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TECHNICAL MEMORANDUM

TO: Diane Escobedo
Washington State Department of Ecology

DATE: September 13, 2018

FROM: Clare Tochilin, SoundEarth Strategies, Inc.

SUBJECT: Total Organic Carbon in Groundwater and Silica Gel Cleanup

SoundEarth Strategies, Inc. (SoundEarth) has prepared this Technical Memorandum to present the results of sampling for total organic carbon (TOC) in a groundwater sample collected from upgradient monitoring well MW8. This sampling was conducted in response to a discussion between SoundEarth and the Washington State Department of Ecology (Ecology) on August 28, 2018 regarding the use of silica gel cleanup in the analysis of diesel- and oil-range petroleum hydrocarbons (DRPH and ORPH) by Northwest Total Petroleum Hydrocarbon method NWTPH-Dx in on-Property wells MW01 through MW06 (Figure 1).

Ecology's Publication No. 10-09-057, revised June 2016, states the following regarding the use of silica gel cleanup in the analysis of groundwater samples for petroleum hydrocarbons:

"Silica gel cleanup should not be used for NWTPH-Dx analyses of groundwater samples unless uncontaminated background samples indicate that naturally occurring organic matter is a significant component of the TPH being detected in the groundwater samples. If silica gel cleanup is used, groundwater samples should be split and analyzed both with and without silica gel cleanup."

The laboratory test method NWTPH-Dx quantifies non-polar petroleum hydrocarbon compounds and also polar organic compounds such as oxygen, nitrogen, sulfur organic acids, alcohols, ketones, phenols, and organic matter. The silica gel absorbs the polar compounds in the groundwater sample. Non-polar petroleum hydrocarbons are not absorbed by the silica gel and are more accurately quantitated.

Groundwater samples collected from monitoring wells MW01 through MW06 were analyzed both with and without silica gel cleanup for DRPH and ORPH. Concentrations of DRPH and ORPH exceeded the MTCA Method A cleanup levels (CULs) in wells MW02, MW03, and MW04 without silica gel cleanup. However, these wells were non-detect for true petroleum using silica gel cleanup. Concentrations of DRPH and ORPH were below the CULs in wells MW01, MW05, and MW06 without silica gel cleanup. Every detection of DRPH and ORPH without silica gel cleanup was flagged by the laboratory as not representative of the standard hydrocarbons used for quantitation (Table 1). When analyzed with silica gel cleanup, concentrations of DRPH and ORPH in all but one groundwater sample (MW05) were not detected above laboratory reporting limits.

Following discussions with Ecology, SoundEarth analyzed a groundwater sample collected on August 29, 2018, from monitoring well MW8, located beyond the southern Property boundary on the south-adjointing

(upgradient) property, for TOC to determine whether or not polar organic compounds are present in uncontaminated groundwater beneath the Property. MW8 has not exhibited detectable concentrations of petroleum hydrocarbons during at least the last four quarters of sampling conducted by Cardno (Figure 1; Table 1). The TOC concentration detected in this monitoring well was 8,720 micrograms per liter ($\mu\text{g/L}$; 8.27 milligrams per liter $[\text{mg/L}]$).

Chapter 3 of United Nations Educational, Scientific and Cultural Organization, and World Health Organization's publication *Water Quality Assessments – A Guide to the Use of Biota, Sediments and Water in Environmental Monitoring – Second Edition* states the following regarding concentrations of TOC in groundwater:

“In surface waters, TOC concentrations are generally less than 10 mg l^{-1} , and in groundwater less than 2 mg l^{-1} , unless the water receives municipal or industrial wastes, or is highly coloured due to natural organic material, as in swamps.”

The table below from the textbook *Organic Geochemistry of Natural Waters* by E.M. Thurman provides typical TOC ranges for a variety of different water sources. According to this reference, the typical TOC concentration for groundwater is 700 parts per billion (ppb; $\mu\text{g/L}$). The TOC concentration of 8,270 $\mu\text{g/L}$ detected in well MW8 is approximately 12.5 times higher than this and is closer to the typical TOC concentrations for eutropic lake, marsh, and bog water, which contain much larger quantities of organic material than are typically found in groundwater.

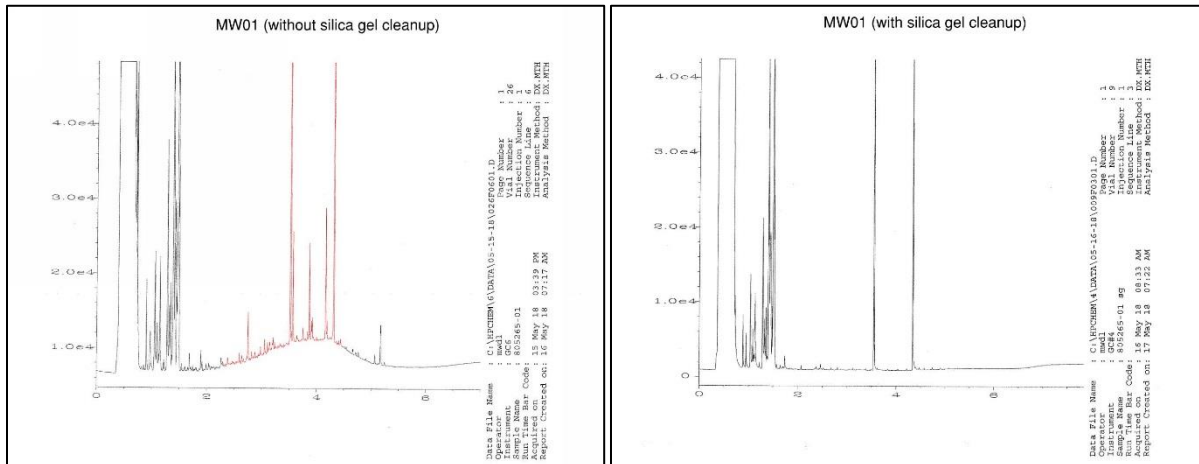
Water	Typical TOC (Range)	Typical TOC present as Particulates
Bog	33 ppm (10 to 60)	4 ppm
Marsh	17 ppm (10 to 60)	3 ppm
Eutropic lake	12 ppm	3 ppm
Oligotrophic lake	2.2 ppm	0.2 ppm
River	7.0 ppm (1 to 10)	2.5 ppm
Precipitation	1.1 ppm	0.1 ppm
Ground Water	700 ppb	
Sea Water	500 ppb	50 ppb
Waste Water	up to 1000 ppm	
Process Waters	very wide range	
Drinking Water	100 ppb to 10 ppm	
Purified Water	1 ppb to 500 ppb	
Ultrapure Water	0.1 ppb to 10 ppb	

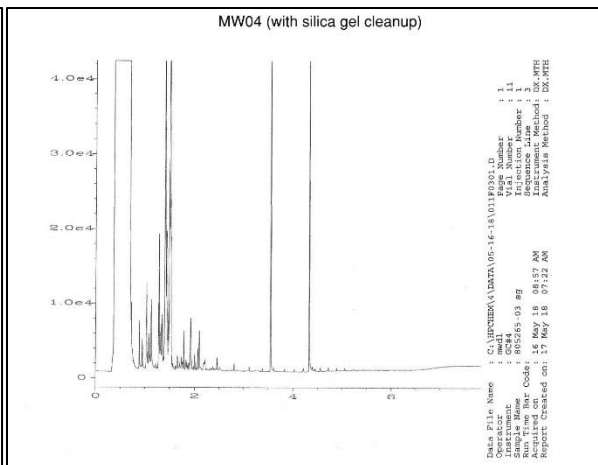
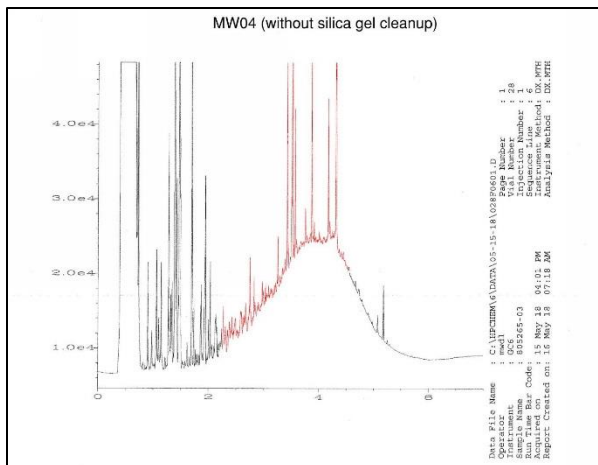
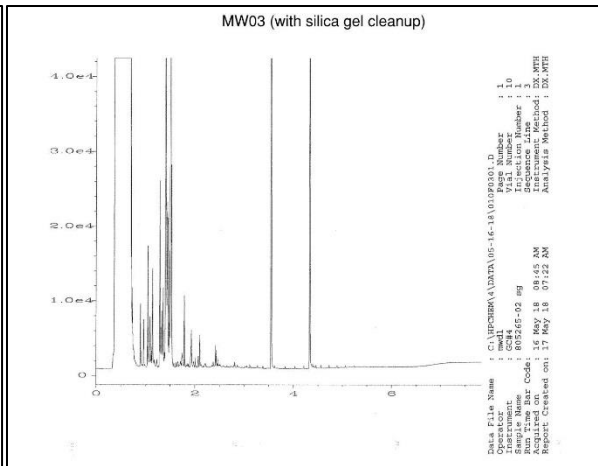
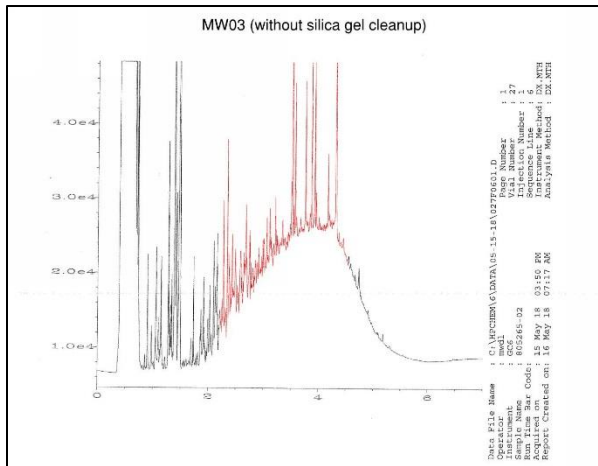
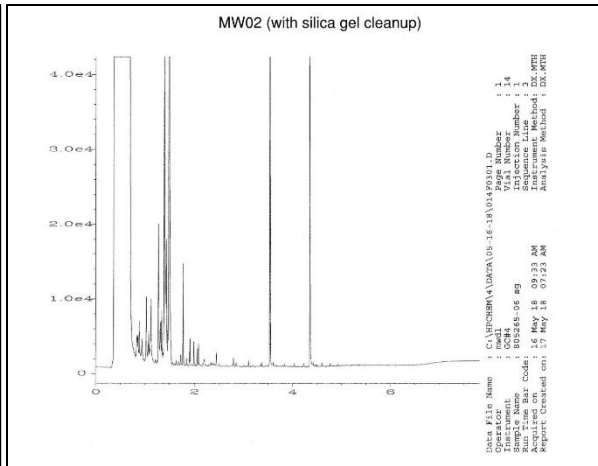
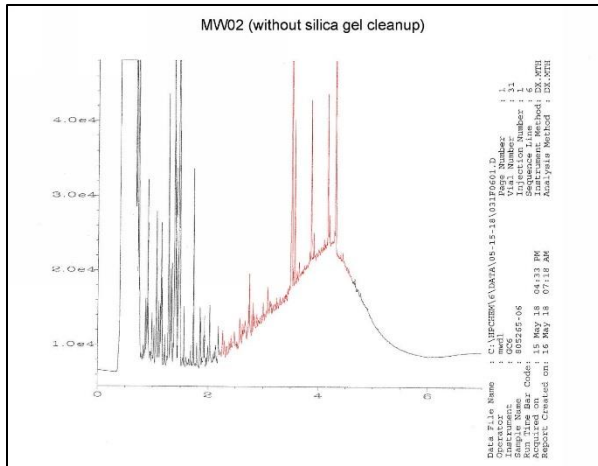
Between 1997 and 2000, Ecology conducted groundwater monitoring for TOC as part of an aquifer study in northwestern Washington (Ecology Publication No. 02-03-007). Groundwater samples collected from 15 monitoring wells at two different sites on 7 to 8 sampling dates over a one-year time period contained

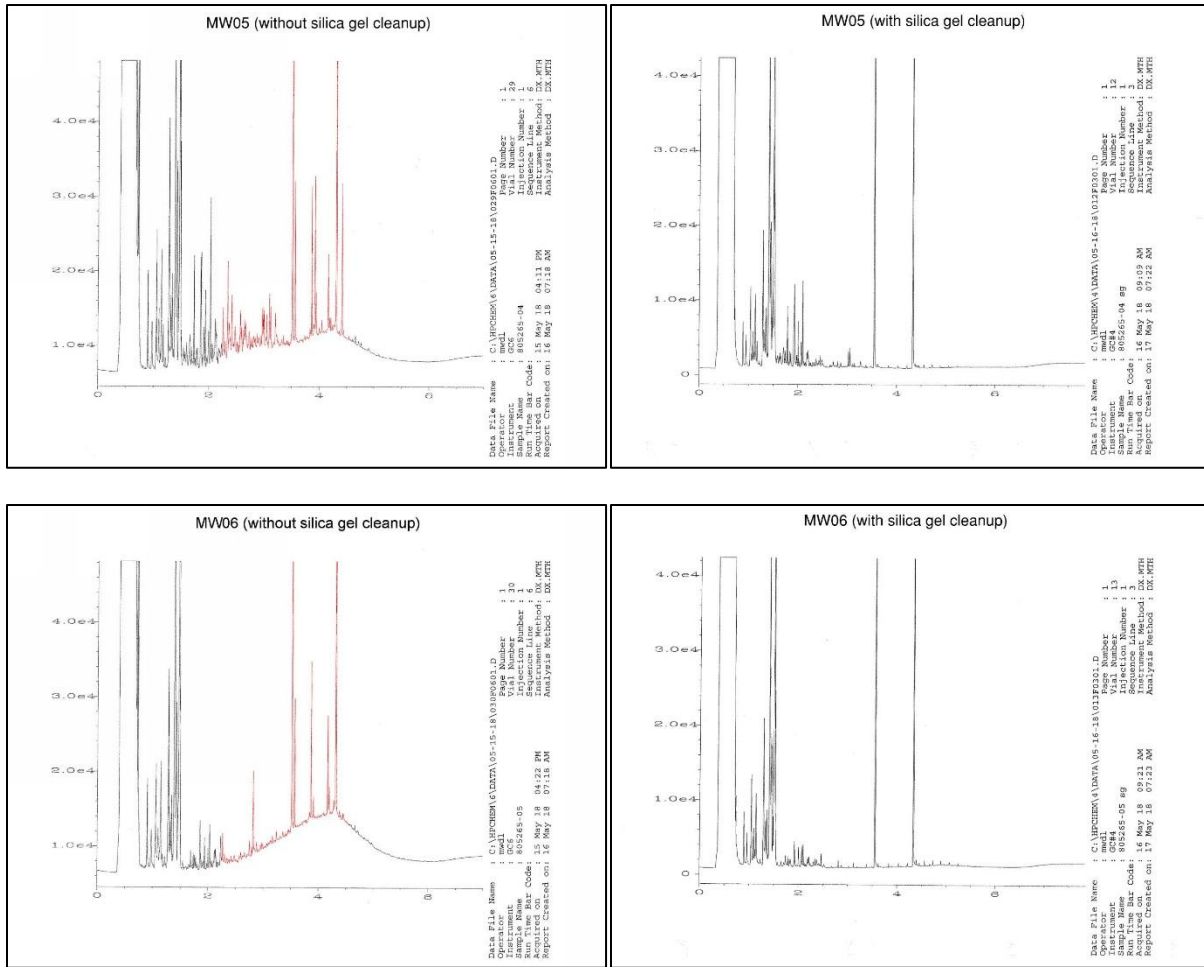
mean TOC concentrations ranging from 0.67 to 4.7 mg/L. At one of the sites, the majority of TOC concentrations were below the laboratory reporting limit of 0.5 mg/L.

Based on our review the references summarized above, the TOC concentration detected in uncontaminated background well MW8 (8.27 mg/L) is significantly higher than typical TOC concentrations in groundwater not impacted with petroleum hydrocarbons or other contaminants. As stated in *Water Quality Assessments – A Guide to the Use of Biota, Sediments and Water in Environmental Monitoring – Second Edition*, TOC values higher than 2 mg/L in groundwater result from the presence of natural organic matter. The TOC value detected in MW8 indicates that a significant amount of naturally occurring polar organic material is present in groundwater beneath the Property.

As shown in the chromatograms below for wells MW01 through MW06, when polar organic compounds (shown in red on the first chromatograms without silica gel cleanup) are removed from the groundwater sample using silica gel cleanup, it is clear that a significant component of the quantified total petroleum hydrocarbons can be attributed to the polar compounds. Based on the high TOC concentration in uncontaminated background well MW8, and a review of DRPH and ORPH chromatograms shown below, we have a high degree of certainty that the DRPH and ORPH concentrations detected in groundwater samples without silica gel cleanup collected at the Property are the result of naturally occurring, non-petroleum polar organic compounds. The presence of this organic material is proven by the high TOC concentration detected in well MW8. Based on this analysis and Ecology’s guidance on the use of silica gel cleanup in the analysis of groundwater samples for petroleum hydrocarbons, the use of this lab method is justified for groundwater samples at the Property. Consequently, the groundwater at the Property is in compliance with MTCA CULs for petroleum hydrocarbons based on use of the proper lab methods.







REFERENCES

Chapman, D. and V. Kimstach. 1996. "Chapter 3 – Selection of water quality variables." *Water Quality Assessments – A Guide to Use of Biota, Sediments and water in Environmental Monitoring*. Edited by Deborah Chapman. Second Edition. UNESCO/WHO/UNEP.

Washington State Department of Ecology. 2002. *Effects of Land Application of Manure on Groundwater at Two Dairies over the Sumas-Blaine Surficial Aquifer*. Publication No. 02-03-007. March.

Thurman, E.M. 2012. *Organic Geochemistry of Natural Waters*. Springer.

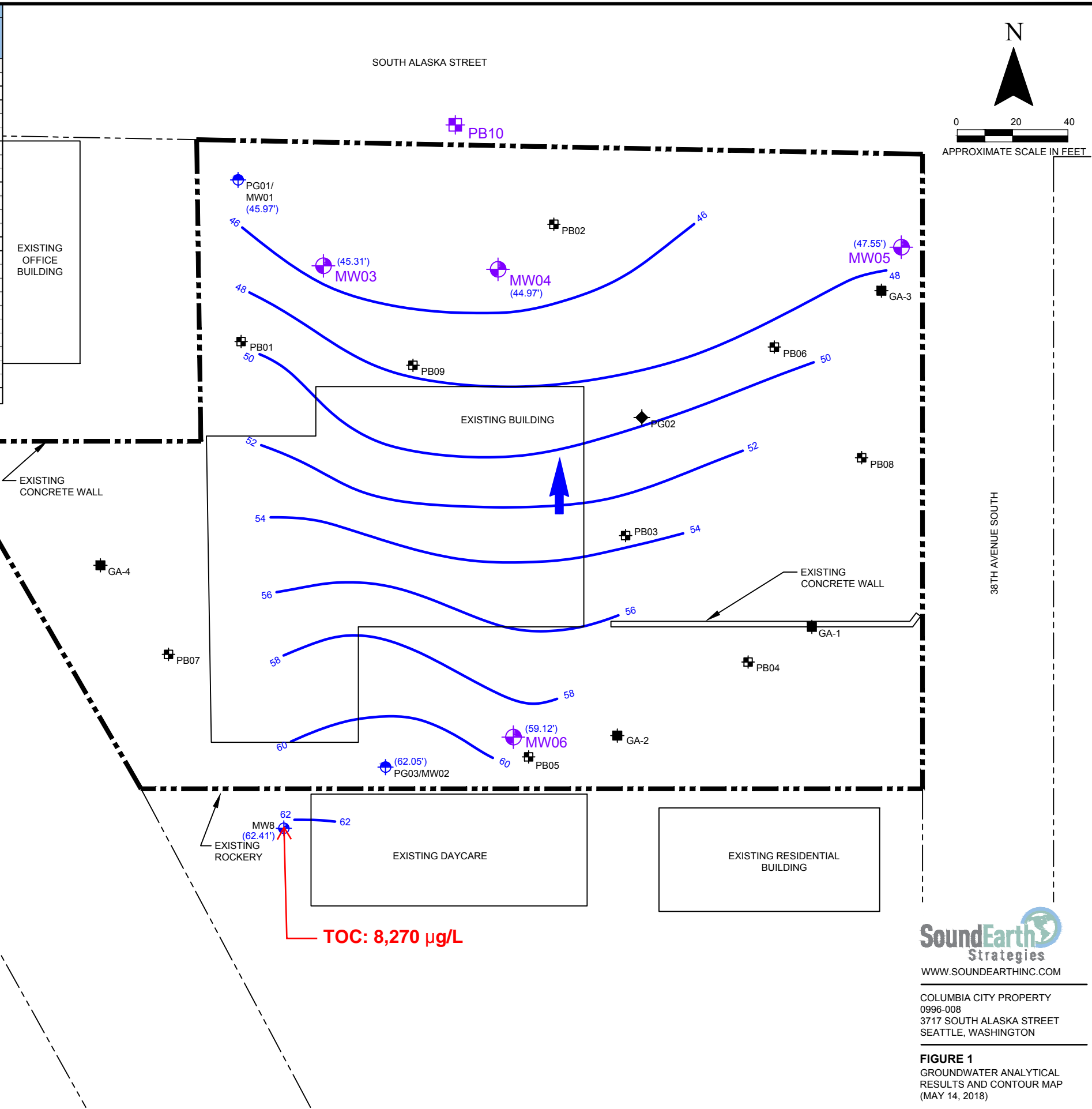
Attachments: Figure 1, Groundwater Analytical Results and Contour Map (May 14, 2018)
 Table 1, Summary of Groundwater Analytical Results for Petroleum hydrocarbons and CVOCs

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Location	Date Sampled	Analytical Results (in µg/L)								
		GRPH	DRPH	DRPH with Silica Gel	ORPH	ORPH with Silica Gel	Benzene	cPAH TEQ	CVOCs	Dissolved Arsenic
Reconnaissance Groundwater Samples										
PB05	05/19/15	230	180	--	1,100	--	<0.35	--	ND	7.07
PB06	05/19/15	110	360	--	530	--	<0.35	--	ND	1.55
Low-Flow Groundwater Samples										
MW01	05/21/15	<100	<50	--	<250	--	<0.35	0.08	ND	2.65
	05/14/18	--	200	<50	<250	<250	--	0.05	--	--
MW02	05/21/15	100	<50	--	<250	--	<0.35	0.08	ND	12.7
	05/14/18	--	610	<50	510	<250	--	0.05	--	5.27
	06/01/18	--	--	--	--	--	--	--	--	6.25
MW03	03/07/18	--	510	--	<400	--	--	0.05	--	--
	05/14/18	--	1,100	<50	560	<250	--	0.05	--	--
MW04	03/07/18	--	350	--	<400	--	--	0.05	--	--
	05/14/18	--	820	<50	520	<250	--	0.05	--	--
MW05	05/14/18	--	320	57	<250	<250	--	0.05	--	--
MW06	05/14/18	--	280	<50	<250	<250	--	0.05	--	6.93
	06/01/18	--	--	--	--	--	--	--	--	8.34
MW8	08/15/17	<100	<91	--	<91	--	<0.50	--	--	--
	10/17/17	<100	<94	--	<94	--	<0.50	--	--	--
	02/01/18	<100	<94	--	<94	--	<0.50	--	--	--
	04/03/18	<100	<100	--	<100	--	<0.50	--	--	--
MW9R	08/21/17	<100	<91	--	<91	--	<0.50	--	--	--
	10/17/17	190	<96	--	<96	--	<0.50	--	--	--
	02/01/18	180	<91	--	<91	--	<0.50	--	--	--
	04/04/18	150	<100	--	<100	--	<0.50	--	--	--
MTCA Method A Cleanup Levels		1,000	500	500	5	0.1	varies	5		

LEGEND

- PURPLE INDICATES SUPPLEMENTAL EXPLORATION LOCATION
- MW8 PRE-DEVELOPMENT GROUNDWATER MONITORING WELL (SOUNDEARTH 2018)
- PG03/MW02 MONITORING WELL (PANGEO 2015)
- GA-4 GEOTECHNICAL BORING (GOLDER ASSOCIATES 2007)
- PG02 GEOTECHNICAL BORING (PANGEO 2015)
- PB10 PUSH-PROBE BORING (SOUNDEARTH 2015 & 2018)
- PROPERTY BOUNDARY
- PARCEL BOUNDARY
- 2-FOOT INTERVAL GROUNDWATER CONTOUR
- (45.97') GROUNDWATER ELEVATION
- GROUNDWATER FLOW DIRECTION
- DCE DICHLOROETHENE
- DRPH DIESEL-RANGE PETROLEUM HYDROCARBONS
- GRPH GASOLINE-RANGE PETROLEUM HYDROCARBONS
- ORPH OIL-RANGE PETROLEUM HYDROCARBONS
- PCE TETRACHLOROETHENE
- RED** RED NOTES CONCENTRATION EXCEEDS MTCA METHOD A CLEANUP LEVEL
- TCE TRICHLOROETHENE
- VC VINYL CHLORIDE
- µg/L MICROGRAMS PER LITER
- MTCA WASHINGTON STATE MODEL TOXICS CONTROL ACT
- < NOT DETECTED AT A CONCENTRATION EXCEEDING THE LABORATORY REPORTING LIMIT



COLUMBIA CITY PROPERTY
0996-008
3717 SOUTH ALASKA STREET
SEATTLE, WASHINGTON

FIGURE 1
GROUNDWATER ANALYTICAL RESULTS AND CONTOUR MAP (MAY 14, 2018)



Table 1
Summary of Groundwater Analytical Results for Petroleum Hydrocarbons and CVOCs
Columbia City Property
3717 South Alaska Street
Seattle, Washington

Location	Sample ID	Date Sampled	Sampled By	Analytical Results (µg/L)												
				GRPH ⁽¹⁾	DRPH ⁽²⁾	DRPH with Silica Gel ⁽³⁾	ORPH ⁽²⁾	ORPH with Silica Gel ⁽³⁾	Benzene ⁽⁴⁾	Toluene ⁽⁴⁾	Ethylbenzene ⁽⁴⁾	Total Xylenes ⁽⁴⁾	PCE ⁽⁴⁾	TCE ⁽⁴⁾	cis-1,2-DCE ⁽⁴⁾	VC ⁽⁴⁾
Reconnaissance Groundwater Samples																
PB05	PB05-20150519	05/19/15	SoundEarth	230	180 ^x	--	1,100	--	<0.35	<1	<1	<3	<1	<1	<1	<0.2
PB06	PB06-20150519	05/19/15	SoundEarth	110	360 ^x	--	530	--	<0.35	<1	<1	<3	<1	<1	<1	<0.2
Low-Flow Groundwater Samples																
MW01	MW01-20150521	05/21/15	SoundEarth	<100	<50	--	<250	--	<0.35	<1	<1	<3	<1	<1	<1	<0.2
	MW01-20180514	05/14/18		--	200 ^x	<50	<250	<250	--	--	--	--	--	--	--	--
MW02	MW02-20150521	05/21/15	SoundEarth	100	<50	--	<250	--	<0.35	<1	<1	<3	<1	<1	<1	<0.2
	MW02-20180514	05/14/18		--	610^x	<50	510^x	<250	--	--	--	--	--	--	--	--
MW03	MW03-20180307	03/07/18	SoundEarth	--	510^x	--	<400	--	--	--	--	--	--	--	--	--
	MW03-20180514	05/14/18		--	1,100^x	<50	560^x	<250	--	--	--	--	--	--	--	--
MW04	MW04-20180307	03/07/18	SoundEarth	--	350 ^x	--	<400	--	--	--	--	--	--	--	--	--
	MW04-20180514	05/14/18		--	820^x	<50	520^x	<250	--	--	--	--	--	--	--	--
MW05	MW05-20180514	05/14/18	SoundEarth	--	320 ^x	57 [*]	<250	<250	--	--	--	--	--	--	--	--
MW06	MW06-20180514	05/14/18	SoundEarth	--	280 ^x	<50	<250	<250	--	--	--	--	--	--	--	--
MW8	MW8	08/15/17	Cardno	<100	<91	--	<91	--	<0.50	<1.0	<1.0	<1.0	--	--	--	--
	MW8	10/17/17		<100	<94	--	<94	--	<0.50	<1.0	<1.0	<1.0	--	--	--	--
	MW8	02/01/18		<100	<94	--	<94	--	<0.50	<1.0	<1.0	<1.0	--	--	--	--
	MW8	04/03/18		<100	<100	--	<100	--	<0.50	<1.0	<1.0	<1.0	--	--	--	--
MW9R	MW9R	08/21/17	Cardno	<100	<91	--	<91	--	<0.50	<1.0	<1.0	<1.0	--	--	--	--
	MW9R	10/17/17		190	<96	--	<96	--	<0.50	<1.0	<1.0	<1.0	--	--	--	--
	MW9R	02/01/18		180	<91	--	<91	--	<0.50	<1.0	<1.0	<1.0	--	--	--	--
	MW9R	04/04/18		150	<100	--	<100	--	<0.50	<1.0	<1.0	<1.0	--	--	--	--
MTCA Method A Cleanup Levels for Groundwater				800/1,000⁽⁵⁾⁽⁶⁾	500⁽⁵⁾		500⁽⁵⁾		5⁽⁵⁾	1,000⁽⁵⁾	700⁽⁵⁾	1,000⁽⁵⁾	5⁽⁵⁾	5⁽⁵⁾	16⁽⁷⁾	0.2⁽⁵⁾

NOTES:

Red indicates concentration exceeding MTCA cleanup level.

Chemical analyses conducted by Friedman & Bruya, Inc., of Seattle, Washington.

⁽¹⁾Analyzed by Method NWTPH-Gx.

⁽²⁾Analyzed by Method NWTPH-Dx.

⁽³⁾Analyzed by Method NWTPH-Dx, with silica gel cleanup.

⁽⁴⁾Analyzed by EPA Method 8260C.

⁽⁵⁾MTCA Cleanup Regulation, Chapter 173-340-900 of the WAC, Table 720-1 Method A Cleanup Levels for Groundwater, revised November 2007.

⁽⁶⁾800 µg/L when benzene is present and 1,000 µg/L when benzene is not present.

⁽⁷⁾MTCA Cleanup Regulation, CLARC, Groundwater, Method B, Non-Carcinogen, Standard Formula Value.

Laboratory Note:

*The pattern of peaks present is not indicative of diesel.

< = not detected at a concentration exceeding the laboratory reporting limit

-- = not measured/not analyzed

µg/L = micrograms per liter

Cardno = Cardno Limited

CLARC = Cleanup Levels and Risk Calculations

CVOC = chlorinated volatile organic compound

DCE = dichloroethene

DRPH = diesel-range petroleum hydrocarbons

EPA = U.S. Environmental Protection Agency

GRPH = gasoline-range petroleum hydrocarbons

MTCA = Washington State Model Toxics Control Act

NWTPH = Northwest Total Petroleum Hydrocarbon

ORPH = oil-range petroleum hydrocarbons

PCE = tetrachloroethene

SoundEarth = SoundEarth Strategies, Inc.

TCE = trichloroethene

VC = vinyl chloride

WAC = Washington Administrative Code