reviewed and signed by the supervisor. Copies may be forwarded to the employee’s training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC’s Initial Demonstration of Capability.

17.3 Training and proficiency is documented in accordance with the *ALS-Kelso Training Procedure* (ADM-TRAIN).

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 There are no known modifications in this laboratory standard operating procedure from the reference method.

19) Summary of Changes Since Last Revision

19.1 Updated to latest ALS format.
19.2 Separated criteria for 200.7 and 6010D.
19.3 Removed reference to CLP.
19.4 Updated to reference 6010D.
19.5 Updated SOP references as necessary.
19.6 Deleted Section 3.6 (old) surrogate definition.
19.7 Section 6.1 – Updated references for prep methods.
19.8 Section 11.2.1.2 – Updated IS concentrations.
19.9 Deleted sections 11.2.2 and 11.2.3.
19.10 Section 11.3.1.1 and 11.3.2.1 – Updated bullets for ICB.
19.11 Section 12.5 – changed to annually.

20) References and Related Documents

20.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Update V, Method 6010D, Revision 4, July 2014.

20.2 USEPA, Methods for Determination of Metals in Environmental Samples, Supplement I, EPA/600/R-94/111, Method 200.7, Revision 4.4, May 1994.

20.3 *Hardness by Calculation, Method 2340B,* Standard Methods for the Examination of Water and Wastewater, 20th ed., 1998.

21) Attachments/Appendices

21.1 Table 1 – Standard A for ICAP 6500 ICP-OES.

21.2 Table 2 – ICP ICV Standards.

21.3 Table 3 – ICP Interference Checks.

21.4 Table 4 – ICAP 6500 Analytical Wavelengths.

TABLE 1
Standard A for ICAP 6500 ICP-OES

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Antimony	(1)	100	5	1000	0.5
Beryllium	(1)	100	5	1000	0.5
Boron	(1)	100	5	1000	0.5
Cadmium	(1)	100	5	1000	0.5
Calcium	Ca stock	1000	0.5	1000	1.0*
Chromium	(1)	100	5	1000	0.5
Cobalt	(1)	100	5	1000	0.5
Copper	(1)	100	5	1000	0.5
Iron	(1)	100	5	1000	0.5
Lead	(1)	100	5	1000	0.5
Magnesium	(1)	100	5	1000	0.5
Manganese	(1)	100	5	1000	0.5
Molybdenum	(1)	100	5	1000	0.5
Nickel	(1)	100	5	1000	0.5
Selenium	(1)	100	5	1000	0.5
Silver	(1)	100	5	1000	0.5
Tin	Elemental Stock	1000	0.5	1000	0.5
Thallium	(1)	100	5	1000	0.5
Titanium	(1)	100	5	1000	0.5
Vanadium	(1)	100	5	1000	0.5
Zinc	(1)	100	5	1000	0.5
Hydrochloric Acid	-	-	50	1000	5%
Nitric Acid	-	-	10	1000	1%

(1) Mixed Standard, QCS-26
* 0.5mL 1000ppm Ca added to 5mL QCS-26(100ppm Ca), 1000mL Final Volume

TABLE 2
ICP ICV Standards

ICV1 Solution

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Aluminum	QCP-CICV-1	1000	2.5	500	5.0
Antimony	Elemental Stock	1000	1.25	500	2.5
Arsenic	QCP-CICV-3	500	2.5	500	2.5
Barium	QCP-CICV-1	1000	2.5	500	5.0
Beryllium	QCP-CICV-1	25	2.5	500	0.125
Cadmium	QCP-CICV-3	250	2.5	500	1.25
Calcium	QCP-CICV-1	2500	2.5	500	12.5
Chromium	QCP-CICV-1	100	2.5	500	0.5
Cobalt	QCP-CICV-1	250	2.5	500	1.25
Copper	QCP-CICV-1	125	2.5	500	0.625
Iron	QCP-CICV-1	500	2.5	500	2.5
Lead	QCP-CICV-3	500	2.5	500	2.5
Magnesium	QCP-CICV-1	2500	2.5	500	12.5
Manganese	QCP-CICV-1	250	2.5	500	1.25
Molybdenum	Elemental Stock	1000	0.25	500	0.5
Nickel	QCP-CICV-1	250	2.5	500	1.25
Potassium	QCP-CICV-1	2500	2.5	500	12.5
Selenium	QCP-CICV-3	500	2.5	500	2.5
Silver	QCP-CICV-1	125	2.5	500	0.625
Sodium	QCP-CICV-1	2500	2.5	500	12.5
Thallium	QCP-CICV-3	500	2.5	500	2.5
Titanium	Elemental Stock	1000	1.0	500	2.0
Vanadium	QCP-CICV-1	250	2.5	500	1.25
Zinc	QCP-CICV-1	250	2.5	500	1.25
Hydrochloric Acid	-	-	25	500	5%
Nitric Acid	-	-	5	500	1%

TABLE 3
ICP Interference Check Solutions

ICSA Solution

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Aluminum	CLPP-ICS-A	5000	50	500	500
Calcium	CLPP-ICS-A	5000	50	500	500
Iron	CLPP-ICS-A	2000	50	500	200
Magnesium	CLPP-ICS-A	5000	50	500	500
Hydrochloric Acid	-	-	25	500	5%
Nitric Acid	-	-	5	500	1%

ICSAB Solution

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Aluminum	CLPP-ICS-A	5000	50	500	500
Antimony	Elemental Stock	1000	0.5	500	1
Barium	CLPP-ICS-B	50	5	500	0.5
Beryllium	CLPP-ICS-B	50	5	500	0.5
Cadmium	CLPP-ICS-B	100	5	500	1
Calcium	CLPP-ICS-A	5000	50	500	500
Chromium	CLPP-ICS-B	50	5	500	0.5
Cobalt	CLPP-ICS-B	50	5	500	0.5
Copper	CLPP-ICS-B	50	5	500	0.5
Iron	CLPP-ICS-A	2000	50	500	200
Lead	CLPP-ICS-B	100	5	500	1
Magnesium	CLPP-ICS-A	5000	50	500	500
Manganese	CLPP-ICS-B	50	5	500	0.5
Nickel	CLPP-ICS-B	100	5	500	1
Silver	CLPP-ICS-B	100	5	500	1
Vanadium	CLPP-ICS-B	50	5	500	0.5
Zinc	CLPP-ICS-B	100	5	500	1
HCl	-	-	25	500	5%
HNO3	-	-	5	500	1%

TABLE 4
ICAP 6500 Analytical Wavelengths

Analyte	Wavelength	
Aluminum	167.0	Low Line
Aluminum	394.4	
Antimony	206.8	
Antimony	217.5	Alternate
Arsenic	189.0	
Barium	455.4	
Beryllium	234.8	
Boron	249.6	
Cadmium	226.5	
Cadmium	214.4	Alternate
Calcium	315.8	
Calcium	393.3	Low Line
Chromium	267.7	
Cobalt	230.7	
Cobalt	228.6	Alternate
Copper	327.3	
Copper	224.7	Alternate
Iron	259.9	
Lead	220.3	
Lithium	670.7	
Magnesium	279.0	High Line
Magnesium	279.5	Low Line
Magnesium	285.2	
Manganese	257.6	
Manganese	260.5	High Line
Molybdenum	202.0	
Nickel	221.6	
Nickel	231.6	Alternate
Phosphorus	214.9	
Phosphorus	178.2	Alternate
Potassium	766.4	
Selenium	196.0	
Silicon	251.6	
Silver	328.0	
Sodium	588.9	Alternate
Sodium	589.5	

TABLE 4 (cont.)
ICAP 6500 Analytical Wavelengths

Analyte	Wavelength	
Strontium	407.7	
Thallium	190.8	
Tin	189.9	
Titanium	336.1	
Vanadium	292.4	
Zinc	206.2	
Zinc	213.8	Alternate

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Ian Richardson
Ian.Richardson@ghd.com
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Inactive Extraction Well EXT-9
Longer-Term Pumping Test Work Plan

Occidental Chemical Corporation
605 Alexander Avenue
Tacoma Washington
Glenn Springs Holdings, Inc.

GHD | 651 Colby Drive Waterloo Ontario N2V 1C2 Canada
007843 | A8 | 403 | Report No 144 | April 1, 2019

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List of Acronyms

Draft 2018 AO	Draft 2018 Agreed Order between Ecology, Glenn Springs Holdings, Inc., and Mariana Properties, Inc.
Amended AOC	2005 Amendment to the Administrative Order on Consent
bgs	below ground surface
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CSI work plan	2012 Comprehensive Supplemental Investigation work plan
CRA	Conestoga-Rovers & Associates (now GHD)
CVOC	chlorinated volatile organic compound or chlorinated volatile organic compounds
°C	degrees Celsius
Ecology	Washington State Department of Ecology
ft	feet
gpd	gallons per day
gpm	gallons per minute
GSH	Glenn Springs Holdings, Inc.
GWETS	OCC existing groundwater extraction and treatment system
GWTP	OCC existing groundwater treatment plant
HACH	Hach Company
HASP	Health and Safety plan
Hylebos	Waterway
lbs	pounds
LST	leachate storage tank
µg/L	micrograms per liter
MTCA	Model Toxics Control Act
NPDES	National Pollutant Discharge Elimination System
OCC	Occidental Chemical Corporation
O&M	Operation and Maintenance
QAPP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act
RTO	regenerative thermal oxidizer
s.u.	standard units of pH
UofW	University of Washington
USEPA	United States Environmental Protection Agency
WAC	Washington Administrative Code
Waterway	Hylebos Waterway
Work Plan	Inactive Extraction Well EXT-9 Longer-Term Pumping Test Work Plan
ZGP	zone-grouping plane

1. Introduction

Occidental Chemical Corporation (OCC) has been working with the Washington State Department of Ecology (Ecology) and the United States Environmental Protection Agency (USEPA) (together referred to as the 'Agencies') to address remaining environmental issues at the 'Occidental' Site associated in part with the former OCC facility located in Tacoma, Washington (Site).

The existing groundwater extraction and treatment system (GWETS) at the OCC Site in Tacoma, Washington began operation in March 1994 to extract and treat contaminated groundwater. Operation of the GWETS is required under Resource Conservation and Recovery Act (RCRA) Permit WAD 009242314 and is incorporated as part of the USEPA Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Administrative Order on Consent, as amended in 2005 (Amended AOC), to provide for corrective actions.

Ecology, Glenn Springs Holdings, Inc. (GSH), and Mariana Properties, Inc. (Mariana) are negotiating a Draft 2018 Agreed Order (Draft 2018 AO). Section VIID of the Draft 2018 AO requires a longer-term groundwater extraction demonstration to provide data and information to evaluate long-term effectiveness, permanence, and implementability of the future hydraulic containment system at the site. The Draft 2018 AO specifies the performance of a longer-term groundwater pumping test at inactive extraction well EXT-9 for the longer-term groundwater extraction demonstration. The data quality objectives of this longer-term groundwater pumping test are presented in Exhibit E of the Draft 2018 AO. The overall objective for the EXT-9 longer-term groundwater pumping test is to evaluate the feasibility of pumping groundwater in close proximity to high pH and high dissolved silica concentration areas.

This Work Plan presents the steps and procedures necessary to complete a longer-term groundwater pumping test at inactive extraction well EXT-9 (EXT-9). The details of the plan have been negotiated through collaborative discussions between GSH/OCC, Ecology, and USEPA.

This Work Plan is organized as follows:

- Section 1 Introduction
- Section 2 EXT-9 Longer-Term Pumping Test Objectives
- Section 3 Scope of Work
- Section 4 Field Procedures
- Section 5 Data Evaluation and Reporting
- Section 6 Schedule
- Section 7 References

2. EXT-9 Longer-Term Pumping Test Objectives

The overall objectives for the EXT-9 longer-term groundwater pumping test is to evaluate the feasibility of pumping groundwater in close proximity to high pH and high dissolved silica concentration areas and to provide data and information to evaluate long-term effectiveness, permanence, and implementability of pumping groundwater near these areas.

Additionally, the EXT-9 longer-term groundwater pumping test is designed in an attempt to address the following specific questions:

- Can groundwater in close proximity to high pH and high dissolved silica concentration areas be pumped without causing plugging in the well or aquifer?
- Does the rate of pumping affect well efficiency or the tendency for plugging?
- If well plugging does occur, can the well be rehabilitated and brought back into service?
- What volume of solids will be generated during treatment of the extracted groundwater?
- What are the physical and chemical characteristics of the solids?
- Can a pumping rate equivalent to that modeled be maintained?

Some of the objectives listed above may or may not be achieved depending on conditions encountered during the testing. For example, if no solids are generated it would not be possible to characterize the solids.

3. Scope of Work

The activities to be performed under this Work Plan are described in the following sections. The specific field procedures to be used in completing these activities are presented in Section 4 of this Work Plan and will be in accordance with the procedures presented in the 2012 Comprehensive Supplemental Investigation (CSI) work plan (CRA, 2012). All field activities will be conducted in accordance with the Site Health and Safety Plan (HASP). The Site HASP will be updated as necessary to provide additional information regarding the EXT-9 longer-term groundwater pumping test and extraction of potentially high pH groundwater. Groundwater sampling and analyses will be conducted in accordance with the procedures presented in Section 4 below and the Quality Assurance Project Plan (QAPP) as presented in the 2012 CSI work plan.

Modifications and/or amendments to the approved Work Plan may be necessary during implementation of the work due to unforeseen field conditions including well fouling, conveyance fouling, carbon bed fouling, or other GWETS upsets. Any proposed changes to the approved Work Plan will be discussed with and approved by the Agencies prior to implementation of any plan changes.

3.1 Groundwater Pumping Test

The EXT-9 longer-term groundwater pumping test will be no more than 30 days total duration and will be conducted at a planned groundwater pumping rate of 20 gallons per minute (gpm). The groundwater pumping test will be conducted to assess well yield and well performance, and to facilitate the collection of water quality samples. The collected well yield/performance data and the results of the water quality samples will be used to assess the potential impacts of pumping in close proximity to high pH and high dissolved silica concentrations in groundwater. To conduct the EXT-9 longer-term groundwater pumping test, a submersible pump and sounding tubes will be temporarily installed in EXT-9. The pump discharge will be connected overland via temporary piping to an existing extraction branch (A-Branch) that is connected to the OCC existing groundwater treatment plant (GWTP). Power for the submersible pump will be provided by a temporary generator. Additionally, EXT-9 and selected neighboring monitoring wells will be instrumented with data logging pressure transducers to monitor groundwater levels before, during, and after the groundwater pumping test. The transducers will be positioned as close as practically possible to the mid-point of the well screens. For the duration of the groundwater pumping test, groundwater level monitoring will be conducted at 20 wells (EXT-9, MW-H-01, MW-EXT-9-Shallow, MW-EXT-9-Intermediate, MW-EXT-9-Deep, 40-25, 40-50, 40-75, 40-100, 11-75, 11-25, 11-45, 11-100, 74-50, 74-75, 74-100 74-130, 11-183, and extraction wells A-3 and A-4). Also, surface water elevation monitoring using a tide gauge will be conducted within the Hylebos Waterway coincident with the groundwater pumping test and groundwater level monitoring. The well locations are shown on Figure 3.1, and the well completion details for the monitoring network are presented in Table 3.1.

Preceding the longer-term groundwater pumping test, a series of variable rate step-drawdown tests will be completed. The step-drawdown testing will be designed to duplicate the initial 2013 post-installation testing. These data will be used to assess the current condition (i.e., efficiency) of EXT-9, and determine if any well redevelopment may be warranted for EXT-9 and/or if any changes to the proposed longer-term groundwater pumping test rate are necessary.

Groundwater pumped during the testing will be conveyed to the OCC GWTP through temporary overland piping connected to the vault for extraction well A-3 and then through the existing A-Branch subterranean conveyance as shown on Figure 3.2. To facilitate the use of the A-Branch conveyance, the standard vacuum extraction system will be offline. EXT-9 effluent produced during the groundwater pumping test upon reaching the GWTP will bypass the GWETS extraction pump and be re-introduced at the head of the system. The EXT-9 effluent will then follow the normal system operations of first being processed through the decanter, then routed to the inclined plate settler. Water passing through the settler will ultimately be collected in the leachate storage tank (LST). Daily batches of collected effluent will be processed through the air stripper prior to final polishing in the two onsite 20,000 pounds (lbs) carbon vessels before being discharged through outfall GWTP-001. Running through the entire GWTP system including the air stripper will provide a real world assessment of the treatability of the EXT-9 effluent. Operation of the full treatment system is also the safest way to process the EXT-9 effluent and will greatly reduce the risk of accidental discharges from unexpected carbon breakthrough or system upsets.

The EXT-9 longer-term groundwater pumping test duration may be limited due to the logistics of pumping, containing, transporting, and treating the accumulated groundwater. This may include such events as well fouling, conveyance fouling, carbon bed fouling, or other GWETS upsets. GWETS upsets which cannot be rectified in timely manner may prevent water transfer or result in filling the LST that would require shutdown of the extraction pump. The installation of the temporary overland conveyance connecting EXT-9 with extraction A-Branch will also impact the accessibility and use ability of POT tenant properties. Timely completion of the testing will limit these impacts.

3.2 Background Water Level Monitoring

Prior to initiating any groundwater pumping at EXT-9, background water level monitoring will be conducted at each of the 20 wells within the proposed monitoring network and a tide gauge in the Hylebos Waterway described in Section 3.1. Data loggers will be installed following the procedures in Section 4.2 below. Data will be collected for a minimum of one week prior to initiating any groundwater pumping tests. These data will be used to assess background conditions in the vicinity of EXT-9 prior to initiating any groundwater pumping tests. The Hylebos Waterway water levels will be used to normalize tidal fluctuations in the groundwater levels. A series of hydrographs will be prepared for each well. An on-Site weather station and data logging barometer will be deployed. Precipitation will be tracked and recorded daily from the on-Site weather station or obtained from online records for the National Oceanic and Atmospheric Administration (NOAA) National Centers for Environmental Information (NCEI) Tacoma Number 1, WA US meteorological station. The data logging barometer is necessary for adjusting the pressure transducer readings from the monitoring network for barometric pressure fluctuations.

3.3 Background Groundwater Quality Monitoring

Prior to initiating the EXT-9 longer-term groundwater pumping test, background groundwater quality samples will be collected from monitoring wells MW-EXT-9-Shallow, MW-EXT-9-Int, MW-EXT-9-Deep and inactive extraction well EXT-9. Groundwater sampling parameters for laboratory analyses and field parameters to be monitored are presented in Table 3.2. Samples from MW-EXT-9-Shallow MW-EXT-9-Int, and MW-EXT-9-Deep will be collected using low-flow purging and sampling techniques described in Section 4.4. The background groundwater quality samples from EXT-9 will be collected after purging of at least 3 well volumes (approximately 370 gallons, which will be verified with on-Site field measurements). The planned step-drawdown testing will remove three well volumes during the fourth step. Therefore, background samples will be collected following the completion of the fourth step. The samples for EXT-9 will be collected from an in-line water spigot installed in the conveyance piping prior to any flow control valves.

These data will provide background groundwater quality conditions and allow monitoring of changes in plume concentrations during and after the groundwater pumping test, as well as confirm the assumptions made in preparing the treatment train process.

All laboratory analyses will be performed by a Washington State Department of Ecology accredited laboratory. Sample volumes, containers, and holding procedures are listed in Table 7.1 of the QAPP (CRA, 2012).

3.4 Groundwater Quality Monitoring During Testing

Groundwater quality samples and field measurements will be collected throughout the EXT-9 longer-term groundwater pumping test as described below. The laboratory and field parameters are presented in Table 3.2.

Field measurements of groundwater pH, specific conductance, oxidation-reduction potential, dissolved oxygen, turbidity, temperature, and salinity will be performed at the time of sampling. The field parameters will be measured in the flow-through cell using the multi-parameter water quality meter calibrated per manufacturer's instructions. Silica measurements in the field will be obtained using a Hach Company (HACH) Model SI-5 field testing kit.

Groundwater sample laboratory analyses will include geochemistry (total dissolved solids and total suspended solids), metals (silica), and Site chlorinated volatile organic compounds (CVOC) as listed in Table 3.2.

Groundwater quality samples and field parameters will be collected from EXT-9, MW-EXT-9-Shallow, MW-EXT-9-Int, and MW-EXT-9-Deep. Field parameters will be monitored daily with groundwater quality samples collected after 1, 5, 10, 15, 20, 25, and 30 days of groundwater pumping. Samples from EXT-9 will be collected from a spigot installed in the conveyance line before any flow control valves. Groundwater quality grab samples from MW-EXT-9-Shallow, MW-EXT-9-Int, and MW-EXT-9-Deep will be collected using bladder pump with dedicated air/water tubing and disposable bladder or similar variable flow DC-submersible pump. Further details are provided in Section 4.4.

3.5 Process Sampling and Observations

The existing GWTP is designed under normal operating conditions to effectively process between 100-120 gpm of water per day. Since the proposed constant rate is 20 gpm, collected effluent from EXT-9 will be stored in the LST for daily batch processing. Processing the pumped groundwater in this fashion will allow efficient use of the GWTP processes shown on Figure 3.3.

3.5.1 Process Sampling

Process samples will be collected each day for the first 5 days to confirm system performance. After five days, process samples will be collected on days 10, 15, 20, 25, and 30. Influent pH will be monitored daily in the field at the well head. A series of five process water samples will be collected from the following process points: decanter feed; stripper feed; stripper discharge; primary bed discharge; and secondary bed discharge. Process water sample analyses will be limited to pH and Site CVOC listed in Table 3.2. Following cessation of the testing, a sample will be collected at the National Pollutant Discharge Elimination System (NPDES) sampling point 002 and analyzed for the parameters listed in the NPDES permit for effluent discharged to the Hylebos Waterway. Analytical results of the sample collected at sampling point 002 will be reported on the discharge monitoring report (DMR) and submitted to Ecology according to NPDES permit requirements. The parameters are listed in Section 4.5.

All sampling and analytical activities will be conducted in accordance with the field procedures presented in Section 4.

3.5.2 Process Observations

In addition to water quality monitoring, process observations will be made daily of all GWTP processes with specific attention paid to air stripper and carbon bed performance. Visual observations can be made through sight glasses installed in the side of the air stripper. These observations should reveal if excessive solids precipitation and/or fouling is occurring within the air stripper trays. Inlet and exit pressures from the carbon beds will be monitored and should bed pressures exceed a difference of 20 psi, the bed will be backwashed.

4. Field Procedures

4.1 Groundwater Pumping Tests

For the EXT-9 longer-term constant rate groundwater pumping test, a submersible pump and two sounding tubes will be installed in the well. The pump assembly will be set just above the top of the screen at between 105 and 110 feet (ft) below ground surface (bgs). Two sounding tubes will be set above the pump intake. The sounding tubes each will consist of a 3/4-inch and 1-inch PVC threaded pipe, to allow deployment of a data logging pressure transducer and a separate port for manual water level monitoring. The pump shall be capable of pumping between 5 and 30 gpm or groundwater from EXT-9. The pump and controlling equipment will be powered at the well head with a portable generator. The pump controller will be installed with a pressure switch to shut the pump down should an emergency condition occur at the GWTP requiring the cessation of groundwater pumping. The groundwater pumping equipment shall include a sampling point (spigot), valves for flow regulation, a totalizing flow meter accurate to 0.5 gpm, and a check valve to prevent backflow into the well.

Prior to initiating any groundwater pumping tests, selected neighboring wells listed in Table 3.1 and the tide gauge in the Hylebos Waterway will be instrumented with data logging pressure transducers to record groundwater levels and tide elevations during subsequent groundwater pumping. A dedicated data logging pressure transducer will be deployed at the surface to record barometric changes during the testing and monitoring.

Pumped groundwater will be conveyed via temporary piping to the vault for extraction well A-3. The temporary piping will be tied into the existing A-Branch subterranean conveyance to transport the pumped groundwater for treatment through the GWTP as shown on Figure 3.2.

4.1.1 Step-Drawdown Test

The testing will consist of a series of variable-rate steps designed to assess the efficiency and specific capacity of EXT-9, the effectiveness of development and provide a baseline for the longer-term constant rate groundwater pumping test. The variable-rate step test will consist of five discrete steps, replicating as close as practical the groundwater pumping rates completed in January 2014 of 5, 12, 17, and 20 gpm plus an additional step at 25 gpm. Each step will be conducted for a minimum of 20 minutes with electronic and manual water levels collected every 1 minute, or more frequently as practical. After 20 minutes the groundwater pumping rate will be adjusted to the next desired rate. The groundwater pumping will continue for another 20 minutes. The process is followed until all five steps are completed. Following the fourth step-rate test, a groundwater sample will be collected using the inline spigot. Prior to shutting down the final step, the pump will be set at 20 gpm in preparation for the 30-day longer-term constant-rate groundwater pumping test.

Following the completion of all five of the planned steps, the well will be allowed to recover for a minimum of 24 hours prior to starting the constant-rate groundwater pumping test.

4.1.2 Longer-Term Constant-Rate Groundwater Pumping Test

The constant-rate groundwater pumping test will be conducted for a period of no more than 30 days at an anticipated rate of 20 gpm. Both electronic and manual water levels will be collected every 1 minute, or more frequently as practical for the first 20 minutes of the test. Manual water level frequency will be reduced to every five minutes for the remaining first hour, then reduced to every half-hour for the remainder of the first 8 hours. After 8 hours of groundwater pumping, manual water level data collection will be reduced to every 2 hours for the remainder of the first 24 hours. After the first day of groundwater pumping (24 hours), water levels will be collected every 8 hours throughout the remainder of testing.

At the end of the constant-rate groundwater pumping test and prior to shutting down the pump, a final groundwater sample will be collected using the inline spigot and analyzed for the analytical parameters in Table 3.2.

4.2 Groundwater and Surface Water Level Monitoring

As noted in Section 4.1, selected neighboring wells, listed in Table 3.1 and shown on Figure 3.1, and the tide gauge in the Hylebos Waterway will be instrumented with dedicated and calibrated data logging pressure transducers to continuously record groundwater levels and tide elevations during groundwater pumping. The groundwater level monitoring locations were selected to be in clusters where possible within the various zone-grouping planes (ZGPs).

Prior to installation, all water level pressure transducers will be tested to confirm the calibration is consistent with manufacturer's specifications. The following procedure will be used to confirm transducer calibration:

i) Program water level pressure transducer per manufacturer's instructions to record at 1-second intervals

ii) Submerge water level transducer in a column of fresh water to a measured depth (shallow or deep depending on the transducer pressure rating/scale) and record transducer readings for approximately 1 minute

iii) Submerge water level transducer in a column of fresh water to a measured depth that is approximately 10 feet above or below the depth from step ii) above and record transducer readings for approximately 1 minute

iv) Remove water level transducer and download the transducer readings

v) Review the transducer readings to ensure that the recorded pressures/depths for steady state readings are equivalent to the two measured submergence depths (in the fresh water column) within manufacturer's specifications (0.05 percent Full Scale accuracy), confirming the water level transducer is recording accurately and functioning in accordance with the factory calibration of the transducer

The transducers will be linked/synchronized to a common clock and programmed to a common 5-minute data logging interval and positioned as close a practically possible to the mid-point of the well screens.

These data will be used to evaluate the aquifer response to the groundwater pumping.

4.3 Groundwater Sampling at Extraction Well EXT-9

A background groundwater quality sample and field parameters will be collected following the fourth step during the variable-rate step testing. During the longer-term constant-rate groundwater pumping test, field parameters will be monitored daily with groundwater quality samples collected after 1, 5, 10, 15, 20, 25, and 30 days of groundwater pumping. Groundwater quality samples will be collected from a sampling port (spigot) placed inline within the conveyance piping before any valves for flow regulation. Groundwater samples will be analyzed for the parameters in Table 3.2.

All laboratory analyses will be performed by a Washington State Department of Ecology accredited laboratory. Sample volumes, containers, and holding procedures are listed in Table 7.1 of the QAPP (CRA, 2012).

Field parameters, with the exception of silica, will be measured in the flow-through cell using a Horiba U-52 water quality meter or equivalent that is calibrated per manufacturer's specifications. Silica measurements in the field will be measured using a HACH Model SI-5 field testing kit.

4.4 Groundwater Sampling at Monitoring Wells MW-EXT-9-Shallow, MW-EXT-9-Int, and MW-EXT-9-Deep

Background groundwater quality samples from MW-EXT-9-Shallow, MW-EXT-9-Int, and MW-EXT-9-Deep will be collected using low-flow sampling techniques described below in Section 4.4.1 with subsequent grab groundwater quality samples collected at each well during the longer-term constant-rate groundwater pumping test using a bladder pump with dedicated air/water tubing and disposable bladder or similar variable flow DC-submersible pump described in Section 4.4.2.

4.4.1 Background Groundwater Sampling

The initial background groundwater samples will be collected using a bladder pump with dedicated air/water tubing and disposable bladder or similar variable flow DC-submersible pump and flow-through cell connected to well-dedicated polyethylene tubing. Field parameters, with the exception of silica, will be measured in the flow-through cell using a Horiba U-52 water quality meter or equivalent that is calibrated per manufacturer's specifications. Silica measurements in the field will measured using a HACH Model SI-5 field testing kit. Groundwater samples will be collected following the purging of three well volumes for the initial background sampling round and following the purging of one well volume for subsequent rounds (after 1, 5, 10, 15, 20, 25, 30 days). Sampling procedures are presented below:

i) Identify the well using the current Site map (update the map if needed) and inspect the well for damage. Note the condition of the surface protection, manhole or cover, and the well cap in the field book

ii) Measure and record, in the field book, the water level in the well using an electric tape water level measuring device to the nearest 0.01 ft

iii) Measure and record, in the field book, the total depth of the well to the nearest 0.1 ft to determine if there any accumulated sediments

iv) Install the sample tubing in the well with the bottom of the tubing (intake) at the midpoint of the available well screen, and connect the pump

v) With the pump controller set to its lowest setting, turn the pump on

vi) Slowly increase the pump speed until discharge occurs

vii) Once discharge occurs, record the visual observation of water quality and adjust the flow to a sustainable pumping rate. Record the groundwater pumping rate for subsequent sampling rounds

viii) Measure and record, in the field book, field parameters (pH, specific conductance, turbidity, temperature, dissolved oxygen, oxidation-reduction potential, salinity, and water level) and visual water quality every 5 minutes for the first well volume and then every 15 minutes for the remaining two well volumes. Stabilization will be considered to be achieved and purging complete after three consecutive readings are within the following limits:

a)	pH	±0.1 unit
b)	Temperature	±3 percent
c)	Specific Conductance	±3 percent
d)	Dissolved Oxygen	±10 percent
e)	Oxidation-Reduction Potential	±10 percent
f)	Water level	±0.2 foot

ix) If the well is purged dry, collect a sample and record the field parameters once the well recovers sufficiently to allow sample collection

x) Prior to sampling, disconnect the discharge tubing from the flow-through cell and fill the sample containers per laboratory instruction. Fill sample containers for CVOC analysis directly from the tubing using zero headspace containers. CVOC samples will be collected in unpreserved vials and analyzed within 7 days to avoid the potential creation of air bubbles by an acid-base reaction between high pH groundwater and the acid preservative. Samples for metals and geochemistry will be unfiltered

xi) Record the conditions at the time of sampling in the field book, including a description of the sample, the date and time of sampling, the sample identification number, the sample location, and the weather conditions

The field parameters listed above will be measured and recorded. Sample containers will be labeled, wrapped in packing material, and immediately placed in a cooler with ice. Samples will be delivered to the analytical laboratory by courier under approved Chain-of-Custody procedures

All laboratory analyses will be performed by a Washington State Department of Ecology accredited laboratory. Sample volumes, containers, and holding procedures are listed in Table 7.1 of the QAPP (CRA, 2012).

4.4.2 Grab Sampling

Field parameters and groundwater quality samples will be collected after 1, 5, 10, 15, 20, 25, and 30 days of groundwater pumping. Field parameters, with the exception of silica, will be measured in the flow-through cell using a Horiba U-52 water quality meter or equivalent that is calibrated per manufacturer's specifications. Silica measurements in the field will measured using a HACH Model SI-5 field testing kit following manufacturer's specifications. One well volume will be pumped using a bladder pump with dedicated air/water tubing and disposable bladder or similar variable flow DC-submersible pump prior to collecting samples for laboratory analyses. Groundwater samples will be analyzed for the parameters in Table 3.2.

All laboratory analyses will be performed by a Washington State Department of Ecology accredited laboratory. Sample volumes, containers and holding procedures are listed in Table 7.1 of the QAPP (CRA, 2012).

4.5 Process Observation and Abbreviated GWTP Operations

For the purposes of this testing, several of the normal GWTP operation parameters will be adjusted to accommodate the testing schedule and requirements. All of the GWTP apparatuses will be online with the exception of previously decommissioned equipment and the groundwater extraction system. The treatment process is presented in Figure 3.3. Groundwater will be continuously delivered from EXT-9 to the GWTP and temporarily stored in the main leachate storage tank (LST). Treatment through the remainder of the GWTP treatment train will be completed in batches to maximize the performance of the air stripper and carbon beds.

Influent will initially flow to the decanter where any free product, if present, will be collected and measured. Water will then flow through the inclined plate settler and ultimately stored in the main LST. The LST is an 110,000 gallon tank and can accommodate several days of continuous groundwater pumping at EXT-9. The available capacity in the LST will be maintained below 30% to allow for periodic short-term shut downs of the treatment process to allow for backwashing as necessary and process observations as part of the testing program while maintaining groundwater pumping from EXT-9.

Carbon bed performance will be assessed by monitoring inlet and exit pressures from the two carbon vessels. A difference of greater 20 psi will suggest fouling of the bed is occurring and the bed will require backwashing. Traditionally during normal operations, beds are backwashed every two weeks independent of pressures as a general maintenance activity to increase the beds operational life. During this testing program backwashing will be held off until determined necessary following pressure observations. If backwashing is unsuccessful in bringing down the beds operational pressures the project team will be notified and a decision made on cessation of the testing.

During periods of non-treatment the air stripper will be taken offline to assess solids precipitation within the unit. If excessive fouling is observed the trays will be cleaned to allow the groundwater pumping tests to continue. Should fouling prevent safe operation of the air stripper the project team will be notified and a decision made on cessation of the testing.

Daily pH monitoring will be conducted at the decanter feed and stripper feed. Ecology has concluded that discharge of treated water from the EXT-9 longer-term groundwater pumping test will not have a reasonable potential to cause a violation of the pH water quality standard in the receiving water as stated in a March 29, 2108 memorandum (Ecology, 2018).

The NPDES effluent limits for the Site are listed below:

- Flow gallons per day (gpd) 216,000
- Chloroform micrograms per liter 75(µg/L)
- Carbon tetrachloride 4.4(µg/L)
- 1,1-dichloroethylene 3.2(µg/L)
- 1,1,2-trichloroethane 5.0(µg/L)
- 1,1,2,2-tetrachloroethane 11(µg/L)
- Trichloroethylene 81(µg/L)
- Tetrachloroethylene 8.9(µg/L)
- Methylene chloride 185(µg/L)
- Vinyl chloride 5.0(µg/L)

Process sampling results indicating breakthrough exceeding the NPDES effluent limits exiting the secondary carbon bed will stop the testing. The following criteria will result in a call to the project team and potentially shutting down of the testing program:

- Process sampling results indicating breakthrough exceeding the NPDES effluent limits exiting the primary carbon bed (note that this will not result in a discharge that exceeds the effluent limits because the water will be treated by the secondary carbon bed)
  - Requires carbon replacement prior to breakthrough of secondary carbon bed to re-establish carbon bed redundancy
- Reduction of flow within the well
  - Loss of flow will stop the testing
- Significant backpressure within the conveyance line
  - Loss of flow will stop the testing
- Significant backpressure within GWTP apparatus
  - Loss of flow will stop the testing
- Excessively high carbon bed pressures
  - Loss of flow within the carbon beds will stop the testing

- Other groundwater pumping interruptions
- Significant GWTP system upset loss of treatment capabilities will stop the testing

4.6 Field Logbook

Field logbooks will be bound documents containing individual field and sample logs. Information recorded will include:

- Project number
- Sample matrix
- Name of sampler
- Sample source
- Time and date
- Pertinent data (i.e., depth)
- Analysis to be conducted
- Sampling method
- Appearance of each sample (i.e., color)
- Preservative added, if any
- Number of sample bottles collected
- Pertinent weather data

Each page of the field logbook will be signed by the sampler.

4.7 Labeling and Packaging

A unique sample numbering system will be used to identify each collected sample. This system will provide a tracking number to allow retrieval and cross-referencing of sample information. The sample numbering system to be used is described as follows:

Example:	G-121695-AA-BBB-XXX
Where:	G-Designates sample Type (GW=Groundwater)
121695:	Date of collection (mm/dd/yy)
AA:	Sampler initials
BBB:	Borehole Location I.D.
XXX:	Unique sample number

QC samples will also be numbered with a unique sample number.

Sample containers will be individually wrapped and placed on ice or cooler packs in laboratory-supplied coolers immediately after labeling. Samples will be delivered to the laboratory by courier under approved Chain-of-Custody procedures as described below.

4.8 Chain of Custody Procedures

Chain-of-Custody forms will be completed for all samples to document the transfer of sample containers. Custody seals will be placed on each cooler. The cooler will then be sealed with packing tape. Sample container labels will include sample number, place of collection, and date and time of collection. All samples will be refrigerated using wet ice at 4°C (±2°C) and delivered to the analytical laboratory within 48 hours of collection. All samples will be delivered to the laboratory by commercial courier or contractor personnel. All samples will be maintained at 4°C (±2°C) by the laboratory.

The Chain-of-Custody record, completed at the time of sampling, will contain, but not be limited to, the sample number, date and time of sampling, and the name of the sampler. The Chain-of-Custody document will be signed, timed, and dated by the sampler when transferring the samples.

Each sample cooler being shipped to the laboratory will contain a Chain-of-Custody form. The Chain-of-Custody form will consist of four copies which will be distributed as follows. The shipper will maintain a copy while the other three copies will be enclosed in a waterproof envelope within the cooler with the samples. The cooler will then be sealed properly for shipment. The laboratory, upon receiving the samples, will complete the three remaining copies. The laboratory will maintain one copy for their records. One copy will be returned to the Quality Assurance/Quality Control (QA/QC) Officer-Field and Analytical Activities (Field QA Office) upon receipt of the samples by the laboratory. One copy will be returned with the data deliverables package.

4.9 Equipment Cleaning

Prior to being placed into a well, all equipment will be cleaned according to the following protocol:

i) Disassemble equipment, if necessary

ii) Non-phosphate detergent wash

iii) Tap water rinse

iv) Distilled water rinse

v) Isopropanol rinse

vi) Air dry

vii) Distilled water rinse

When practicable, sampling equipment will be wrapped in aluminum foil to prevent it from becoming contaminated. When cleaning pressure transducer equipment, the isopropanol rinse shall not be used. Wash waters shall be collected in a coverable container for subsequent transfer to the Site treatment plant.

4.10 Waste Material Handling

Solid wastes (e.g., Tyvek coveralls, gloves) will be containerized and disposed of in accordance with the appropriate regulations.

Wastewater and decontamination solvents shall be placed in separate containers and covered. At the end of every day, all containers will be securely covered and full containers will be transferred to an on-Site staging area. All containers will be properly labeled as to contents in conformance with all federal and state regulations.

5. Data Evaluation and Reporting

The groundwater pumping test and water quality sample results will be summarized in a report detailing well and GWTP performance. The data collected will be used to develop hydrographs, maps, and figures to convey the results obtained and aid in the planning and design of the proposed replacement groundwater treatment plant and associated extraction system. A final report will be prepared to describe the performance of EXT-9 during the groundwater pumping test, the influence of the groundwater pumping test on surrounding groundwater levels and quality, and the performance of the GWTP. In addition, if the testing is terminated prior to the completion of 30 days of groundwater pumping, a detailed description of the observed issues and complications necessitating the early cessation of groundwater pumping will be included in the report.

The data and results from the previous short-term groundwater pumping test performed on inactive extraction well EXT-9 under the June, 2013 'Extraction Well Pilot Test Installation Work Plan' will also be included in this report.

6. Schedule

The schedule will depend on approval of this Work Plan and completing repairs and upgrades (installation of new regenerative thermal oxidizer [RTO]) to the Tacoma GWTP. The RTO was delivered in March 2018, installed in April 2018, with startup and shake down expected to be completed in May 2018. Once this work plan is approved and the GWTP is online and proven operating effectively, the groundwater pumping test will be scheduled in consultation with Ecology.

During the groundwater pumping test, weekly progress updates will be provided to highlight well and GWTP operations. Field status updates will be scheduled to begin 2 weeks prior to the start of the testing to discuss background data collection and data logger deployment. Ecology will be notified a minimum of 7 days prior to the start of the testing.

7. References

CRA, 2012. Comprehensive Supplemental Investigation Work Plan, ref. no. 7843 (111), April.

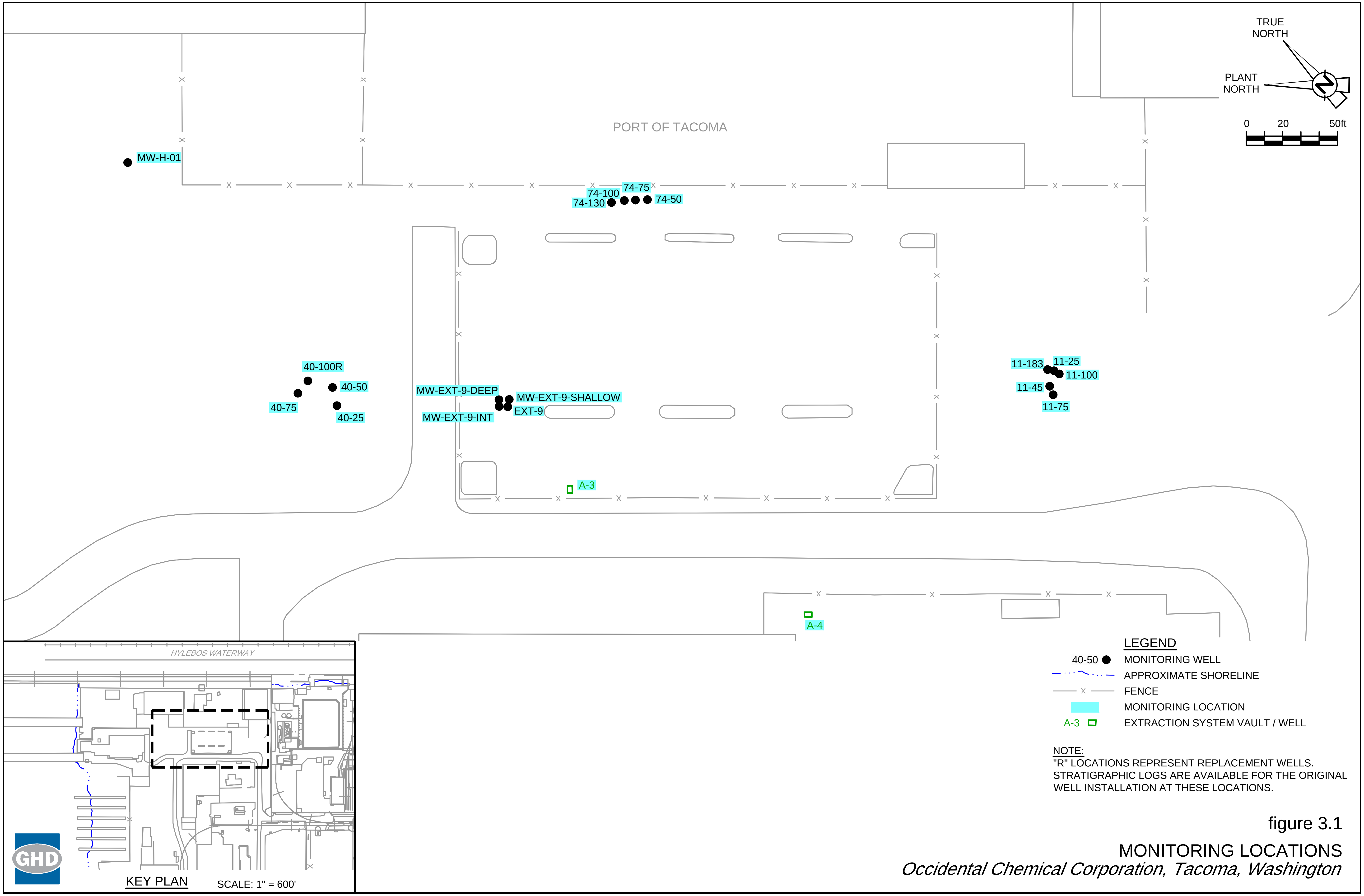
CRA, 2014. Site Characterization Report, Groundwater and Sediment Remediation, Occidental Chemical Corporation, Tacoma, Washington, August. (Also known as the Remedial Investigation Report [RI Report]).

Ecology, 2013. Model Toxics Control Act Regulation and Statute: MTCA Cleanup Regulation Chapter 173-340 WAC, Model Toxics Control Act Chapter 70.105D RCW, Uniform Environmental Covenants Act Chapter 64.70 RCW.

Ecology, 2018. Memorandum, Extraction Well No. 9 Pump Test - Receiving Water pH Evaluation, March 29, 2018

GHD, 2017. Feasibility Study Report, Occidental Chemical Corporation, Tacoma, Washington, January.

UofW, 2017. Examination of Silica Precipitation, Gelation and Hydraulic Fouling in Occidental Chemical Corporation (OCC) Soils, Report to Project Sponsors, Gregory Korshin and Mark Benjamin, University of Washington, January.



KEY PLAN

SCALE: 1" = 600'

LEGEND

40-50 ● MONITORING WELL

─ · · ~ · · ─ APPROXIMATE SHORELINE

── x ── FENCE

▬ MONITORING LOCATION

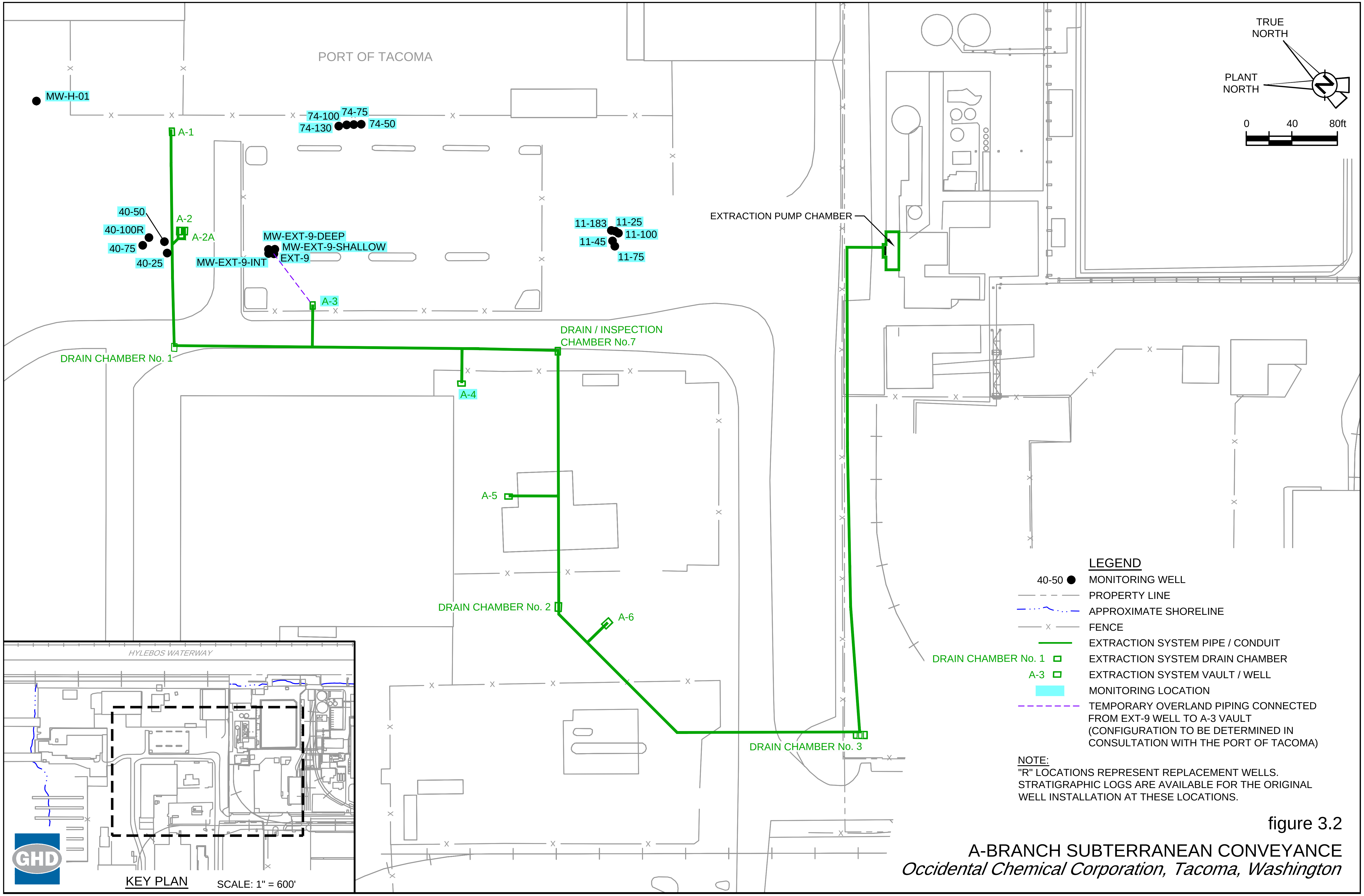
A-3 ☐ EXTRACTION SYSTEM VAULT / WELL

NOTE:
"R" LOCATIONS REPRESENT REPLACEMENT WELLS.
STRATIGRAPHIC LOGS ARE AVAILABLE FOR THE ORIGINAL
WELL INSTALLATION AT THESE LOCATIONS.

figure 3.1

MONITORING LOCATIONS

Occidental Chemical Corporation, Tacoma, Washington



LEGEND

40-50 ●	MONITORING WELL
— — —	PROPERTY LINE
-·-·-	APPROXIMATE SHORELINE
— x —	FENCE
——	EXTRACTION SYSTEM PIPE / CONDUIT
DRAIN CHAMBER No. 1 ☐	EXTRACTION SYSTEM DRAIN CHAMBER
A-3 ☐	EXTRACTION SYSTEM VAULT / WELL
🟦	MONITORING LOCATION
- - - -	TEMPORARY OVERLAND PIPING CONNECTED FROM EXT-9 WELL TO A-3 VAULT (CONFIGURATION TO BE DETERMINED IN CONSULTATION WITH THE PORT OF TACOMA)

NOTE:
"R" LOCATIONS REPRESENT REPLACEMENT WELLS. STRATIGRAPHIC LOGS ARE AVAILABLE FOR THE ORIGINAL WELL INSTALLATION AT THESE LOCATIONS.

figure 3.2

A-BRANCH SUBTERRANEAN CONVEYANCE

Occidental Chemical Corporation, Tacoma, Washington

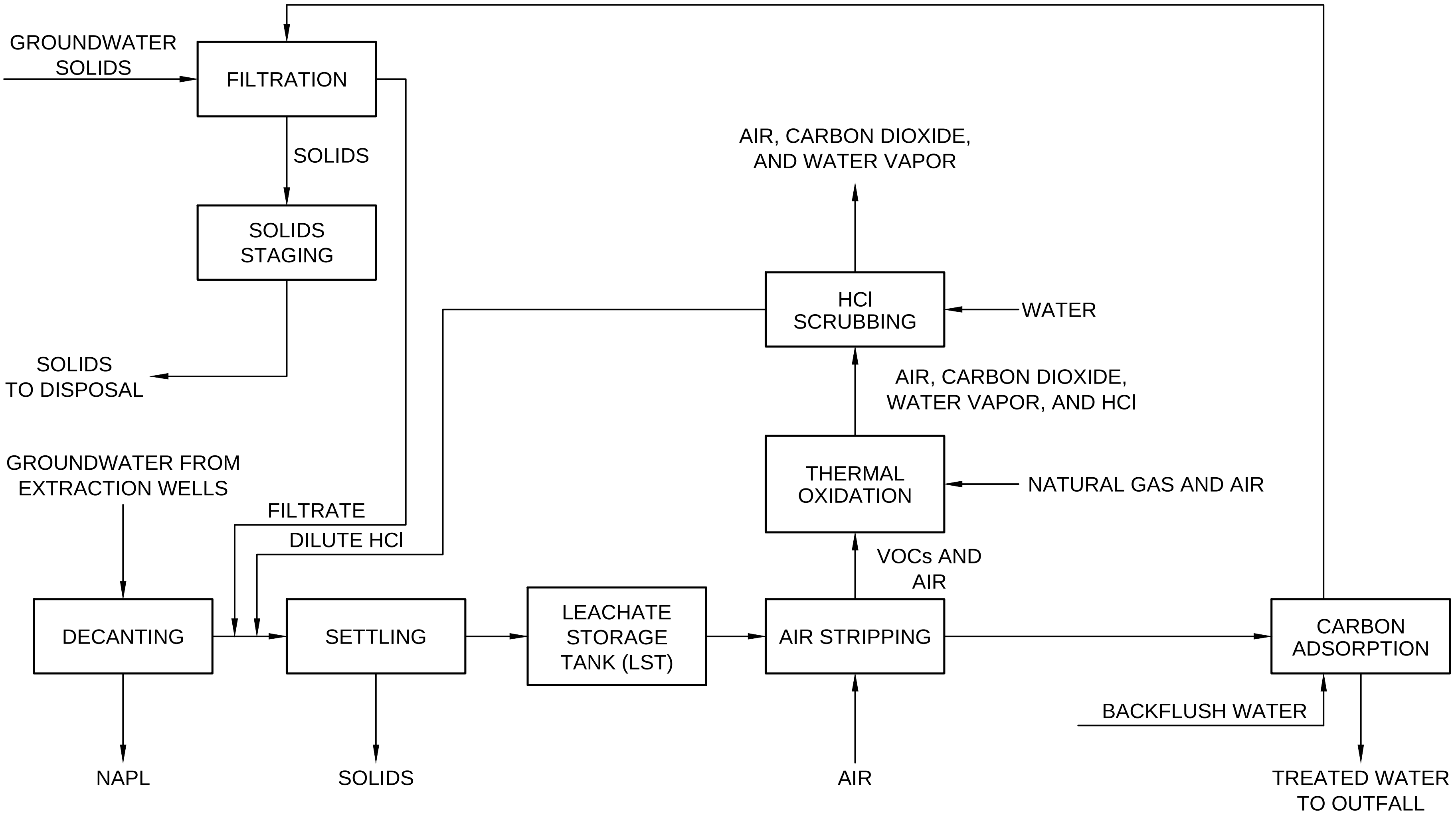


figure 3.3

TREATMENT PROCESS FLOW SCHEMATIC
GROUNDWATER TREATMENT FACILITY

Occidental Chemical Corporation, Tacoma, Washington

Table 3.1

Summary of Well Completion Details
Inactive Extraction Well EXT-9 Longer-Term Pumping Test Work Plan
Occidental Chemical Corporation
Tacoma Washington

						Screened Interval		Screened Interval		Data Logger Deployment	Data Logger Deployment		
Location	Easting	Northing	Ground Elevation (ft NGVD)	Reference Elevation (ft NGVD)	Well Diameter (in)	Bottom (ft BGS)	Top (ft BGS)	Bottom (ft NGVD)	Top (ft NGVD)	mid-point of screen (ft BGS)	mid-point of screen (ft NGVD)	Monitoring Zone	Approximate Radial Distance from EXT-9 (ft)
Monitoring Wells													
11-25	1167006.5	715972.4	12.32	12.06	2.0	25.00	20.00	-12.68	-7.68	22.50	-10.44	25	300
11-45	1166998.9	715968.0	12.24	11.80	4.0	44.86	34.86	-32.62	-22.62	39.86	-28.06	50	298
11-75	1166997.1	715963.3	12.25	11.91	2.0	75.40	70.40	-63.15	-58.15	72.90	-60.99	75	299
11-100	1167007.4	715969.2	12.32	11.77	2.0	98.32	93.32	-86.00	-81.00	95.82	-84.05	100	303
11-183	1167004.5	715975.4	12.35	12.02	4.0	182.97	172.97	-170.62	-160.62	177.97	-165.95	>160	297
40-25	1166710.5	716232.4	12.40	11.90	2.0	23.50	18.50	-11.10	-6.10	21.00	-9.10	25	94
40-50	1166715.7	716241.2	12.46	11.90	2.0	49.06	44.06	-36.60	-31.60	46.56	-34.66	50	97
40-75	1166699.9	716252.2	12.49	12.06	2.0	76.20	71.20	-63.71	-58.71	73.70	-61.64	75	115
40-100R	1166708.5	716253.3	12.62	11.73	2.0	97.80	92.80	-85.18	-80.18	95.30	-83.57	100	111
74-50	1166911.6	716195.1	11.74	11.43	2.0	50.00	45.00	-38.26	-33.26	47.50	-36.07	50	137
74-75	1166906.7	716199.5	11.74	11.49	2.0	75.00	70.00	-63.26	-58.26	72.50	-61.01	75	133
74-100	1166902.1	716203.6	11.74	11.34	2.0	100.00	95.00	-88.26	-83.26	97.50	-86.16	100	130
74-130	1166896.3	716207.7	11.78	11.21	2.0	130.00	125.00	-118.22	-113.22	127.50	-116.29	130	126
MW-EXT-9-DEEP	1166776.6	716172.9	12.58	12.14	2.0	202.00	197.00	-189.42	-184.42	199.50	-187.36	>160	6
MW-EXT-9-INT	1166774.2	716170.2	12.56	11.95	2.0	155.00	150.00	-142.44	-137.44	152.50	-140.55	160	5
MW-EXT-9-SHALLOW	1166780.8	716169.0	12.59	12.21	2.0	123.00	118.00	-110.41	-105.41	120.50	-108.29	130	4
MW-H-01	1166720.8	716408.1	11.41	10.93	2.0	167.25	162.25	-155.84	-150.84	164.75	-153.82	160	248
Extraction Wells													
EXT-9	1166777.4	716166.7	12.57	12.17	6.0	130.00	110.00	-117.43	-97.43	100.00*	-87.83	100	0
A-3	1166771.1	716113.1	12.10	7.65	10.0	68.40	38.40	-56.30	-26.30	53.40	-45.75	25	56
A-4	1166818.7	715969.2	11.00	7.34	10.0	68.50	38.50	-57.50	-27.50	53.50	-46.16	25	200

Notes:

ft NGVD - feet National Geodetic Vertical Datum
ft BGS - feet below ground surface
in - inches
* - approximate; transducer will be set above the pump intake

Table 3.2

Summary of Groundwater Sample Analytical and Field Parameters
Inactive Extraction Well EXT-9 Longer-Term Pumping Test Work Plan
Occidental Chemical Corporation
Tacoma, Washington

Site CVOC

1,1,2,2-Tetrachloroethane
1,1,2-Trichloroethane
1,1-Dichloroethene
Carbon Tetrachloride
Chloroform (Trichloromethane)
Methylene Chloride
Tetrachloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
Trichloroethene
Vinyl Chloride

Geochemistry

Total Dissolved Solids
Total Suspended Solids

Metals

Silica

Field Parameters *

pH
Temperature
Specific Conductance
Dissolved Oxygen
Oxidation Reduction Potential
Turbidity
Salinity
Silica

Note:

* Field Parameters collected on-Site using field meter and HACH® kit (silica).

CVOC - Chlorinated volatile organic compounds

Appendices

Appendix A

Ecology March 29, 2018 memorandum; 'Extraction Well No. 9 Pump Test – Receiving Water pH Evaluation'

1889

STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
PO Box 47775 • Olympia, Washington 98504-7775 • (360) 407-6300
711 for Washington Relay Service • Persons with a speech disability can call (877) 833-8641

MEMORANDUM

TO: Kerry Graber, Occidental Chemical Site Manager
FROM: Chuck Hoffman, Environmental Engineer CH
SUBJECT: Extraction Well No. 9 Pump Test – Receiving Water pH Evaluation
DATE: March 29, 2018

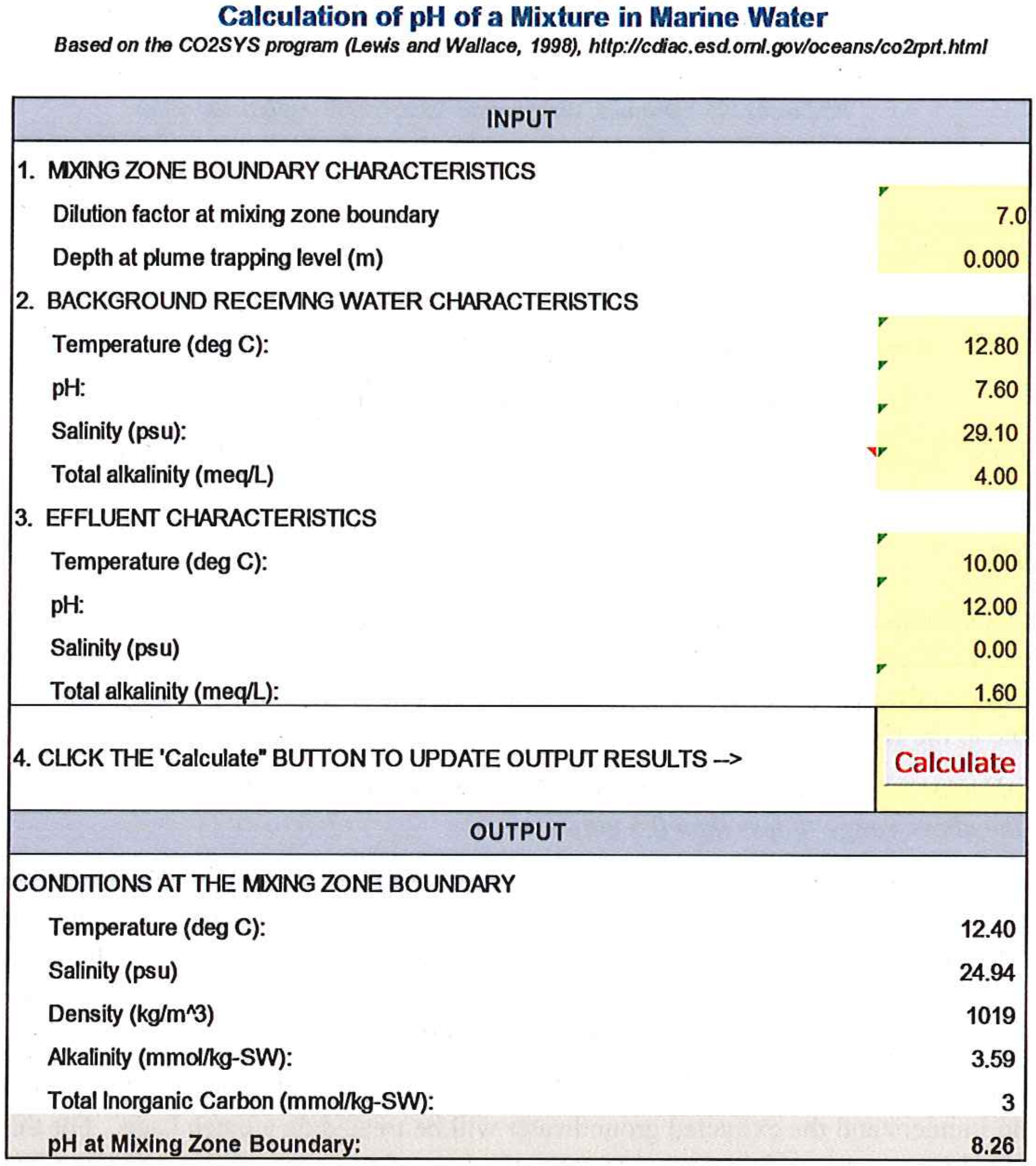
Occidental Chemical (Occidental) has concern regarding that the discharge of groundwater from the extraction Well No. 9 test would violate the pH water quality standard, if the pH of the extracted groundwater is greater than 8.5 standard units (s.u.). The water quality standard for pH applicable to the Hylebos Waterway follows:

> *pH must be within the range of 7.0 to 8.5 with a human-caused variation within the above range of less than 0.5 units.*

When we reissued the NPDES permit in 2015, I calculated mixing of the treatment plant effluent with the receiving water as a part of the evaluations to determine if the effluent would have a reasonable potential to cause a violation of water quality standards. For those evaluations, I used a treatment plant flow of 92,700 gallons per day (gpd) combined with a cooling water flow of 504,000 gpd to model effluent mixing in the receiving water during the critical condition.

Occidental has proposed a pumping rate of 20 gallons per minute (28,000 gpd) for the Well No. 9 test and I understand the extracted groundwater will be treated on a batch basis. For this evaluation, I assumed Occidental would treat three days of extracted groundwater as a batch. The total treated flow would be 84,000 gallons of groundwater that would discharge with 504,000 gallons of cooling water. I used the same characteristics for the cooling water as I used for the permit evaluation. For the groundwater pH, I assumed a worse case, and highly unlikely, pH of 12 s.u. for the entire 84,000 gallons.

For the first part of the evaluation I evaluated the pH that would result from mixing the cooling water and treated groundwater prior to discharge. The pH of this mix is 8.24 s.u. An image of the spreadsheet that Ecology uses to calculate pH of mixtures follows:

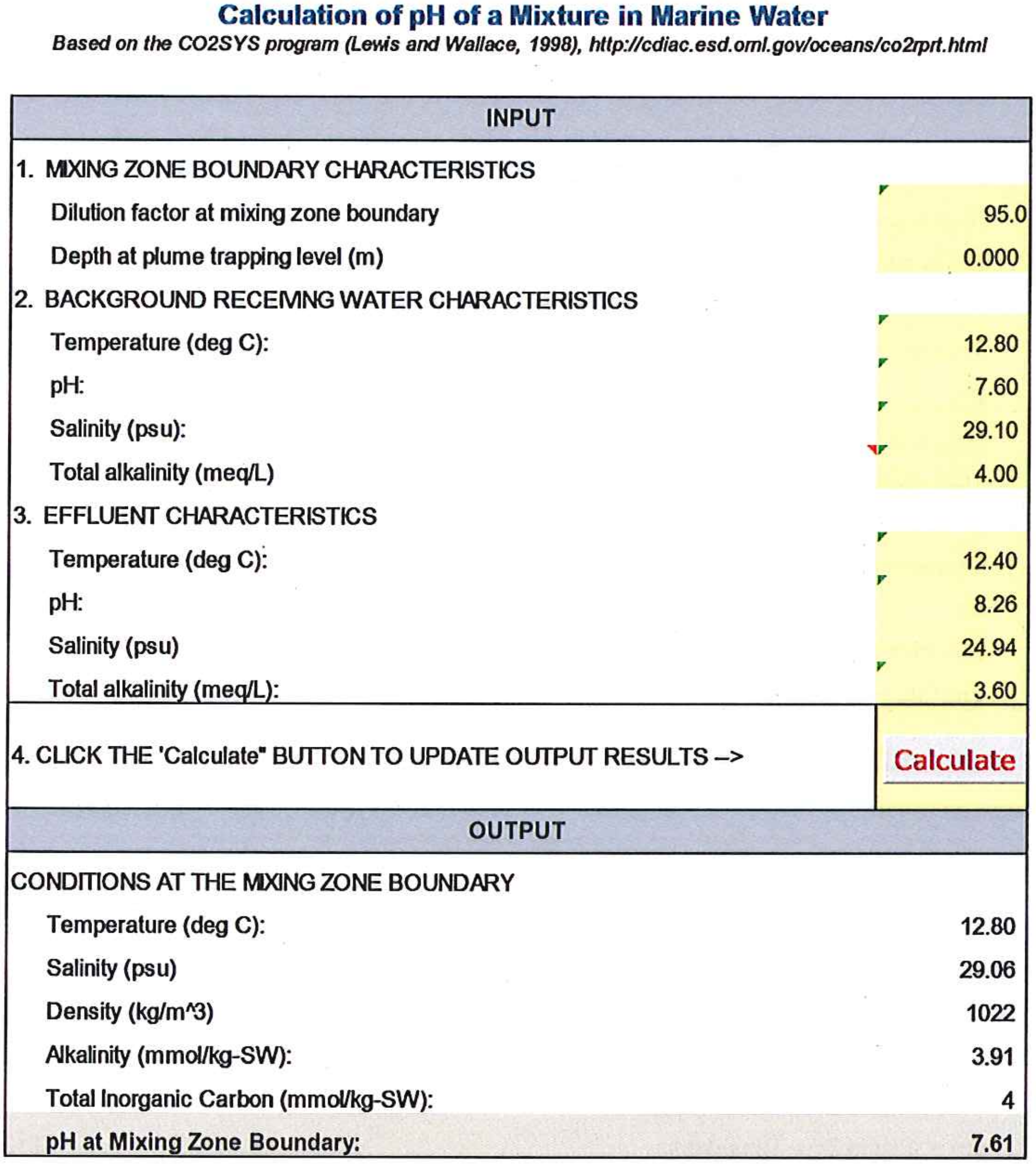


Calculation of pH of a Mixture in Marine Water

Based on the CO2SYS program (Lewis and Wallace, 1998), http://cdiac.esd.ornl.gov/oceans/co2rprt.html

INPUT	
1. MIXING ZONE BOUNDARY CHARACTERISTICS	
Dilution factor at mixing zone boundary	7.0
Depth at plume trapping level (m)	0.000
2. BACKGROUND RECEIVING WATER CHARACTERISTICS	
Temperature (deg C):	12.80
pH:	7.60
Salinity (psu):	29.10
Total alkalinity (meq/L)	4.00
3. EFFLUENT CHARACTERISTICS	
Temperature (deg C):	10.00
pH:	12.00
Salinity (psu)	0.00
Total alkalinity (meq/L):	1.60
4. CLICK THE 'Calculate" BUTTON TO UPDATE OUTPUT RESULTS -->	Calculate
OUTPUT	
CONDITIONS AT THE MIXING ZONE BOUNDARY	
Temperature (deg C):	12.40
Salinity (psu)	24.94
Density (kg/m^3)	1019
Alkalinity (mmol/kg-SW):	3.59
Total Inorganic Carbon (mmol/kg-SW):	3
pH at Mixing Zone Boundary:	8.26

The next step is to calculate pH at the boundary of the chronic mixing zone. I used a similar chronic dilution factor as I used for the permit evaluations because the treatment plant flows are similar. The effluent characteristics in the following spreadsheet are the results from the calculations to determine the pH of the treated groundwater/cooling water mixture. I used the same receiving water characteristics as used for the permit evaluations. The calculations result in a pH increase of 0.01 s.u. at the boundary of the chronic mixing zone, less than the 0.5 s.u. increase allowed by the water quality standard.

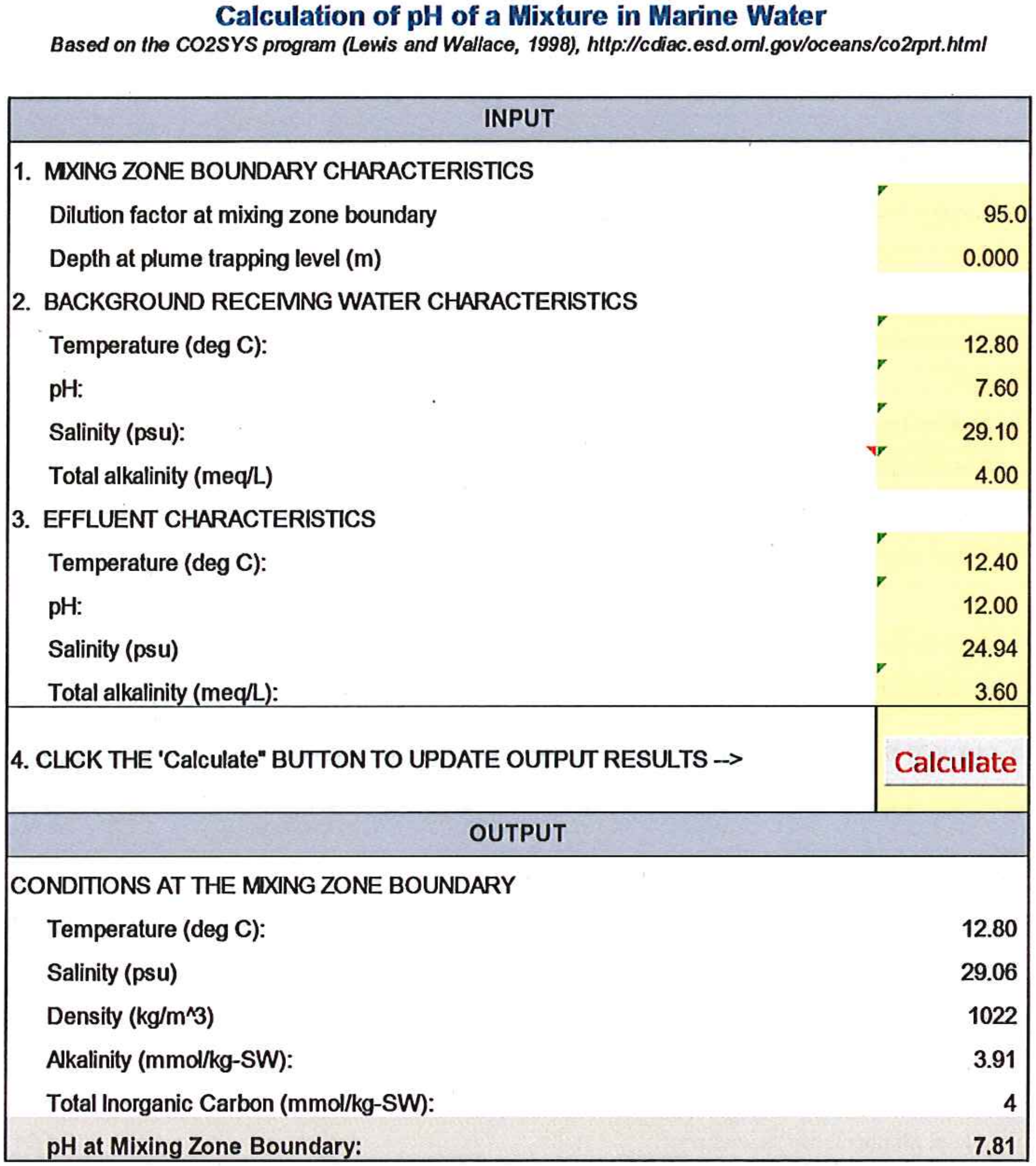


Calculation of pH of a Mixture in Marine Water

Based on the CO2SYS program (Lewis and Wallace, 1998), http://cdiac.esd.ornl.gov/oceans/co2rprt.html

INPUT	
1. MIXING ZONE BOUNDARY CHARACTERISTICS	
Dilution factor at mixing zone boundary	95.0
Depth at plume trapping level (m)	0.000
2. BACKGROUND RECEIVING WATER CHARACTERISTICS	
Temperature (deg C):	12.80
pH:	7.60
Salinity (psu):	29.10
Total alkalinity (meq/L)	4.00
3. EFFLUENT CHARACTERISTICS	
Temperature (deg C):	12.40
pH:	8.26
Salinity (psu)	24.94
Total alkalinity (meq/L):	3.60
4. CLICK THE 'Calculate" BUTTON TO UPDATE OUTPUT RESULTS -->	Calculate
OUTPUT	
CONDITIONS AT THE MIXING ZONE BOUNDARY	
Temperature (deg C):	12.80
Salinity (psu)	29.06
Density (kg/m^3)	1022
Alkalinity (mmol/kg-SW):	3.91
Total Inorganic Carbon (mmol/kg-SW):	4
pH at Mixing Zone Boundary:	**7.61**

For an extreme evaluation, I assumed the entire discharge (treated groundwater and cooling water) has a pH of 12 s.u. The calculation results in pH 7.81 s.u. at the chronic mixing zone boundary (shown in the following image). This is for example only and does not mean Ecology would permit a discharge of that volume with pH 12 s.u.



Calculation of pH of a Mixture in Marine Water

Based on the CO2SYS program (Lewis and Wallace, 1998), http://cdiac.esd.ornl.gov/oceans/co2rprt.html

INPUT	
1. MIXING ZONE BOUNDARY CHARACTERISTICS	
Dilution factor at mixing zone boundary	95.0
Depth at plume trapping level (m)	0.000
2. BACKGROUND RECEIVING WATER CHARACTERISTICS	
Temperature (deg C):	12.80
pH:	7.60
Salinity (psu):	29.10
Total alkalinity (meq/L)	4.00
3. EFFLUENT CHARACTERISTICS	
Temperature (deg C):	12.40
pH:	12.00
Salinity (psu)	24.94
Total alkalinity (meq/L):	3.60
4. CLICK THE 'Calculate" BUTTON TO UPDATE OUTPUT RESULTS -->	Calculate
OUTPUT	
CONDITIONS AT THE MIXING ZONE BOUNDARY	
Temperature (deg C):	12.80
Salinity (psu)	29.06
Density (kg/m^3)	1022
Alkalinity (mmol/kg-SW):	3.91
Total Inorganic Carbon (mmol/kg-SW):	4
pH at Mixing Zone Boundary:	7.81

In conclusion, the discharge of treated water from the extraction Well No. 9 pump test, conducted under the assumptions in this memorandum, will not have a reasonable potential to cause a violation of the pH water quality standard in the receiving water.