

Kent Highlands Landfill Groundwater Compliance Evaluation

Prepared for



May 2019

Prepared by

Parametrix

Kent Highlands Landfill Groundwater Compliance Evaluation

Prepared for

Seattle Public Utilities

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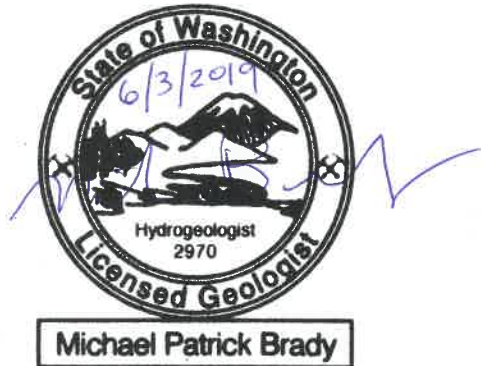


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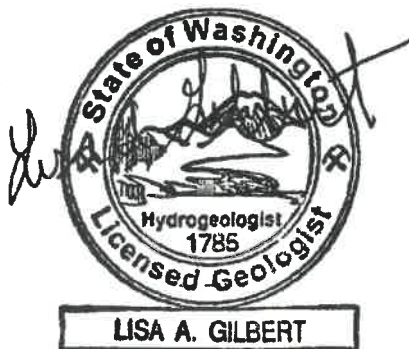
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Kent Highlands Landfill Groundwater
Compliance Evaluation.
Prepared by Parametrix and EHS-International, Inc.
Seattle, WA. May 2019.

CERTIFICATION

The technical material and data contained in this document were prepared under the supervision and direction of the undersigned, whose seal, as a professional hydrogeologist licensed to practice as such, is affixed below.



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ACRONYMS AND ABBREVIATIONS

µg/L	micrograms per liter
ARARs	applicable or relevant and appropriate requirements
CAP	Cleanup Action Plan
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
City	City of Seattle
CLARC	Cleanup Levels and Risk Calculations
COCs	contaminants of concern
DCE	cis-1,2-dichloroethene
DO	dissolved oxygen
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
ft/ft	Feet per Feet
GA	Gravel Aquifer
GCMP	Groundwater Compliance Monitoring Plan
INMI	International Manganese Institute
kg/L	kilograms per liter
LA	Landfill Aquifer
LOA	Lower Outwash Aquifer
MCL	Maximum Contaminant Level
mg/L	milligrams per liter
MNA	monitored natural attenuation
MOA	Middle Outwash Aquifer
MTCA	Model Toxics Control Act
nM	Nanomoles
NOAEL	no-observed adverse effect level
NPL	National Priorities List
ORC-A	Oxygen Release Compound – Advanced®
PCE	tetrachloroethylene
PMTDI	provisional maximum tolerable daily intake
POC	point of compliance
Qal	Quaternary Alluvial

ACRONYMS AND ABBREVIATIONS (CONTINUED)

Qpfc	Quaternary Pre-Fraser Coarse Grained
Qva	Quaternary Vashon Advance Outwash
Qvi	Quaternary Vashon Ice-contact
Qvt	Quaternary Vashon Till
RA	Risk Assessment
RAA	Recent Alluvium Aquifer
redox	oxidation-reduction
RI	remedial investigation
RVs	regulatory standards
SA	Sand Aquifer
SCLs	Shewhart control limits
Site	Kent Highlands Landfill
SPU	Seattle Public Utilities
TCE	trichloroethylene
TL	tolerance limit
UCL95	upper 95 confidence limit on the mean
UOA	Upper Outwash Aquifer
VOC	volatile organic compound
WAC	Washington Administrative Code
WHO	World Health Organization

1. INTRODUCTION AND BACKGROUND

The Kent Highlands Landfill (Site) encompasses approximately 114 acres of land located on the hillside and upland just west of the Green River Valley (see Figure 1). The landfill is composed of King County parcel numbers 726020115, 1522049066, 1522049008, 1522049007, 1522049012, 0002000001, 0002000023, 0002000005, 0002000010, 0002000012, and 0002000022. The landfill occupies a historical natural ravine that extended from the Des Moines Upland easterly towards the Green River Valley floor. The elevation of the Site near the landfill ranges from 325 feet down to 35 feet above sea level. An engineered filling of a natural ravine on the hillside occurred from 1968 to 1986.

Seattle Public Utilities (SPU) used the landfill from 1968 to 1986 mainly for disposal of domestic and municipal garbage; however, from 1983 to 1986 industrial waste and construction debris also were disposed of. The Site was placed on the National Priorities List (NPL) in 1990 under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The U.S. Environmental Protection Agency (EPA) reached an agreement with the Washington State Department of Ecology (Ecology) for Ecology to be the lead agency overseeing cleanup actions, and subsequently cleanup at the Site has been performed under the regulations presented in the Model Toxics Control Act (MTCA; Chapter 173-340 Washington Administrative Code [WAC]).

1.1 Objectives

Ecology performs periodic reviews of the Site every five years. The Fourth Periodic Review for the Kent Highlands Landfill (Ecology 2014) identified the following action item, and this report has been prepared to address this objective:

Evaluate Additional Cleanup Measures for Ongoing Exceedances of Regulatory Values in Ground Water. Ecology is requesting that further engineering evaluations be conducted to determine ways to reduce ongoing ground water quality exceedances at various downgradient points of compliance. Although there has been some decline in contaminant concentrations with time, it is now clear that the existing leachate collection system is not going to be able to reduce vinyl chloride, manganese, and iron concentrations to applicable cleanup levels (regulatory values) at the point of compliance within a reasonable time frame.

To provide background to support and evaluate remedial options, Section 1 of this report summarizes findings of the remedial investigation and risk assessment used to establish the Site compliance criteria. In Section 2, current Site conditions and applicable or relevant and appropriate requirements (ARARs) are reviewed to assess whether any changes have occurred that could affect the compliance determination, and in Sections 3 and 4 current groundwater quality conditions for manganese, iron, and vinyl chloride are summarized. Finally, in Section 5 current remediation status and additional potential remedial options and their costs and benefits are evaluated, and in Section 6 recommendations are provided.

1.2 Remedial Investigation and Risk Assessment

A remedial investigation (RI) of the Site was conducted in 1991 to identify the nature and extent of contamination emanating from the Site and evaluate potential impacts to human health and the environment (CH2MHill 1991). Several media-specific investigations were conducted to evaluate Site characteristics and contamination extent, including hydrogeologic conditions beneath the landfill and the surrounding area, and groundwater and leachate occurrence, movement, and quality.

The RI found no indications in groundwater of leachate contamination (concentrations above primary drinking water standards) migrating offsite, and no effects of the landfill on water quality in samples collected from the Green River. Water quality in Midway Creek, which flows through the eastern end of the Site at the toe of the landfill, was determined to be degraded by contaminants originating from urban runoff upstream of the landfill.

The Risk Assessment (RA) completed as part of the RI (CH2MHill 1991) determined that although the groundwater quality in the upper zone of the Recent Alluvium Aquifer (RAA) had been affected by leachate, there would be no future exposures in groundwater since landfill-derived contaminants would not migrate to a shallow well installed on the east side of the Green River. The RI determined groundwater flow is easterly discharging to the Green River. The Green River is the ultimate discharge point of local groundwater flow as characterized by upward hydraulic heads from underlying aquifers into the shallow RAA, indicating there is no or limited groundwater flow locally beneath the Green River due to the vertical gradient. Installation of a commercial well on the east side of the Green River was believed to be unlikely because of the poor water quality and low yield potential. Installation of a groundwater well along any of the Site boundaries was also believed to be very unlikely because of regulatory constraints and availability of water from the municipal water supply.

Surface water was determined to be a potential pathway for future exposure. Therefore, groundwater cleanup standards were established using surface water criteria due to the proximity to the Green River, a natural discharge point of the local aquifers.

1.3 Cleanup Action Plan and Remedy

The Cleanup Action Plan (CAP) determined that the MTCA Method B cleanup standards contained in WAC 173-700 through WAC 17-340-760 were demonstrated in the RA prepared for the RI to have been met at this Site under existing conditions. The proposed closure actions were expected to provide continued protection of human health and the environment; therefore, the risk levels posed by the Site were expected to further decrease as the actions were implemented.

Following the RI, construction of the Site's remedy was completed in 1995 and included landfill gas, stormwater, and leachate control measures. Active groundwater remediation was not included in the Site remedy since no risks were determined by the RA to be present via the groundwater or surface water migration and exposure routes.

1.4 Hydrogeologic Conceptual Model

Prior investigations show the subsurface hydrogeology of the Site is complex, with perched groundwater zones in addition to regional confining layers and aquifers. Booth & Waldron (2004) map the upland surface geology of the subject property primarily composed of Quaternary Vashon Till (Qvt) deposits. Lower in elevation, the Qvt directly overlies Quaternary Vashon Advance Outwash (Qva) deposits. Quaternary Pre-Fraser Coarse Grained (Qpfc) deposits are mapped below the Qva at further lower elevations along the historical ravine. At the base of the upland, Quaternary Vashon Ice-contact (Qvi) deposits are mapped, and at the base of the Green River Valley are Quaternary Alluvial (Qal) deposits.

The RI of the Site (CH2MHill 1991) delineated these geologic units of the area into site-specific hydrostratigraphic units including:

- The Landfill Aquifer (LA)
- Recent Alluvium Aquitard
- Recent Alluvium Aquifer (RAA)

- Upper Outwash Aquifer (UOA)
- Middle Outwash Aquifer (MOA)
- Lower Outwash Aquifer (LOA)
- Upper Silt Aquitard, Sand Aquifer (SA)
- Lower Silt Aquitard
- Gravel Aquifer (GA)

The physical conceptual Site model developed for the RI is attached as Figure 2. As shown on the figure, the discharge point for the landfill is within the RAA in the Green River Valley. Groundwater monitoring is evaluated in wells completed in the two downgradient aquifers: the SA and RAA, and compliance is determined based on three RAA wells (KMW-10A, KMW-17, and KMW-19A) located near the toe of the landfill near the discharge point with the Green River Valley (Figure 3).

The SA is the regional shallow aquifer of the Des Moines Upland. It is unconfined on the western upland portion of the Site and becomes confined on the lower eastern portion of the Site. The SA is primarily recharged through lateral flow from the west and also through vertical flow from the overlying LOA. Groundwater from the SA discharges to the RAA, although within the landfill area, a small amount is intercepted by the leachate collection system.

The RAA consists of saturated sand and silty sand deposited by the Green River channel and overbank flood deposits. Except for local areas where silt beds confine the aquifer, the RAA is generally under water table conditions. The RAA is recharged by precipitation, the Green River, Midway Creek, and the SA, GA, LA, and lower alluvial aquifers.

At the discharge point of the SA at the toe of the landfill, the SA is immediately below the RAA. The SA has higher hydraulic heads, indicating an upward vertical groundwater gradient from the SA to the RAA. Similarly, lower alluvial deposits have flowing artesian head above the hydraulic head of the RAA indicating that the RAA and Green River are the ultimate local discharge points for groundwater flow.

1.5 Groundwater Compliance Criteria

In 1996, the Kent Highlands Landfill Groundwater Compliance Monitoring Plan (CH2MHill 1996; GCMP) was implemented for the Site and established the criteria for confirmation monitoring that are used to determine groundwater compliance. Since the CAP determined that the Method B cleanup standards were demonstrated to have been met at the Site under existing conditions, the objective of the confirmation monitoring is to confirm that groundwater quality at the Site does not deteriorate from that which was documented during the RI, does not deteriorate from upgradient or background groundwater quality, and does not exceed regulatory standards. The compliance monitoring wells established by the GCMP (KMW-10A, KMW-17, and KMW-19A) are completed in the RAA and located near the toe of the landfill near the discharge point with the Green River Valley.

The compliance monitoring plan for manganese and iron uses control charts with three components including Shewhart control limits (SCLs), background conditions/tolerance limit (TLs), and regulatory standards (RVs). The GCMP states that an out-of-compliance condition for groundwater would occur for conventional and inorganic parameters if the baseline conditions (SCL, TL, and RV) were all exceeded in any of the compliance wells (RAA wells KMW-10A, KMW-17, and KMW-19A) for two consecutive monitoring events.

Under the GCMP, SCLs were established for all wells and parameters, except for those that showed excessive variability during the period following the RI, including manganese and iron concentrations in compliance well KMW-19A. Ecology determined in the Third Periodic Review that compliance for KMW-19A would be determined solely by comparison to the TL and RV.

For volatile organic parameters, such as vinyl chloride, exceedances of the RVs are used in determining compliance. The upper 95 confidence limit on the mean (UCL95) of the most recent eight quarterly measurements is calculated for the parameter and compared with the RV.

At the time of the RI, laboratory detection levels for some chemicals were higher than cleanup standards and many contaminants were eliminated as primary contaminants of concern (COCs). Vinyl chloride, iron, and manganese were included as COCs due to exceedances of applicable cleanup standards at the time the GCMP was established in 1996.

2. COMPLIANCE UPDATES

This section reviews compliance determinations as presented in Ecology's Five-Year Review reports, including a proposed change to the point of compliance, and presents updates to the conditions that were used to prepare the RA exposure assessment.

2.1 Compliance Determinations

In the Second Periodic Review, Ecology (2003) identified that manganese was out of compliance in monitoring well KMW-19A because concentrations exceeded the TL and RV, and vinyl chloride was out of compliance in wells KMW-10A and KMW-17 due to exceedances of the RV. The Third and Fourth Periodic Reviews (Ecology 2009, 2014) continued to observe these findings, and noted that iron was out of compliance in well KMW-19A.

In the Third Periodic Review (Ecology 2009), Ecology agreed to change the method for determining compliance based on a request from the SPU to modify the procedure to be in accordance with MTCA, WAC 173-340-720 (9)(c)(iii)(A). This subsection requires compliance for carcinogenic compounds to be determined through calculation of the true mean concentration. Ecology accepted the proposal, while noting that the provisions of WAC 173-340-720(9)(e) must also be met. Also, the true mean must be a running average reflecting the previous four quarters of data. The running averages must themselves meet cleanup levels for at least two years (a total of eight running averages) for the Site to be considered in compliance.

2.2 Point of Compliance Revision

At the time of the RI in 1991, the location of the eastern property boundary and point of compliance was sited along Frager Road. In 2007, SPU conducted additional research with regard to the legal property boundary and found documentation that showed the property line to be at the western edge of the Green River east of Frager Road. SPU has requested recognition and approval of the revised property boundary and acknowledgement that the point of compliance (POC) in this portion of the Site be moved from KMW-17 to KMW-17Z. KMW-17Z is closer to the revised property boundary than KMW-17 and is more representative of groundwater conditions just prior to the discharge to the Green River.

In the Third Periodic Review Ecology noted:

The City is requesting that the property boundary along the Green River side of the Site be adjusted based on historical research conducted by the City. The effect of the proposed adjustment would be to move the property line closer to the river. If Ecology agrees with the adjustment, based on review by the Attorney General's office, the City requests that well KMW-17Z be substituted for KMW-17 as the compliance well in this part of the Site. The proposed replacement well is further downgradient, and typically has lower contaminant concentrations.

To date, the revised point of compliance has not been accepted by Ecology or the Attorney General's office. Based on the documentation and location of KMW-17Z, the point of compliance revision appears to meet applicable MTCA criteria for the Site.

2.3 Exposure Assessment Update

The physical conceptual site model developed for the Site during the RI (see Figure 2) shows the local groundwater flow regime for potential human exposure to landfill contaminants via the groundwater migration route. The RI determined that landfill-derived contaminants would not migrate to a shallow well installed on the east side of the Green River because vertical gradients beneath the RAA are upward. Groundwater measurements collected in well pairs since the RI (Parametrix 2015) have continued to indicate upward vertical gradients.

An updated water well inventory was completed in 2019 for the area surrounding the Site (Parametrix and EHSI 2019) to address one of the action items identified in the Fourth Periodic Review (Ecology 2014) to evaluate whether any new wells have been installed downgradient of the landfill since the RI. The updated water well inventory shows no active or potentially active drinking water wells within 1,000 feet of the landfill. However, a well was recently completed in 2016 (the Stearns Well) on the adjoining property south of the landfill along Frager Road. This well is within approximately 1,500 feet of the landfill. Although the well is not directly downgradient of the landfill since groundwater flow is toward the east, SPU has recommended that the well owner be contacted to identify how the well is being used.

As noted in the RA, exposure to landfill contaminants via the groundwater migration route appears to be controlled at the Site. Additional discussion regarding the groundwater compliance related to manganese and iron, and vinyl chloride is provided in the following sections.

3. MANGANESE AND IRON

Section 3.1 describes work previously presented to address the out-of-compliance condition for manganese and iron identified in the Second Periodic Review (Ecology 2003). Section 3.2 reviews applicable manganese and iron ARARs, Section 3.3 summarizes local and regional background concentrations, and Section 3.4 presents recommendations for RV changes.

3.1 Second Periodic Review Response

The Second Periodic Review Response (Floyd|Snider 2007) analyzed conditions that would lead to the observed high degree of variability and elevated manganese concentrations in well KMW-19A, as summarized below. These conditions are also applicable to iron.

In general, biological degradation of organic materials present in the landfill causes groundwater to become anaerobic, creating reducing conditions where naturally occurring manganese leaches from aquifer materials into groundwater. Because of the extreme sensitivity of manganese to changes in oxidation-reduction (redox) conditions, the observed variations in manganese concentrations in compliance well KMW-19A likely reflect changing manganese solubility as redox conditions vary in groundwater. In addition to leachate impacts, redox conditions also vary due to naturally occurring conditions.

At the time of the Second Period Review Response, it was noted that manganese concentrations in SA well KMW-12A that flows toward KMW-19A were trending downward but remained greater than those in KMW-19A. The variations in manganese concentrations in KMW-19A may be a function of how much SA groundwater (as represented by the quality at KMW-12A) is reaching KMW-19A. There is likely to be little opportunity for oxygenation of groundwater as it leaves the SA and enters the RAA. The RAA is overlain by 20 feet of silty deposits of the RA Aquitard, which act as a barrier for recharge with oxygenated groundwater. Furthermore, the floodplain area between the landfill and the Green River is largely a wetlands area that is naturally low in oxygen and rich in organic materials, providing little opportunity for oxygenation of groundwater and precipitation of manganese prior to discharge to the Green River. As groundwater does discharge into the oxygen-rich river waters, however, manganese is likely to immediately precipitate into a solid phase.

The Second Periodic Review Response recommended using the MTCA Method B groundwater value of 2.2 milligrams per liter (mg/L) as the RV instead of the secondary criteria of 0.05 mg/L.

3.2 Applicable or Relevant and Appropriate Requirements Review

ARARs for manganese and iron are reviewed in the following sections.

3.2.1 Manganese

A secondary standard of 0.05 mg/L has been established for manganese (WAC 173-200), but this criterion is based on water discoloration, not health risks

Manganese is an essential nutrient for humans and animals (EPA 2004). Adverse health effects can be caused by inadequate intake or overexposure, although manganese deficiency in humans is thought to be rare because manganese is present in many common foods.

No Maximum Contaminant Level (MCL) has been established for manganese. However, the World Health Organization (WHO) has established a guideline of 0.4 mg/L (WHO 2011). The WHO study states that no quantitative information is available to indicate toxic levels of manganese in the diet of humans, and because of the homeostatic control that humans maintain over this mineral, manganese is generally not considered to be very toxic when ingested with the diet. The upper range manganese intake value of

11 milligrams per day from dietary studies is considered a no-observed adverse effect level (NOAEL). This NOAEL was used to calculate the 0.4 mg/L guideline.

Ecology's Cleanup Levels and Risk Calculations (CLARC) database contains information to help establish cleanup levels for hazardous waste sites to comply with MTCA (Ecology 2015). A Method B non-carcinogenic risk-based standard of 2.24 mg/L has been established for manganese in groundwater.

3.2.2 Iron

A secondary standard of 0.3 mg/L has been established for iron (WAC 173-200), but this criterion is based on water discoloration, not health risks. No health-based guideline values for iron have been proposed, although an analysis by WHO (WHO 2003) proposed a drinking water standard of about 2 mg/L as a precaution against storage of excessive iron in the body. This was based on a provisional maximum tolerable daily intake (PMTDI) of 0.8 milligrams per kilogram of body weight, which applies to iron from all sources except for iron oxides used as coloring agents, and iron supplements taken during pregnancy and lactation or for specific clinical requirements. Allocation of 10 percent of this PMTDI to drinking water gives a value of about 2 mg/L, which does not present a hazard to health. The taste and appearance of drinking water will usually be affected below this level, although iron concentrations of 1 to 3 mg/L can be acceptable for people drinking anaerobic well water.

Ecology (2015) has established a Method B non-carcinogenic risk-based standard of 11.2 mg/L for iron in groundwater. Criteria for iron in surface water are 1 mg/L based on Aquatic Life Fresh/Chronic exposure (Clean Water Act §304; Ecology 2015).

3.3 Local and Regional Background Concentrations

Background conditions at the Site have been characterized at SA well KMW-13 and RAA well KMW-15A, as reflected in the calculated TLs. The most recent TLs calculated for manganese and iron (Parametrix 2019) in the SA (0.75 mg/L and 1.20 mg/L) and RAA (0.548 mg/L and 13.26 mg/L), respectively, are above the current RVs of 0.05 mg/L and 0.3 mg/L.

The background conditions at the Site are within the range of regional data. Woodward et al. (1995) evaluated naturally occurring concentrations of manganese and iron from over 200 water samples from groundwater wells (221 samples for iron, 220 samples for manganese) in southwestern King County as an areawide study and found many occurrences above RVs.

- Manganese concentrations exceeded the MCL of 0.05 mg/L in 44 percent of the groundwater samples with an overall average concentration of 40 micrograms per liter (µg/L).
- Iron concentrations exceeded the MCL of 0.3 mg/L in 15 percent of the groundwater samples with an overall average concentration of 35 µg/L.

Woodward et al. also evaluated manganese and iron concentrations for the RAA (Qal deposits) and the SA (Qva deposits), as summarized below:

- In the RAA, manganese concentrations averaged 25 µg/L in the RAA, ranging from <1 up to 800 µg/L, and iron concentrations averaged 41 µg/L in the RAA, ranging from <3 µg/L up to 2,700 µg/L.
- In the SA, manganese concentrations averaged 19 µg/L in the SA, ranging from <1 up to 810 µg/L and iron concentrations averaged 25 µg/L in the SA, ranging from <3 up to 10,000 µg/L.

The range of redox conditions and naturally occurring manganese concentrations in aquifer materials in the region also make it difficult to identify a natural background concentration for manganese in groundwater (represented by the TL). Therefore, it may not be appropriate to compare manganese

concentrations in downgradient wells to the TL as a measure of compliance. Manganese concentrations in the other two compliance wells are also higher than the TL.

3.4 Current Conditions

Historical concentrations of manganese and iron at the Site are summarized in Appendix A and time-series plots showing trends in concentrations over time are presented in Figures 4 and 5. Concentrations of manganese and iron in well KMW-19A continue to exceed both the TL and RV and constitute an out-of-compliance condition for the Site.

Manganese concentrations at the Site are above the RV of 0.05 mg/L in all eleven of the monitored wells. In most of the wells, manganese concentrations are currently lower than those measured during the RI, with the most notable decreases occurring in SA wells KMW-12A and KMW-16B, although manganese concentrations in SA background well KMW-13 have increased slightly. The highest manganese concentrations at the Site occur in SA well KMW-18A. Current manganese concentrations in RAA well KMW-19A are comparable to those in SA wells KMW-12A and KMW-16B and in RAA wells KMW-10A and KMW-16A. Lower manganese concentrations are generally observed in RAA wells KMW-17 and KMW-17Z than in RAA background well KMW-15A.

Iron concentrations at the Site are above the RV of 0.3 mg/L in seven of the 11 monitored wells (KMW-10A, KMW-15A, KMW-16A, KMW-17, KMW-17Z, KMW-19A, and KMW-13), and have been consistently higher in the RAA wells. Since the RI, iron concentrations have decreased in SA well KMW-12A but have increased in SA well KMW-13. Iron concentrations have decreased in some of the RAA wells (KMW-10A, KMW-16A, and KMW-17) but have stabilized or increased in some wells near the Green River over the past approximately 10 years (background well KMW-15A and wells KMW-17Z, and KMW-19A). Concentrations in well KMW-19A are currently the highest observed at the Site.

As summarized in the Second Periodic Review Response, the anaerobic conditions causing the observed manganese and iron concentrations are believed to be related to a variety of factors including biological decay of leachate-impacted groundwater and naturally occurring low oxygen conditions related to the wetlands. Manganese and iron are expected to precipitate when they encounter the more oxygenated waters of the Green River.

The iron increases in the RAA wells over the past few years, including KMW-19A and background well KMW-15A may be related to increased beaver activity that has created wetland areas. KMW-19A is located south of the landfill toe where leachate flow would primarily be cross-gradient, but near natural spring discharges to Midway Creek where surface water has been documented to contain from 500 µg/L up to 1,000 µg/L of dissolved iron. There has been recent beaver dam creation on Midway Creek, and the entire area surrounding KMW-19A has been affected by surface water. This can be seen in aerial photographs of the Site documenting encapsulation of previously forested land with wetlands between the years 2009 and 2012. The years of wetland formation correspond to increases in iron concentrations in well KMW-19A and the concentrations may be affected by resulting surface water-groundwater interactions.

These observations indicate evaluation of iron and manganese in the shallow RAA, particularly for compliance well KMW-19A, may not be useful in determining compliance due to natural interference in the data.

3.5 Discussion and Recommendations

As stated in the Third Periodic Review (Ecology 2009), manganese and iron do not present a human health or ecological risk at the concentrations present in groundwater at the Site but could cause aesthetic problems such as staining of porcelain fixtures. Therefore, for manganese, it is recommended, as stated in the Second Periodic Review Response, that the MTCA Method B groundwater value of

2.24 mg/L be used as the RV instead of the secondary criteria of 0.05 mg/L. For iron, it is recommended that the MTCA Method B groundwater value of 11.2 mg/L be used as the RV instead of the secondary criteria of 0.3 mg/L.

Further support for the recommended revisions to the RVs is the lack of potential exposures to these secondary contaminants. The increased dissolved oxygen in surface waters of the Green River, the natural discharge point of the RAA, will result in precipitation of manganese and iron. The previously completed RA shows no risks east of the Green River in shallow wells and the updated well inventory shows no active groundwater wells within 1,000-feet of the landfill. The Site property boundary extends to the Green River.

4. VINYL CHLORIDE

Section 4.1 describes work previously presented to address the out-of-compliance condition for vinyl chloride identified in the Second Periodic Review (Ecology 2003), Section 4.2 reviews applicable ARARs, Section 4.3 summarizes current trends in vinyl chloride concentrations, and Section 3.4 summarizes the status.

4.1 Second Periodic Review Response

The Response to the Second Periodic Review (Floyd|Snider 2007) included a Geoprobe investigation and installation of new monitoring well KMW-17Z further downgradient from well KMW-17. The Geoprobe investigation was conducted downgradient of well KMW-17 to evaluate the presence or absence of vinyl chloride closer to where groundwater discharges to the Green River. A groundwater sample was collected from Geoprobe boring FS-1 and found to contain vinyl chloride, cis-1,2-dichloroethene, and acetone. Based on this information a new groundwater monitoring well was installed within 5 feet of FS-1 and identified as well KMW-17Z. This new well was screened at an equivalent elevation to KMW-17.

Groundwater modeling using EPA's natural attenuation model BIOSCREEN (EPA 1996) was performed to estimate the vinyl chloride concentration at the point of discharge to the Green River and to develop proposed remediation levels using groundwater concentrations measured in wells KMW-17 and KMW-17Z. BIOSCREEN accounts for advection, dispersion, sorption/desorption, and biodegradation processes. Inputs to the model used Site-specific data (gradient, porosity, etc.) that remain valid. However, the predicted timeframe for reaching compliance at the Site was too soon since the modeling data were compared to a vinyl chloride RV of 0.25 µg/L (the Method C groundwater cleanup value) instead of the Method B groundwater cleanup level of 0.029 µg/L at that time.

4.2 ARAR Review

During the RI, the practical quantitation limit for vinyl chloride was 10 µg/L, above the primary MCL of 2 µg/L, and the RV was initially established at 10 µg/L. Due to advances in laboratory methodology, Ecology lowered the RV in the Second Periodic Review (Ecology 2003) to the MTCA Method B groundwater cleanup level of 0.029 µg/L. In 2005, the EPA published final guidelines for carcinogen risk assessment, revising preceding versions of the guidelines. The updated guidelines showed an updated human health criterion for exposure to surface water (and freshwater organisms) of 0.025 µg/L. In 2009, Ecology updated the state surface water human health risk criteria to match the EPA levels. Subsequently, in the Third Periodic Review (Ecology 2009) the RV for vinyl chloride was reduced from 0.029 µg/L to the current RV of 0.025 µg/L.

The current vinyl chloride RV of 0.025 µg/L for the Site was established based on cancer risks to a person drinking the surface water of the Green River or groundwater near the landfill while also eating fish biota from the Green River. As public drinking water supply is available to nearly all surrounding properties, this situation is not likely, and the chance of exposure is further reduced since vinyl chloride is expected to volatilize rapidly in surface water as shown by WHO (WHO 1999), which determined that volatilization of vinyl chloride in surface water occurs within 1 to 40 hours.

4.3 Current Conditions

Vinyl chloride concentrations measured in groundwater through 2018 are summarized in Appendix A and time-series plots for vinyl chloride by aquifer are presented in Figure 6. Vinyl chloride concentrations continue to be above the RV in compliance wells KMW-10A and KMW-17, and in well

KMW-17Z located near the Green River at the proposed point of compliance, because the UCL95 of the most recent eight measurements exceed the established RV of 0.025 µg/L.

The time series plots show overall decreasing trends in vinyl chloride concentrations in both the RAA and the SA. In the RAA, vinyl chloride has been decreasing in compliance wells KMW-10A, KMW-17, and KMW-17Z and remains non-detected in compliance well KMW-19A and KW-15A (upgradient). In the SA, vinyl chloride has been decreasing in well KMW-12A and remains non-detected in wells KMW-08A, KMW-13 (upgradient), KMW-16B, and KMW18A. The continuing decreases in vinyl chloride concentrations are due to natural attenuation of the landfill contaminants.

In September 2018 (Parametrix 2019), the only wells where vinyl chloride concentrations were above the RV of 0.025 µg/L were KMW-17 (0.362 µg/L), KMW-17Z (0.0669 µg/l), and KMW-12A (0.0921 µg/L). KMW-12A is located south-southeasterly of the toe of the landfill near the natural historical surface water discharge point of the historical ravine. KMW-17 and KMW-17Z are located near natural aquifer discharge points in the Green River Valley.

4.4 Discussion and Summary

Vinyl chloride is a product of aerobic and anaerobic degradation of chlorinated solvents (such as tetrachloroethylene [PCE] and trichloroethylene [TCE]) released from waste disposed at the Site. The current RV of 0.025 µg/L is based upon humans drinking locally contaminated surface or groundwater while simultaneously consuming fish that have been exposed to the contaminant. There is no current documented surface water consumption near the landfill, and volatilization of vinyl chloride is a rapid process for removal of vinyl chloride introduced into surface waters, with a half-life ranging from about 1 to 40 hours. Although vinyl chloride is currently above the RV at the discharge point to the Green River, no exposure is believed to be occurring. The updated water well inventory (Parametrix and EHSI 2019) shows there are no active or potentially active wells within 1,000 feet of the landfill, and nearly all properties surrounding the Site are supplied with public drinking water.

5. POTENTIAL REMEDIAL OPTIONS AND ASSOCIATED COSTS

Ecology has requested SPU determine remedial options at the Site that could reduce concentrations of vinyl chloride to below RVs at the recommended modified point of compliance (the SPU property boundary at the Green River). To provide support for potential remedial options, Section 5.1 summarizes geochemical processes occurring in landfills that are expected to be present in Site groundwater. Sections 5.2 through 5.4 present potential remedial options and their costs, and Section 5.5 provides a summary of remedial options.

Remedial options evaluated in this section include monitored natural attenuation (MNA), air sparging/air stripping and vapor extraction, and injection of chemical adjuncts, including ORC-Advanced® and Plumestop™.

5.1 Review of Landfill Geochemical Processes

The concentrations of all three COCs are related to biodegradation of landfill contaminants through aerobic and anaerobic processes. Available oxygen is quickly used by microbes and anaerobic degradation begins near the refuse. Methanogenesis occurs next following conversion of available carbon dioxide to methane. As all available carbon dioxide become spent by microbes, the process switches to sulfate reduction as sulfate is converted to hydrogen sulfide. Once sulfate is spent by microbes, the next reduction is through iron conversion from ferrous iron to ferric. This creates more soluble iron within groundwater. Once iron conversion is spent, the next reduction is manganese dioxide oxidized to manganese (-2). Similarly, this creates more soluble manganese within the aquifer. Following manganese dioxide reduction is nitrate reduction to nitrogen. Two of the primary inorganic COCs for the Site (soluble manganese and iron) are tied to the anaerobic processes occurring at the landfill:

- Aerobic: Oxidation-reduction
- Anaerobic: Methanogenesis
- Anaerobic: Sulfate Reduction
- Anaerobic: Iron-reduction (creates more soluble Ferric Iron)
- Anaerobic: Manganese-reduction (creates more soluble Manganese)
- Anaerobic: Nitrate reduction

Anaerobic degradation at the Site is key to the natural reductive dechlorination of chlorinated solvents such as PCE and TCE to their daughter product cis-1,2-dichloroethene (DCE) and vinyl chloride. The apparent natural degradation pathway often requires anaerobic conditions as all available electrons are spent through the degradation process.

EPA guidance (1998) states that in general, reductive dechlorination of chlorinated ethenes occurs by sequential dechlorination from PCE to TCE to DCE to vinyl chloride to ethene. Depending upon environmental conditions, this sequence may be interrupted, with other processes then acting upon the products. With sufficient quantities or appropriate types of electron donors (e.g., slow but steady H₂-production), the final end-product of anaerobic reductive dehalogenation can be ethene. Reductive dehalogenation of chlorinated solvent compounds is associated with the accumulation of daughter products and an increase in chloride. One or more of the following generally is observed at a site where reductive dechlorination of alkenes is ongoing:

- 1) Ethene is being produced (even low concentrations are indicative of biodegradation);
- 2) Methane is being produced;

- 3) Iron II is being produced;
- 4) Hydrogen concentrations are between 1-4 nanomoles (nM); and
- 5) Dissolved oxygen concentrations are low.

This aerobic to anaerobic degradation process is important for understanding the production of landfill contaminants of iron, manganese, and vinyl chloride. Source removal at the Site is not an option. Therefore, remedial actions undertaken at the Site are best suited for implementation downgradient of the degradation/reduction zone at the toe of the landfill near the discharge point with the Green River.

5.2 Monitored Natural Attenuation

5.2.1 Natural Attenuation Modeling

The EPA's analytical model BIOSCREEN can be used to determine whether natural attenuation processes are capable of meeting site-specific remediation objectives at some distance downgradient of a source. EPA's analytical model BIOCHLOR is a similar analytical model designed to simulate remediation by natural attenuation of dissolved solvents such as vinyl chloride at chlorinated solvent release sites.

The BIOSCREEN modeling conducted as a response to the Second Periodic Review (Floyd|Snider 2007) was updated using current vinyl chloride concentrations. Additionally, new modeling using BIOCHLOR (EPA 2000) was completed to evaluate natural attenuation of vinyl chloride at the Site, and the results were compared to the RV of 0.025 µg/L. The modeling results provide an updated projection of the timeframe for achieving compliance at the property boundary with the Green River, located 200 feet away from KMW-17, and for well KMW-17Z, located 140 feet downgradient from well KWM-17. The BIOCHLOR model has an updated feature that allows evaluation of source decay, a process that would be expected at the Site.

5.2.1.1 Model Inputs

The model was calibrated using vinyl chloride and hydraulic gradient data for several different scenarios.

Basic inputs to the model are listed below. Most of the input parameters were the same as used in the 2007 modeling, although some were adjusted as noted during the model calibration process so that the model results accurately reflected the existing Site conditions. Copies of the modeling scenarios are attached in Appendix B.

- Hydraulic Conductivity: 0.005 centimeters per second (cm/sec)
- Hydraulic Gradient: 0.004357 ft/ft (changed from 0.004 ft/ft, see above)
- Porosity: 0.35
- Estimated plume length: 280 (Changed from 200 up to 280 feet)
- Soil bulk density: 1.67 kilograms per liter (kg/L)
- Octanol-water partitioning coefficient (Koc): 56
- Fraction organic carbon (foc): 0.005 mg/L
- Model area length: 200 feet
- Modeled area width: 1,000 feet (changed from 250 feet up to 1,000 feet to closely resemble the toe of the landfill)

- Simulation time: 50 years (changed from 100 years down to 50 years, as 50 years is the current date of the landfill)
- Source thickness: 30 feet
- Source Area Width: 500 feet

The BIOSCREEN and BIOCHLOR scenarios were modeled using 2018 vinyl chloride concentrations and the groundwater gradient of 0.004357 ft/ft observed between KMW-17 and KMW-17Z during 2018. Previous calculations (Floyd|Snider 2007) used the four-year running quarterly average of the vinyl chloride concentration and the average hydraulic gradient of 0.004 ft/ft in the RAA measured between KMW-17 and the Green River at KWS-1 from 1999 to 2004.

The BIOSCREEN model projects first-order of decay degradation. One BIOCHLOR scenario projects first-order of decay using a continuous source, and the other BIOCHLOR scenario projects first-order of decay using a degrading source, which is expected of a landfill. The evaluation of degrading sources is the most effective way to determine ongoing natural attenuation at sites (EPA 1999).

The degradation of the source area (near KMW-17) was evaluated using a natural log linear regression technique (Newell et al. 2002) to determine the degradation constant of the source area. The degradation constant is the most fundamental evaluation with respect to contaminants from sources such as a closed landfill, where there are no longer additional new sources. The degradation constant effectively evaluates the decay of the source area over time to allow for future projection of contamination through natural degradation. The solution of the degradation for the Site is:

$$Y = e^{-0.0752X} \quad \text{where } Y = \text{concentration of vinyl chloride in } \mu\text{g/L}, X \text{ is years since 2005.}$$

Or more appropriately written for the Site:

$$X = -\ln(Y) / 0.0752$$

5.2.1.2 Model Results

Calibration of the model for the three scenarios resulted in adjusted solute half-lives for vinyl chloride of ranging between 0.67 years up to 1.9 years, which are within the range of literature values for net vinyl chloride degradation (0.00183/day to 0.0052/day) cited by Aronson and Howard (1997).

The inputs and model results are shown on Table 1. The updated models calculate vinyl chloride is currently out of compliance at the Green River discharge point based upon the 2018 data. The models calculate current groundwater concentrations discharging into the Green River to be between approximately 0.033 $\mu\text{g/L}$ and 0.034 $\mu\text{g/L}$, which is 0.08 to 0.09 $\mu\text{g/L}$ above the RV. The model indicates that at a distance of approximately 250 feet, or the opposite side of the Green River, current vinyl chloride values are in compliance with the RV.

Table 1. Results of Updated BIOSCREEN and BIOCHLOR Modeling for Vinyl Chloride

Model Type	Date	Vinyl Chloride Concentrations (µg/L)		
		KMW-17	KMW-17Z	Green River
Input Parameters	2018	0.362	0.0669	0.034 BS /0.033 BC
Model Output				
BIOSCREEN	2024	0.26	0.049	0.025
	2036	0.13	0.025	0.013
BIOCHLOR Constant Source	2023	0.28	0.052	0.025
	2037	0.135	0.025	0.012
BIOCHLOR Decaying Source	2025	0.214	0.049	0.024
Ks = 0.0752	2034	0.105	0.025	0.013

BS - BIOSCREEN predicted value

BC - BIOCHLOR predicted value

5.2.1.3 MNA Graphing Projections

Figure 7 shows a visual representation of the BIOSCREEN and BIOCHLOR modeling results. Vinyl chloride concentrations measured in compliance wells KMW-17 and KMW-17Z, and also for compliance well KMW-10A and background (indicator) wells KMW12A and KMW-18A during the period from 1998 to 2018 were plotted. Figure 7 also shows precipitation measured at the King County Star Lake precipitation gauge during this time period (King County 2018). Data for compliance well KMW-19A were not plotted as this well has been in compliance with the current RV for vinyl chloride for some time. As shown on the figure, all the wells show a similar degradation trend consistent with the degradation constant calculated for the Site.

The degradation constant calculated for the Site predicts KMW-17 would be in compliance with the RV (0.025 µg/L) in the year 2054.

$$(2054 - 2005) = -LN(0.025) / 0.0752 \text{ (Equation presented above)}$$

The model results are projected from the 2018 data to show when groundwater is predicted to be in compliance with the RV and predict compliance at the Green River would be achieved through MNA between approximately 2023 and 2025. Compliance at KMW-17Z by MNA is predicted to be achieved between approximately 2034 and 2037. As discussed above, the BIOCHLOR decaying source model is anticipated to be the most likely scenario as the landfill contaminants degrade over time.

Indicator well KMW-12A appears to have a similar vinyl chloride concentration trend (Figure 7). Although the well was not included in the BIOSCREEN and BIOCHLOR model runs, based upon a comparison with KMW-17Z, compliance at KMW-12A would likely be achieved around the years 2040 to 2045. Indicator wells KMW-10A and KMW-18A are currently below the RV with concentrations having degraded over the past 20 years.

The current methodology of MNA in addition to the other source control measures already implemented at the Site will likely achieve compliance with RVs at the Green River within an estimated timeframe of 4 to 6 years dependent upon hydrologic variability, and at KMW-17Z within an estimated timeframe of 15 to 18 years. It should be noted that all the model projections show concentrations at well KMW-17 to be below the MTCA Method A groundwater cleanup level of 0.2 µg/L by the year 2033, or approximately 14 years from present.

5.2.1.4 Discussion and Summary

The updated BIOSCREEN and BIOCHLOR model results project compliance at the Green River discharge point with respect to vinyl chloride to the current RV of 0.025 µg/L would be achieved by approximately 2023 to 2025 when KMW-17 concentrations have been reduced to 0.214 to 0.280 µg/L. KMW-17Z is modeled to be compliant with the current RV between 2034 and 2037 when KMW-17 concentrations reduce to 0.105 to 0.135 µg/L. Overall the modeling results when combined with an updated of the risk assessment show vinyl chloride concentrations at the point of compliance and subsequently in KMW-17Z achieved by current natural attenuation within a reasonable time frame.

5.2.2 Existing Site Data Supporting MNA

EPA guidance states that selection of MNA as a remedy requires documentation of decreasing trends in contaminant concentrations, and also consideration of other data indicating that contaminant mass is being destroyed, not just being diluted or adsorbed to the aquifer matrix. Site monitoring data have historically been collected for volatile organic compounds (VOCs) and for other parameters that can be used to evaluate conditions favorable to MNA, including chloride, iron, manganese, total organic carbon, and sulfate.

If reductive dechlorination were occurring, the data would be expected to indicate decreases in PCE, and initial increases and then decreases in TCE, DCE and vinyl chloride. During reductive dechlorination, cis-1,2-DCE is a more common intermediate than trans-1,2-DCE, and 1,1-DCE is the least prevalent of the three DCE isomers when they are present as daughter products.

Site VOC trends in TCE and daughter products cis-1,2-DCE and vinyl chloride are presented in Figures 8, 9, and 6 and support the occurrence of MNA. Concentrations of parent compound PCE have generally been non-detected. All detected DCE occurs in the form of cis-1,2-DCE.

In the SA, TCE and cis-1,2-DCE concentrations in well KMW-12A generally decreased over time, with some increases during the period from about 2006 to 2008. In the RAA, TCE and cis-1,2-DCE concentrations in well KMW-17 showed some fluctuations and increases until approximately 2008 but have recently stabilized. Vinyl chloride concentrations in well KMW-12A have decreased over time. Vinyl chloride in wells KMW-17 and KMW-17Z increased during the period between approximately 2001 to 2009 but have since been decreasing.

At the Site, concentrations of other parameters are consistent with anaerobic conditions that are favorable to degradation. For example, in wells completed near the landfill toe, the elevated concentrations of manganese and iron, as discussed in Section 3, support anaerobic conditions that would lead to reducing conditions. The observed concentrations of nitrate and sulfate in downgradient wells are similar to or generally lower than in background wells and are consistent with MNA occurring. Chloride concentrations in these areas are inconclusive, but the increases that would be expected due to reductive dichlorination may not be detectable due to the relatively low concentrations of chlorinated hydrocarbons.

5.2.3 Suitability of Continued MNA as a Remedy

MNA is generally implemented as a remedy at sites where there are limited human health risks due to site and development constraints, public drinking water is available, and costs of other types of remediation would be excessive. The Site meets these criteria. Not only is MNA already being successfully implemented since the initial cleanup actions, but there are no public water supply wells in the immediate vicinity, and no other land uses between the Site and the Green River due to ownership by SPU. Any remaining concerns would be related to private water supply wells in and surrounding the landfill that could potentially withdraw contaminated groundwater. Although MNA would not reduce

manganese and iron concentrations, these pose solely odor and taste issues, and do not present a human health risk.

SPU plans to implement a low-flow sampling protocol at the monitoring wells during future sampling events at the Site. The protocol will include measuring dissolved oxygen (DO) and redox. These parameters will add useful information to confirm that conditions are consistent with MNA. Other parameters that could be tested to measure MNA progress are ethene and carbon dioxide, which can be achieved using current laboratory analysis standards and are not cost-prohibitive.

To confirm that MNA is operating as a remedy, per EPA guidance it is recommended that monitoring include analysis of EPA's required MNA parameters in selected wells including the SA and RAA background wells, the three compliance wells, and KMW-12A.

5.3 Other Remedial Options

In addition to MNA, other remedial options considered were air sparging/air stripping with vapor extraction, and injection of chemical adjuncts. Supporting information for remedial options is presented in Appendix C.

5.3.1 Air Sparging/Air Stripping with Vapor Extraction

Air sparging/air stripping is a more active remedial approach that attempts to volatilize contaminants and increase overall dissolved oxygen by introducing air into the water of the aquifer. The increased dissolved oxygen enhances natural aerobic degradation of volatile contaminants by bacteria. Additionally, air sparging would create manganese and iron precipitates that would remove the dissolved manganese and iron from the groundwater into insoluble forms. Oxidation with aeration of groundwater is one of the main treatment approaches by drinking water systems. It takes 0.14 mg/L of dissolved oxygen to oxidize 1 mg/L of dissolved iron and 0.27 mg/L of dissolved oxygen to oxidize 1 mg/L of dissolved manganese. Increasing dissolved oxygen concentrations at the Site to 0.4 mg/L in the RAA would allow for aerobic degradation of the vinyl chloride and oxidation of the dissolved iron and manganese into precipitates.

SPU currently uses two sparging ponds to treat landfill runoff and seeps. The water is sparged in a pond to treat for ammonia and volatile contaminants prior to discharge directly to the Green River. Similar subsurface sparging techniques can be used in situ to oxygenate the groundwater at the toe of the landfill and allow for enhanced microbial degradation of the volatile contaminants, specifically vinyl chloride, and dissolution of manganese and iron prior to aquifer discharge to the Green River.

To not disrupt upland processes, this remedial method would be applied at the toe of the landfill where vinyl chloride has already been anaerobically reduced from PCE/TCE. Oxygenation of groundwater at the toe would allow for aerobic bacteria to further reduce vinyl chloride into non-toxic substances such as ethene. Several sparging wells would need to be used across the toe of the landfill to enhance dissolved oxygen within the groundwater.

Existing landfill gas extraction wells (such as KIGW-1, KIGW-23, and KIGW-24) could potentially be used as stripping wells to withdraw volatilized contaminants; however, these wells are 200 feet upgradient of the toe. New vapor extraction wells may need to be implemented for air sparging/air stripping and vapor extraction to be feasible.

5.3.2 Injection of Chemical Adjuncts

Chemical and nutrient injections to stimulate and enhance microbial degradation of volatile compounds, such as vinyl chloride, is an effective way to treat groundwater in-situ. Various chemical and nutrient injections use either aerobic or anaerobic methodologies. Since one of the goals of the

treatment for the Site would also be to treat for dissolved manganese and iron, the aerobic degradation pathway is likely best.

Oxygen Release Compound – Advanced®

Oxygen Release Compound – Advanced® (ORC-A) is manufactured by Regenesis and has been proven to effectively increase aerobic degradation rates when injected into the subsurface. Typical applications require the use of direct-push drilling technology to apply ORC-A site wide across the plume and distributed entirely across the aquifer.

However, the Site is a closed landfill and multiple ORC-A injections would likely be required. Instead, existing unused monitoring wells of two to four inches in diameter at the toe of the landfill could be used to deploy multiple ORC-A treatment socks. The ORC-A treatment socks can be strung together in a well to allow for ORC-A to slowly release oxygen for a period of up to one year. After one year, the socks could be replaced with new canisters and redeployed. The downsides are that the treatment of the aquifer would be limited to where current unused wells exist and the treatment would be highly localized generally within 15 feet of the wells. Due to the anaerobic conditions likely at the toe of the landfill, there is likely very strong demand for oxygen, that may not allow for iron or manganese precipitation. However, this is a more active approach than simply MNA and could provide highly localized areas of enhanced microbial degradation upgradient prior to discharge to the Green River.

The other potential for ORC-A is to use direction injections into the aquifer; however, due to ongoing leachate concerns, multiple injections would likely be needed over time to maintain oxygen levels.

ORC-A socks would be localized treatment surrounding upgradient wells. The true downgradient degradation of contaminants may be limited due to the current state of electron donor demand. However, this option has limited overall costs and is more proactive than simply MNA alone.

PlumeStop™

The other injection option is PlumeStop™ which is a Liquid Activated Carbon™ technology that can be injected into the subsurface creating a carbon reactive barrier in the groundwater. This technology would be deployed at the toe of the landfill to treat the leachate end of the plume. This would have to be injected into both the RAA and SA aquifers below the Site, but only one injection cycle would be needed, and the reactive barrier would continue to catch, trap, and degrade contaminants for decades. At the Site, it appears a 10-foot-wide by 1,000-foot-long reactive barrier could be implemented at the toe of the landfill. This would continue to reduce dissolved phase contaminants such as vinyl chloride over time and remove the electron donor demand downgradient of the landfill, likely allowing manganese and iron to precipitate in the RAA due to increased dissolved oxygen from nearby RAA groundwater flow.

The PlumeStop™ methodology is likely one of the most proactive measures that could be taken at the landfill as a reactive barrier would create a biological habitat for trapping and ultimately degrading contaminants for decades. This technology has been similarly applied at other sites where nearby surface waters need protection (Regenesis 2019).

5.4 Cost Evaluation

Costs of potential remedial options must be considered to weigh whether they are worth the anticipated benefits. The three remedial options presented rely upon microbial degradation of the contaminants, and the timelines in achieving compliance are variable. The costs for each approach are summarized below.

- MNA uses the current methodology to achieve project goals. Compliance of vinyl chloride is predicted to be achieved between 2023 and 2035 at the Green River, and approximately

between the year 2034 and 2041 at KMW-17Z. Manganese and iron would likely remain above background conditions due to the anaerobic conditions upgradient. The only added costs would be laboratory analysis for MNA parameters at a few selected wells.

- Annual cost (\$5,000 per year for analysis of additional MNA parameters)
- Manpower (no change from current levels)
- Air sparging is a more active treatment technology that increases aerobic degradation of contaminants and would likely allow for manganese and iron compliance. Compliance would likely be achieved sooner due to volatilization of contaminants (roughly estimated 2023 Green River/2027 KMW-17Z, or sooner) There would be several significant added costs incurred due to the more proactive remedial approach.
 - Installation (\$100,00 to \$175,000)
 - Annual cost (\$7,500 per year for power supply)
 - Manpower (a minimum of weekly calibration of the system)
 - Operations and maintenance (estimated \$5,000)
- Chemical Injection of ORC-A. This method combines MNA with more increased aerobic processes. Compliance would likely be achieved sooner than MNA alone (roughly estimated at 2025 Green River/2033 KMW-17Z).
 - Product cost (\$5,000 for ORC-A socks annually)
 - Annual cost (\$5,000 per year for analysis of additional MNA parameters)
 - Manpower (annual replacement of ORC-A socks)
- Chemical Injection of Liquid Activated Carbon™ through PlumeStop™. This method uses creation of a subsurface 1,000-foot reactive barrier at the toe of the landfill in the SA and RAA. Compliance would likely be achieved sooner than MNA alone (roughly estimated 2022 Green River/2025 KMW-17Z) and would be sustained regardless of hydrogeologic conditions.
 - Installation cost (\$50,000 estimated)
 - Product cost (\$150,000 for PlumeStop™ and Regenesis design)
 - Annual cost (\$7,500 per year for analysis of additional MNA parameters)
 - Manpower (None more than current levels)

5.5 Summary of Remedial Options

Balancing human health risks with the relative costs of various options is important when selecting appropriate remediation methodology. As noted above, RVs for the Site have been established based on upon current or future human consumption of surface water or fish. Exceedances of RVs for manganese and iron do not constitute human health risks but are instead associated with taste and odor. Since vinyl chloride is a known human carcinogen, the focus of the remediation should be on vinyl chloride.

MNA appears to be the most feasible and cost-effective remedial option for resolving downgradient vinyl chloride concentrations in groundwater. BIOSCREEN and BIOCHLOR modeling using current vinyl chloride data predicts that groundwater discharging to the Green River could be in compliance with the RV in as little as 4 years, therefore, the costs to implement additional remedial technologies are likely

not warranted. Additionally, SPU owns all the land between the landfill and the Green River and there is no risk of potential exposure from drinking water.

To provide further evaluation of the effectiveness of ongoing MNA, SPU plans to measure additional parameters including DO and redox in routine groundwater monitoring well samples, and analyze the data using EPA guidance to further confirm that MNA is occurring consistent with the conceptual site model. In addition, it is recommended that SPU include additional analyses for EPA's required natural attenuation screening parameters in selected wells including background and compliance wells to demonstrate that attenuation of the site contaminants is occurring at rates sufficient to be protective of human health and the environment.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Vinyl chloride, iron, and manganese remain out of compliance at the landfill. These contaminants are tied to the natural degradation of the landfill source materials; source removal of landfill contaminants is not feasible. Of these parameters, only vinyl chloride presents a potential human health risk. Ecology requirements prohibit completion of any new groundwater wells within 1,000 feet of landfills (WAC 173-160), and this limits the potential for human exposure risk through drinking water. Current data indicates that vinyl chloride concentrations are decreasing due to natural attenuation, and updated BIOSCREEN and BIOCHLOR modeling indicates that concentrations are expected to be in compliance at the Green River in as little as 4 years. Compliance could be achieved at well KMW-17Z in approximately 15 years.

Manganese and iron are naturally occurring and abundant elements whose chemical behavior are dominated by pH and redox reactions (International Manganese Institute [INMI] 2013). Landfills can create slightly reducing geochemical conditions in the surrounding environment and cause manganese and iron to be leached from the soils. The resulting concentrations in groundwater may be elevated over natural background. However, surface water – groundwater interactions complicate evaluation of landfill conditions. Natural concentrations of manganese in groundwater are dependent upon factors such as rainfall chemistry, aquifer lithology, geochemical environment, groundwater flow paths and residence time. Some of these factors can be highly variable over relatively small spatial and temporal scales.

Four potential remedial approaches are discussed: MNA, implementation of ORC-A socks, implementation of Plumestop™, and air sparging/air stripping and vapor extraction. All approaches are feasible at the Site under the current biologic and hydrogeologic conditions.

MNA combined with development restrictions appears to be the most feasible and cost-effective methodology and is anticipated to achieve compliance with necessary RVs for vinyl chloride within a reasonable timeframe. MNA would solely address vinyl chloride, whereas the other remedial options presented would degrade vinyl chloride while simultaneously causing manganese and iron to precipitate and reduce groundwater concentrations of the inorganic COCs. However, as discussed in Section 3.5, there are no exposure risks related to iron and manganese prior to discharge to the Green River. Therefore, the driving factor in cleanup is vinyl chloride concentrations due to its carcinogenicity which MNA shows compliance at the discharge point in as little as 4 years.

Secondarily, ORC-A injection via canisters of unused wells near the toe of the landfill may assist in aerobic degradation of primary contaminants and precipitation of secondary contaminants to more rapidly reduce vinyl chloride concentrations. ORC-A socks would be highly localized and not likely create a necessary reactive barrier. Plumestop implementation is more-proactive in creating such a reactive barrier, but costs again are likely to exceed \$200,000 within the first year of implementation. Another expensive approach (>\$180,000 initially) is to institute an air sparging/air stripping and vapor extraction system at the Site. However, the costs of these additional technologies likely outweigh their advantages based on the current state of the groundwater plume, natural degradation processes, and future risk near and surrounding the landfill.

6.2 Recommendations

Manganese and iron are naturally occurring elements that are released from soils and elevated concentrations in Site wells are likely due to a combination of geochemical processes including their location in the wetland area between the landfill and the Green River that is naturally low in oxygen and

rich in organic materials. Currently their RVs are established based on secondary criteria that are not related to human health or environmental risks and there are no exposures prior to discharge to the Green River. Therefore, it is recommended that the RVs be modified. For manganese, it is recommended that the MTCA Method B groundwater value of 2.2 mg/L be used as the RV instead of the secondary criteria of 0.05 mg/L. For iron, it is recommended that the MTCA Method B groundwater value of 11.2 mg/L be used as the RV instead of the secondary criteria of 0.3 mg/L.

SPU recommends that well KMW-17Z be substituted for KMW-17 as the compliance well in that area of the Site near the Green River.

For vinyl chloride, MNA has been implemented at the Site since the closure of the landfill, and substantial decreases in concentrations have been observed near the point of compliance. Overall, human health risks have been mitigated by SPU's remedial approach along with restrictions on development and installation of new wells placed by Ecology and the City of Kent. Updated groundwater modeling predicts that vinyl chloride concentrations at the Green River will be in compliance with current RVs through continued MNA in as little as 4 years; therefore, continued use of MNA as a remedial approach is recommended.

To provide further evaluation of the effectiveness of ongoing MNA, SPU plans to measure additional parameters including DO and redox in routine groundwater monitoring well samples and analyze the data using EPA guidance to further confirm that MNA is occurring consistent with the conceptual site model. Testing for additional EPA-required natural attenuation screening parameters is also recommended to demonstrate that attenuation of the site contaminants is occurring at rates sufficient to be protective of human health and the environment.

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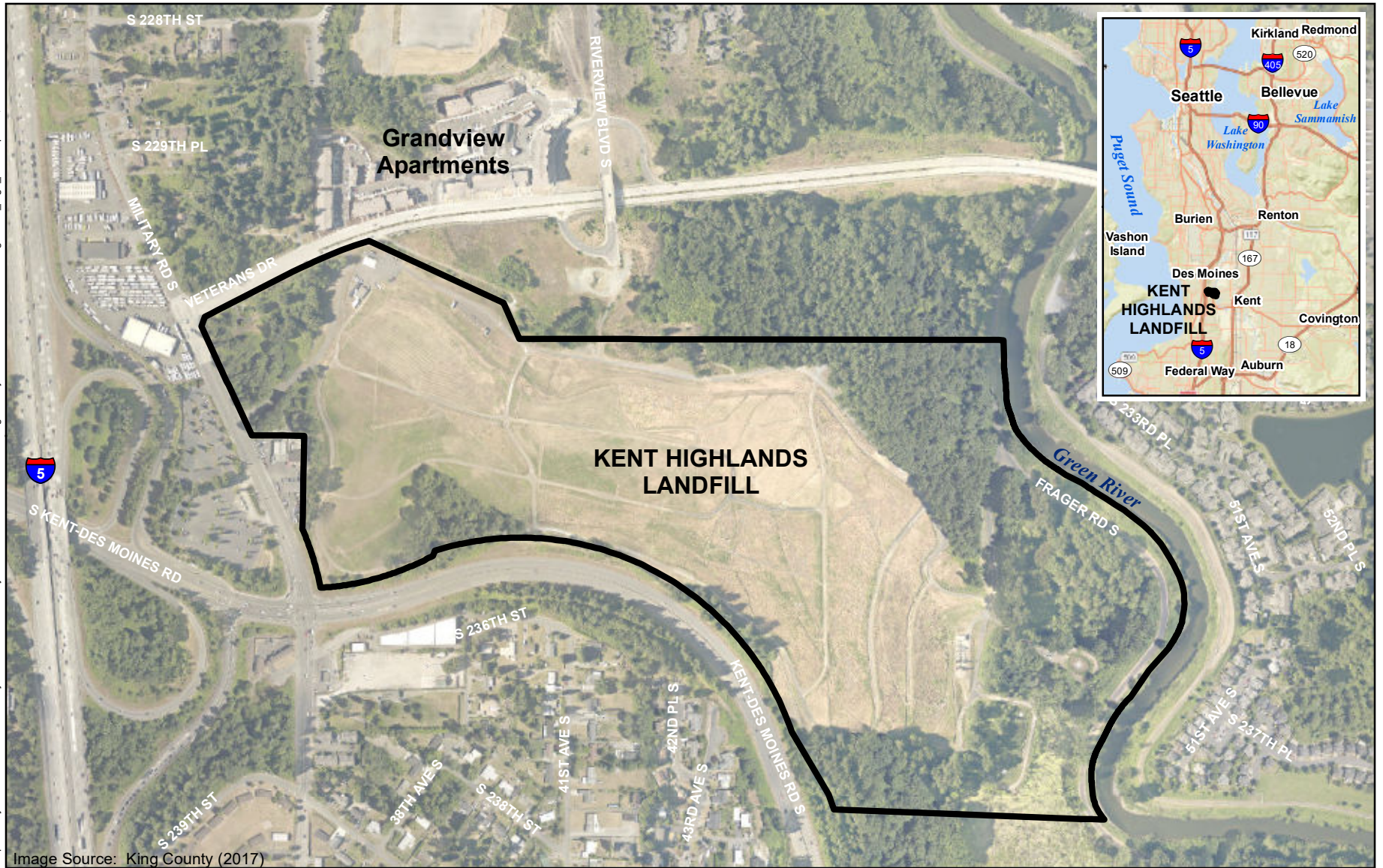
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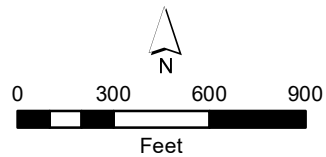
Figures



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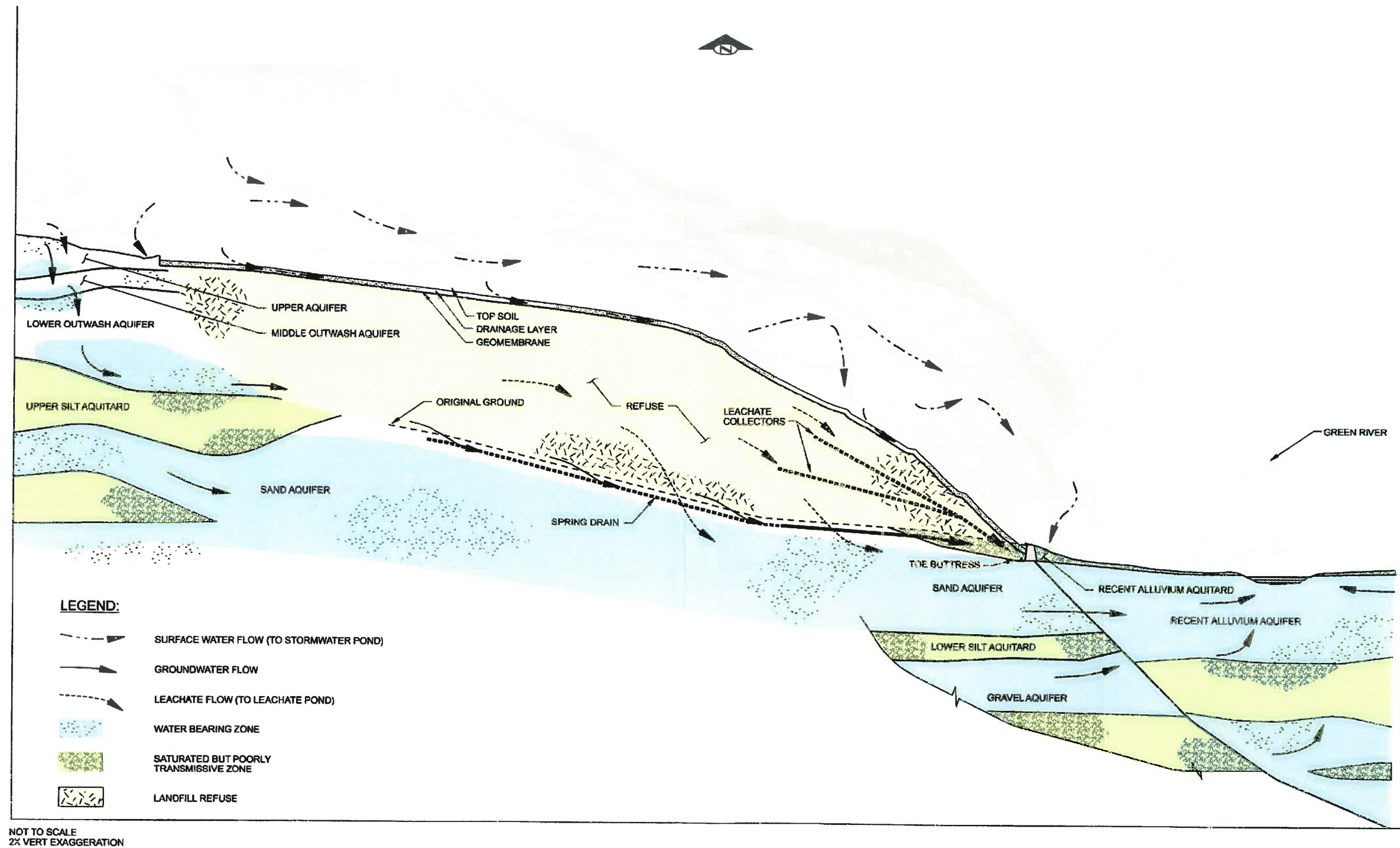


Parametrix
ENGINEERING . PLANNING . ENVIRONMENTAL SCIENCES



 City of Seattle, Seattle Public Utilities Owned Parcel
Boundary That Includes Kent Highlands Landfill

Figure 1
Site Location Map
Kent Highlands Landfill
Kent, Washington



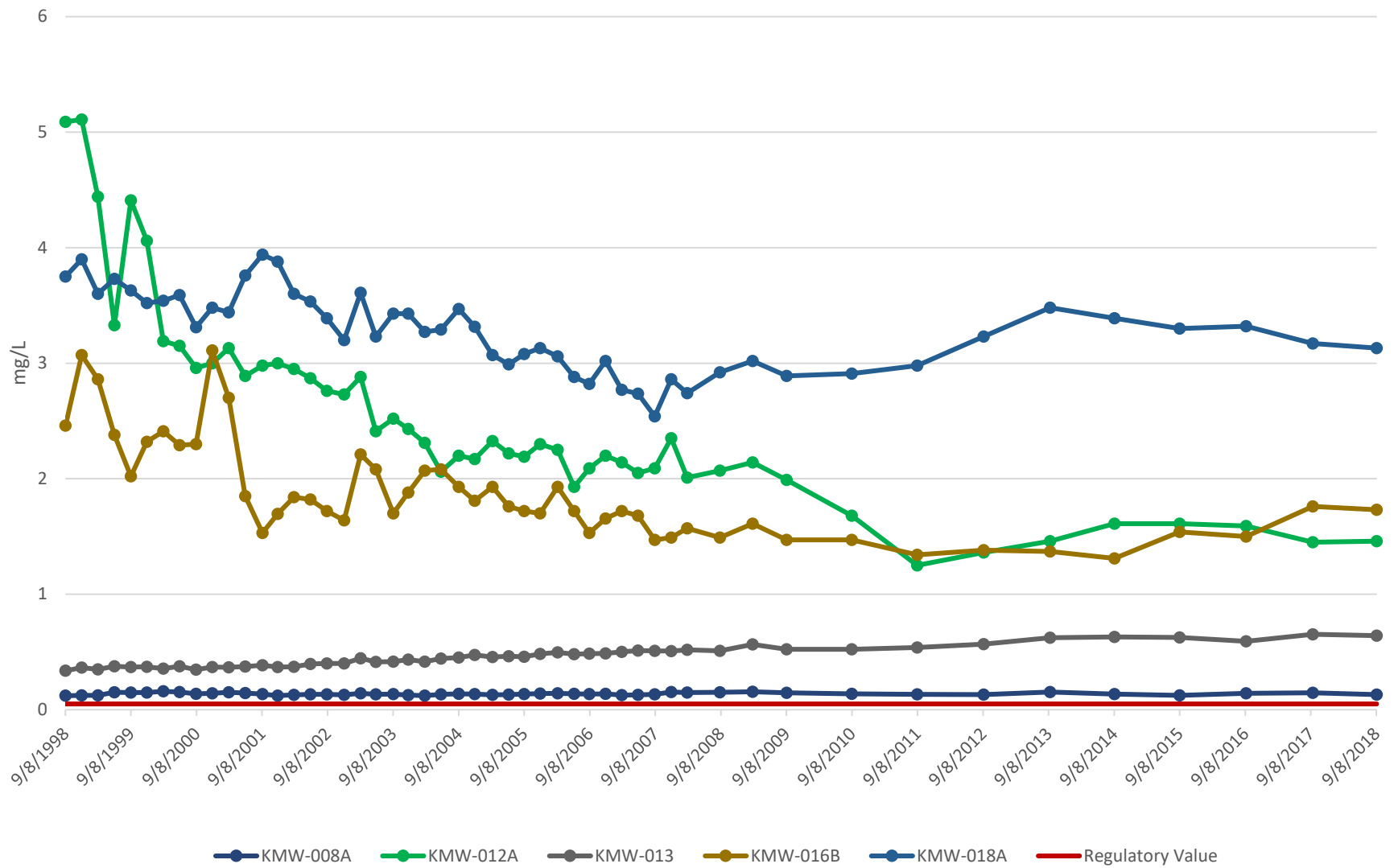
Seattle
Public
Utilities

FLOYD | SNIDER
strategy • science • engineering

Kent Highlands Landfill
City of Seattle

Dissolved Manganese

Sand Aquifer



Recent Alluvium Aquifer

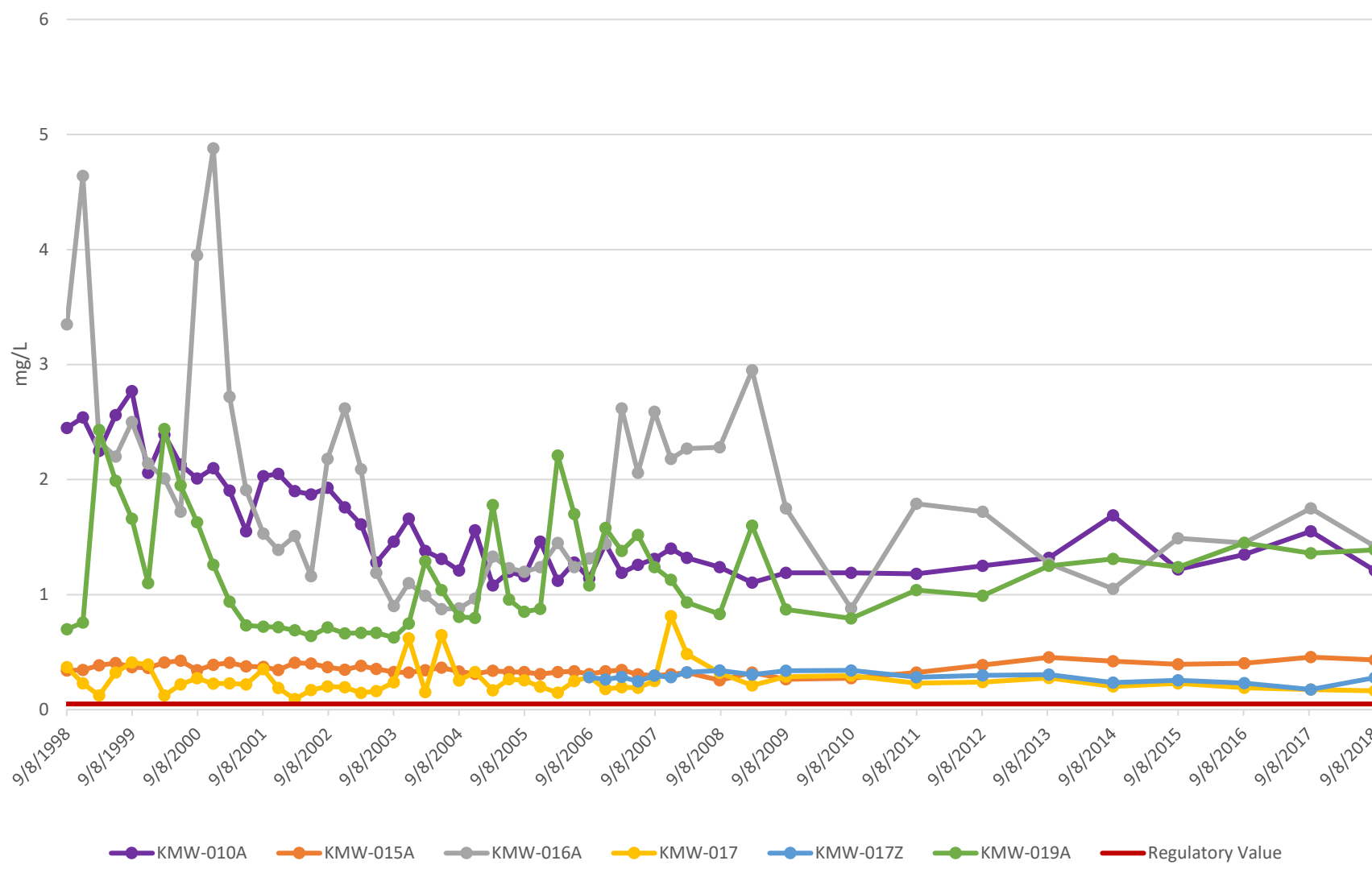
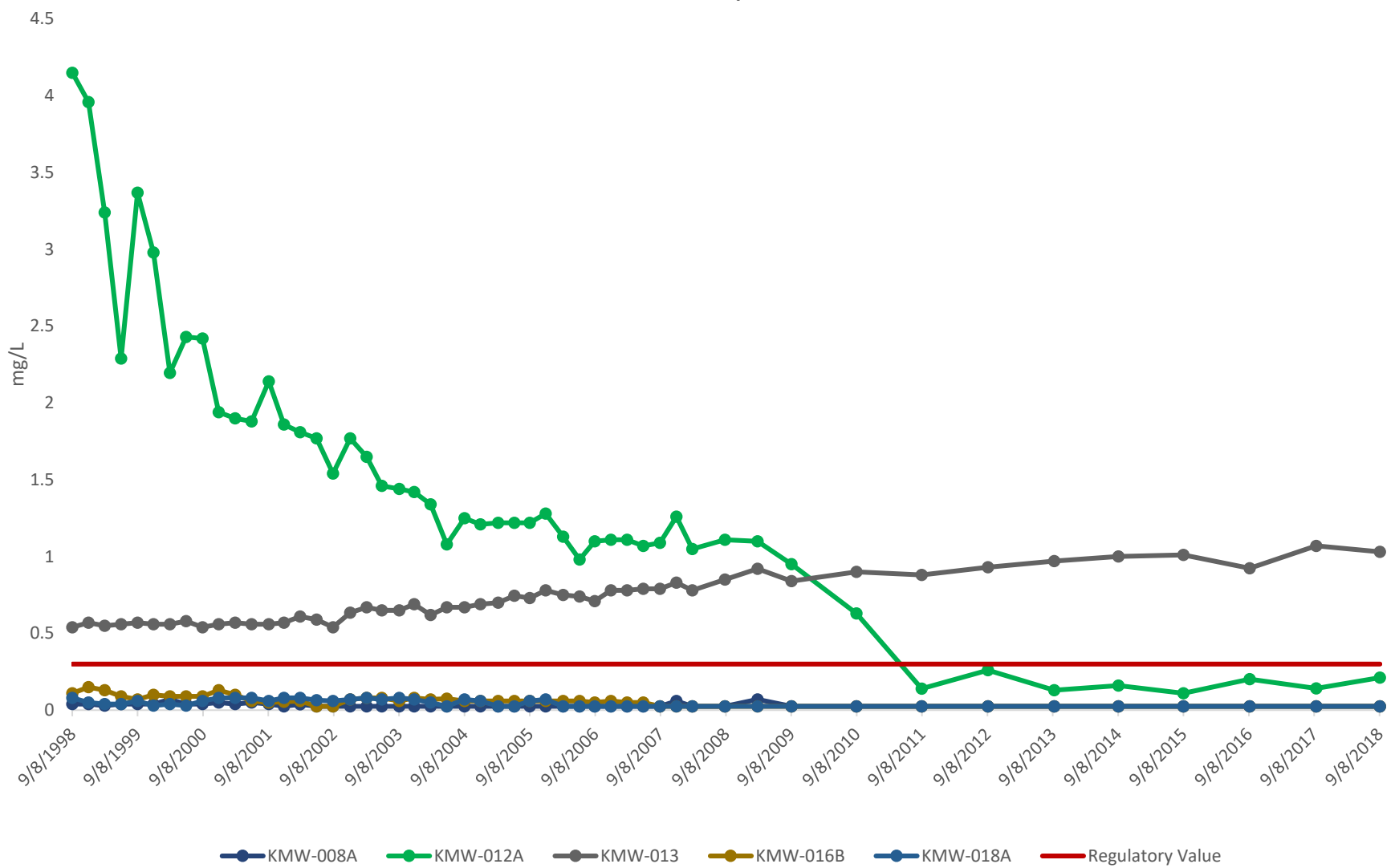


Figure 4
Dissolved Manganese Results
Kent Highlands Landfill

Dissolved Iron

Sand Aquifer



Recent Alluvium Aquifer

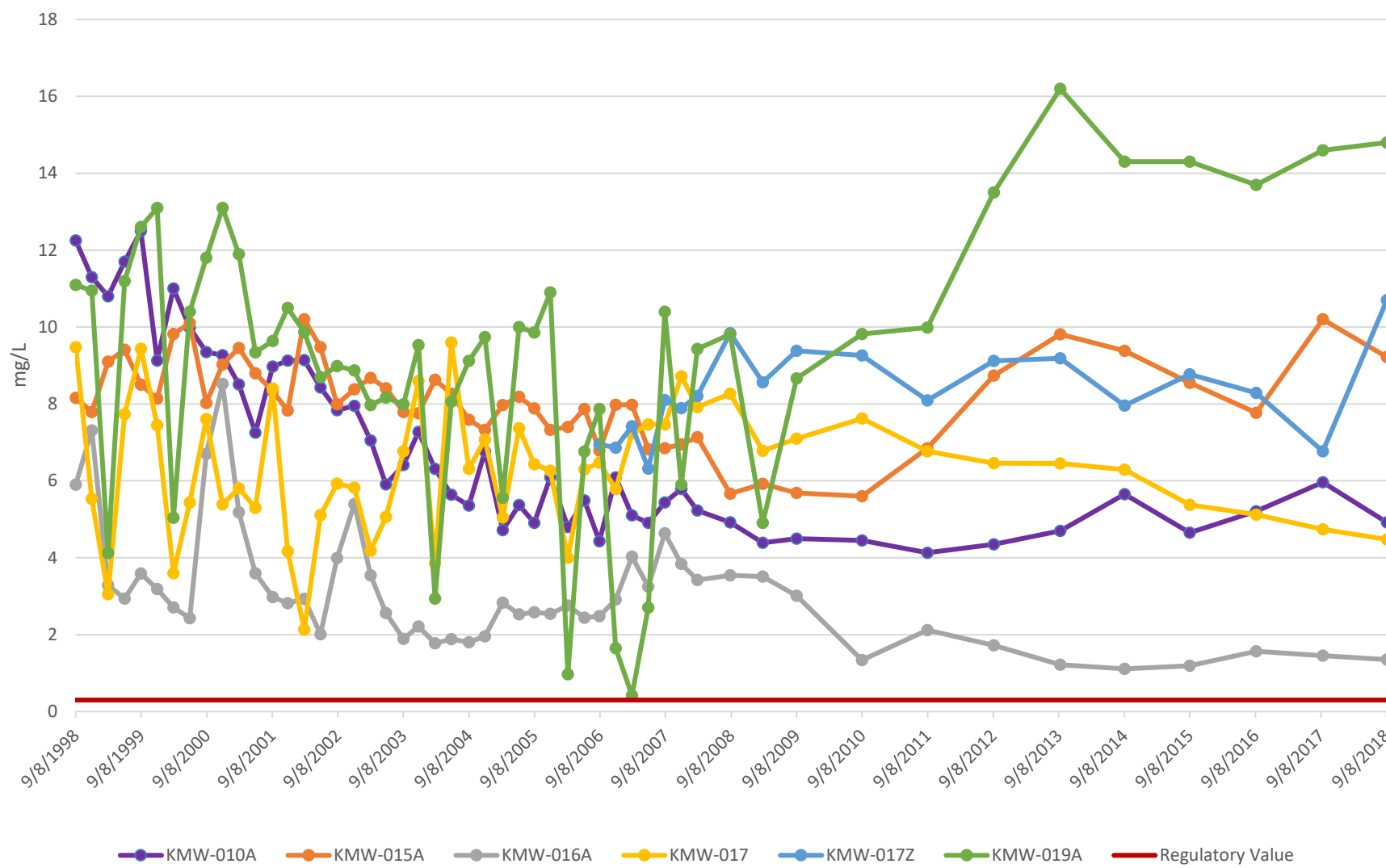
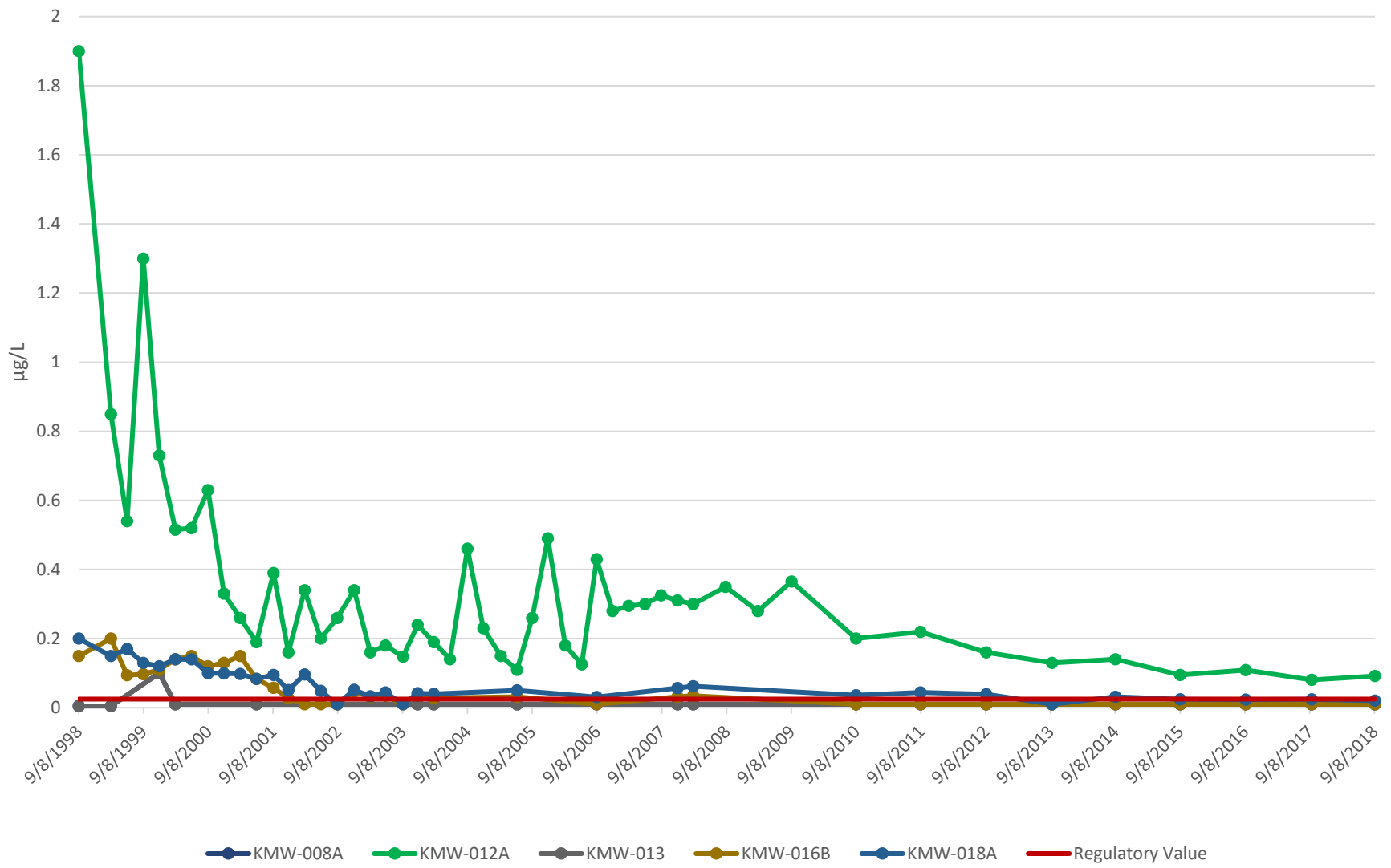


Figure 5
Dissolved Iron Results
Kent Highlands Landfill

Vinyl Chloride

Sand Aquifer



Recent Alluvium Aquifer

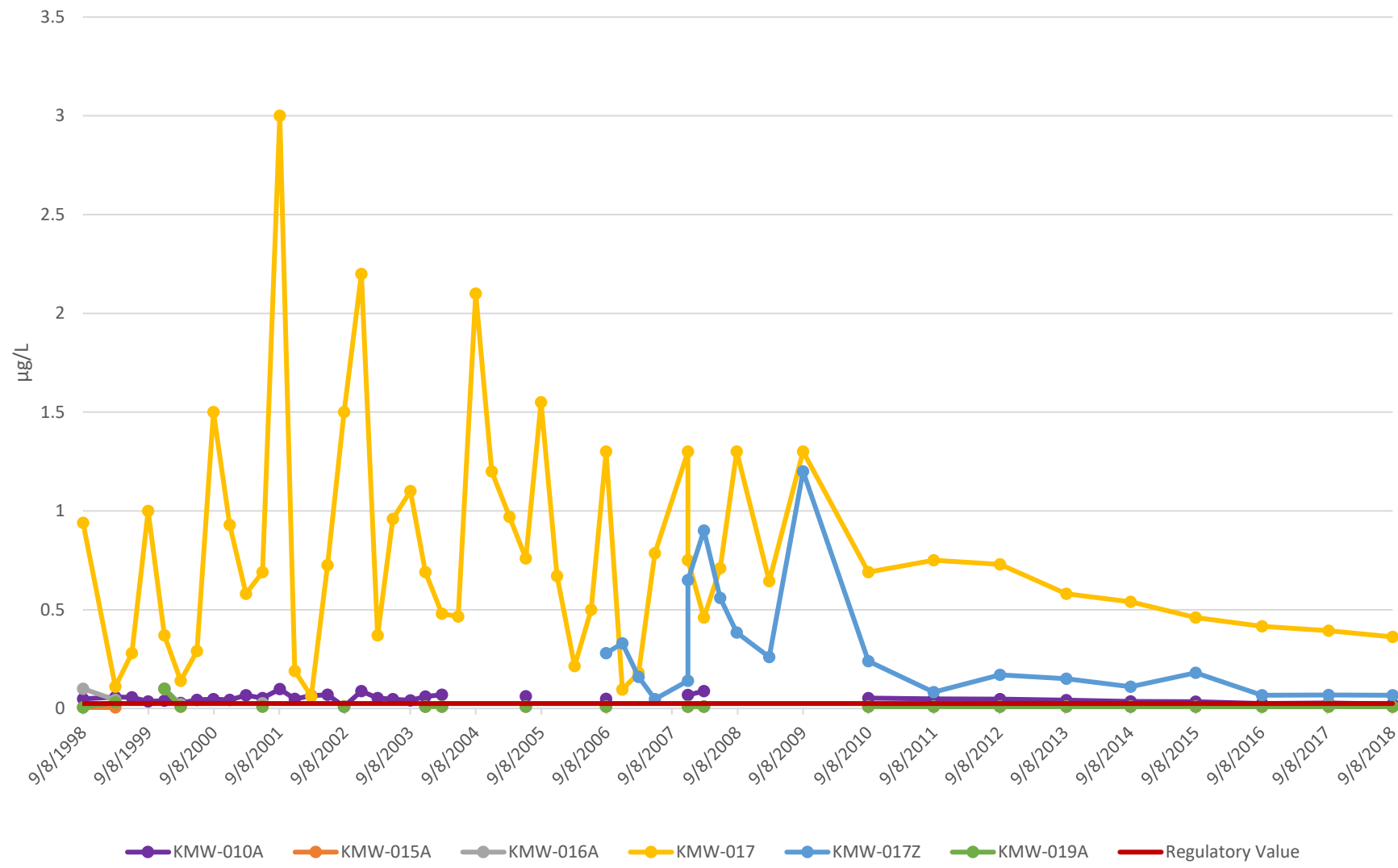
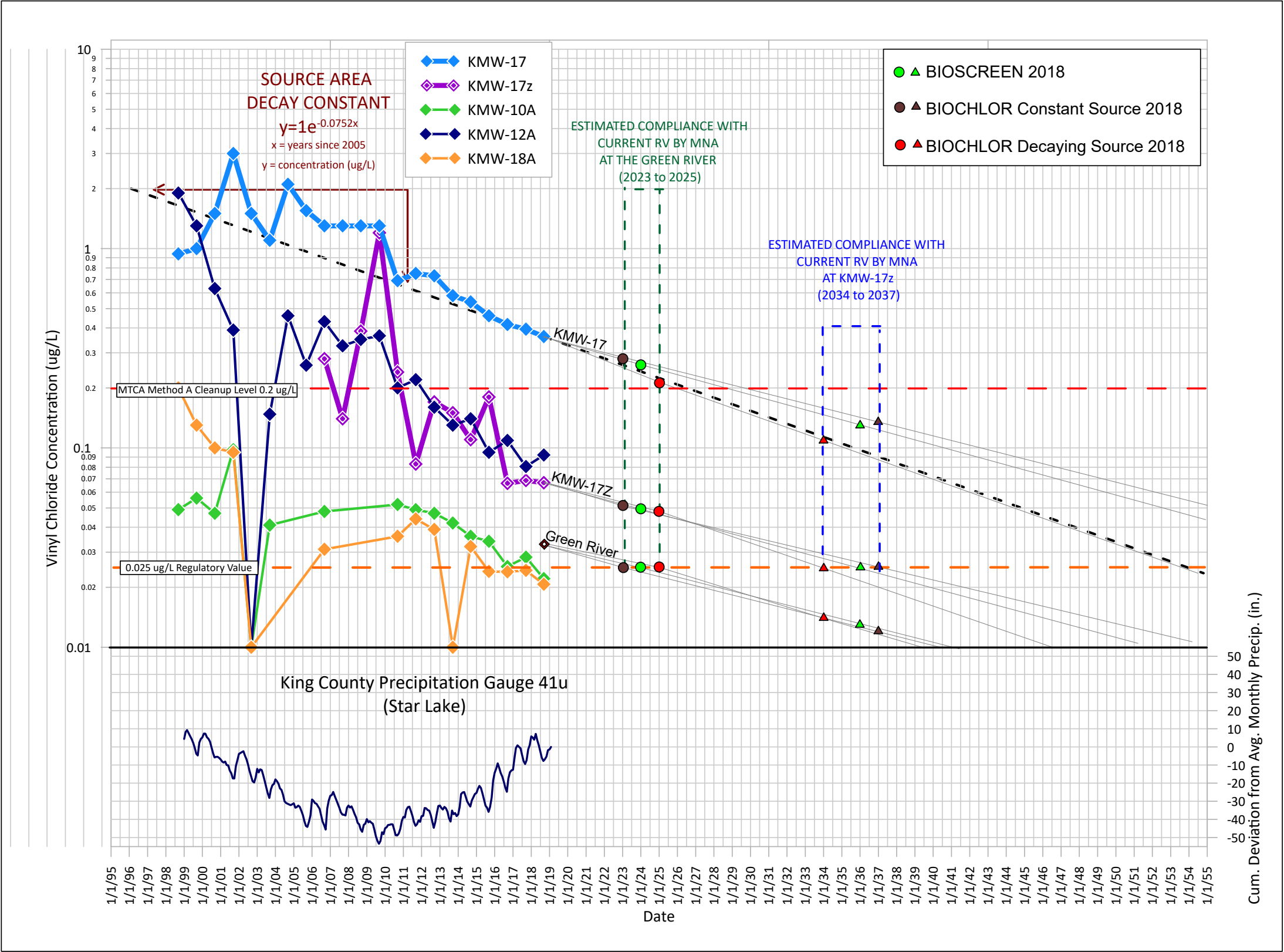


Figure 6
Vinyl Chloride Results
Kent Highlands Landfill



EHS-International, Inc.
1011 SW Klickitat Way, Suite 104
Seattle, Washington 98134
Ph: 206.381.1128
Fax: 206.254.4279

KENT HIGHLANDS LANDFILL
Compliance Analysis

SEATTLE PUBLIC UTILITIES
Kent, Washington

PROJECT MANAGER:
K. EASTHOUSE
CREATED BY:
M. BRADY
DATE:
1999 - 2018 DATA

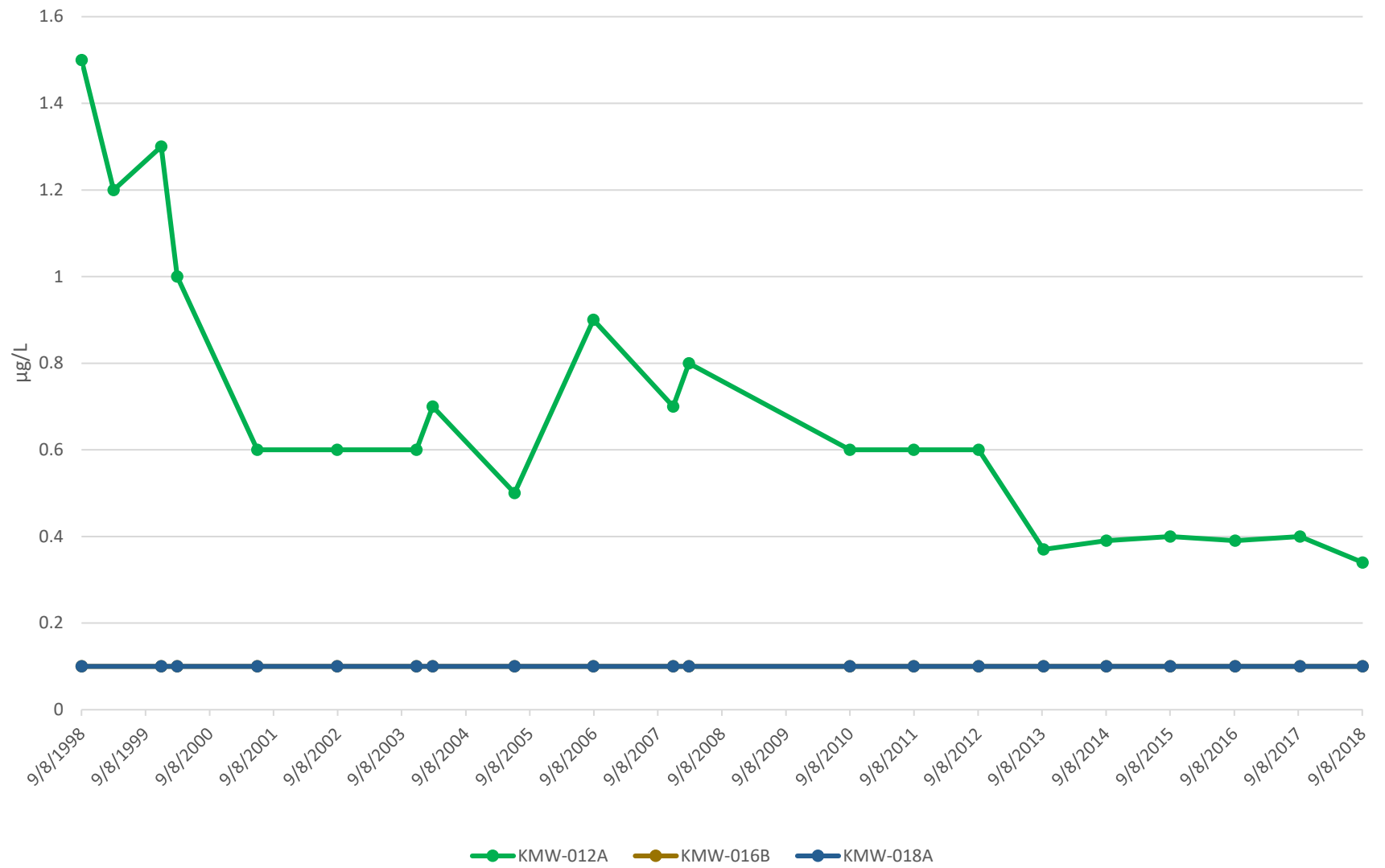
EHSI PROJECT #:
10887

ISSUE DATE:
MARCH 2019

Figure 7
Vinyl Chloride Degradation Hydrograph
Kent Highlands Landfill
Kent, Washington

Trichloroethene

Sand Aquifer



Recent Alluvium Aquifer

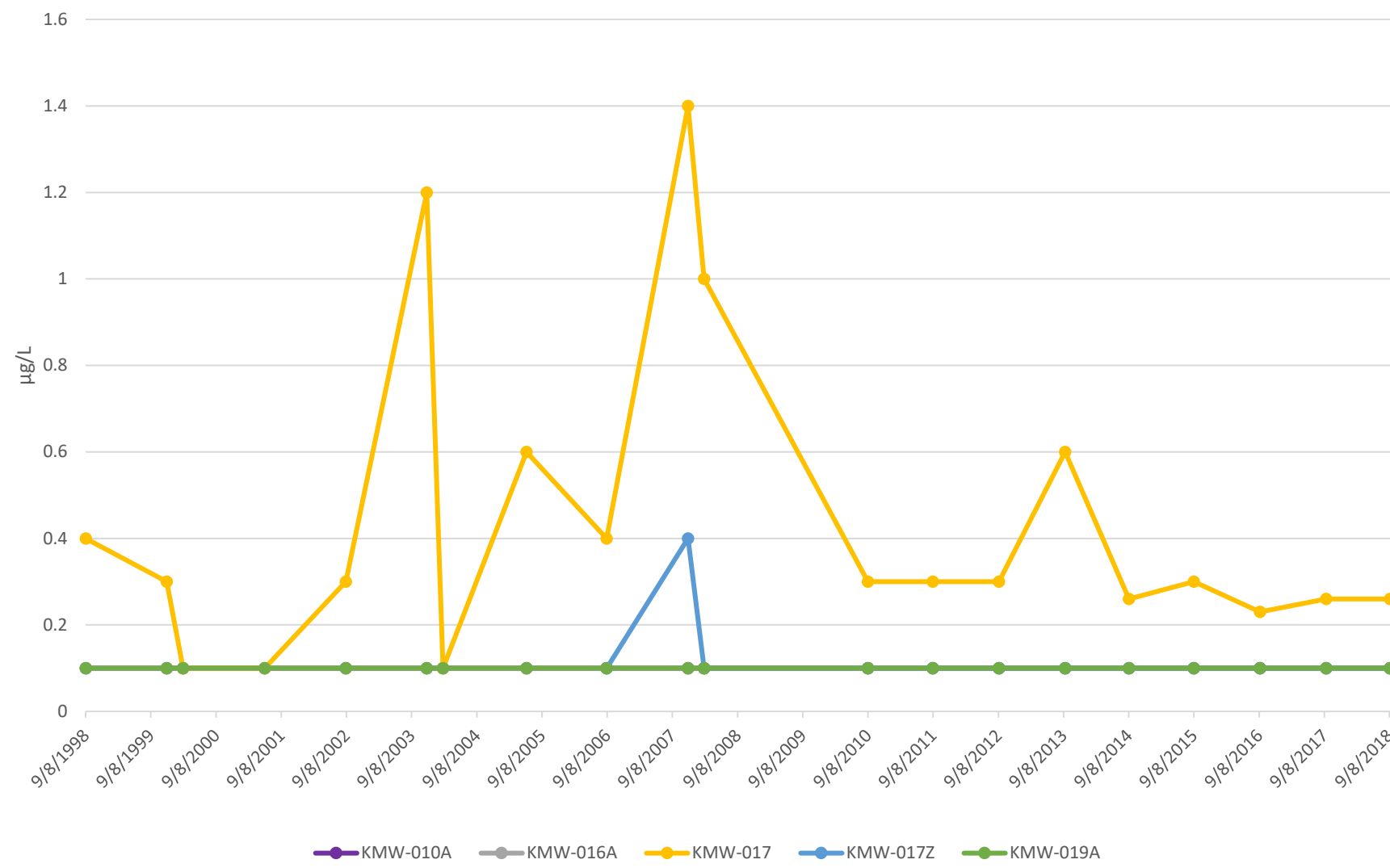


Figure 8
Trichloroethene Results
Kent Highlands Landfill

cis-1,2-Dichloroethene

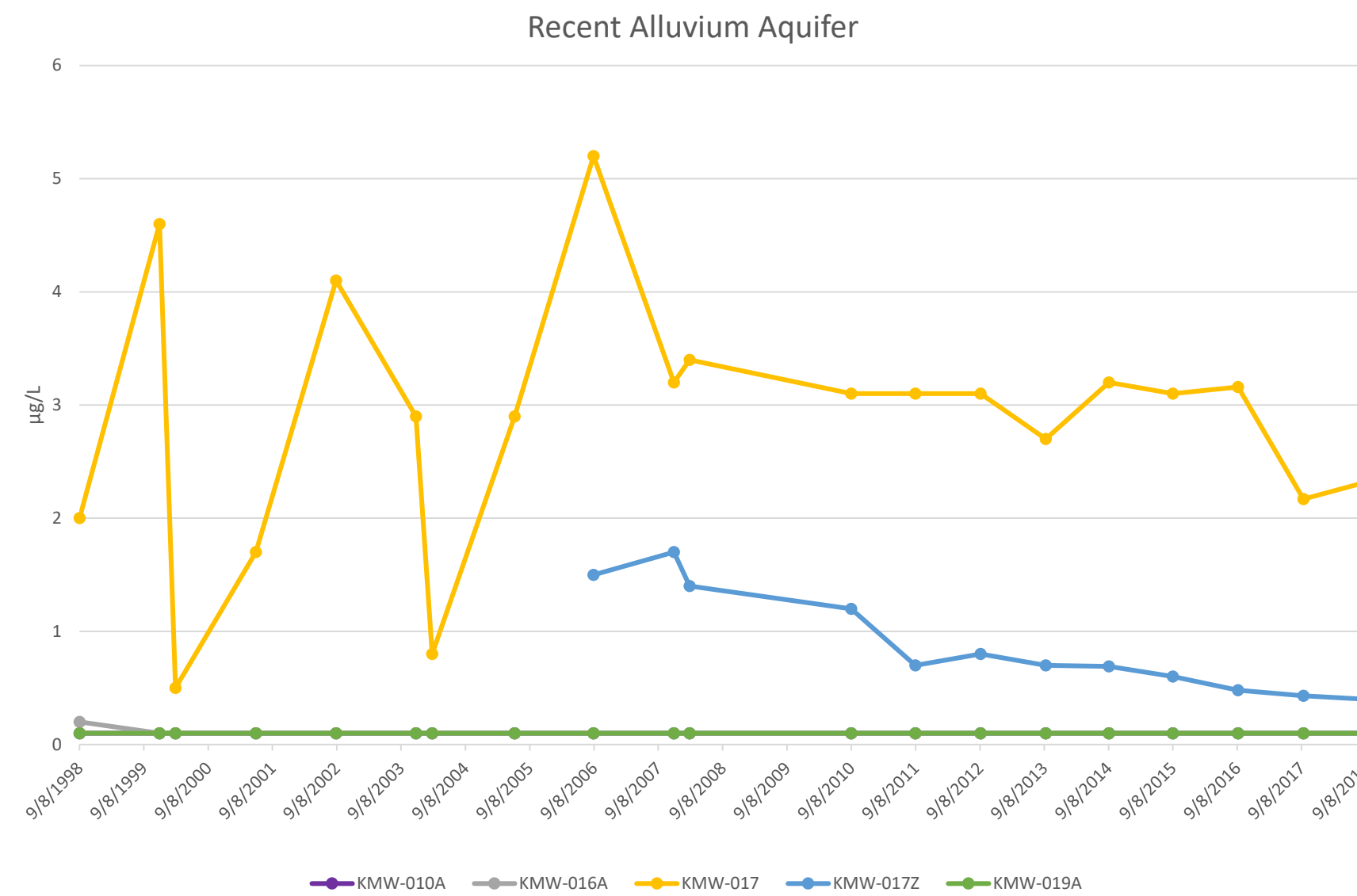
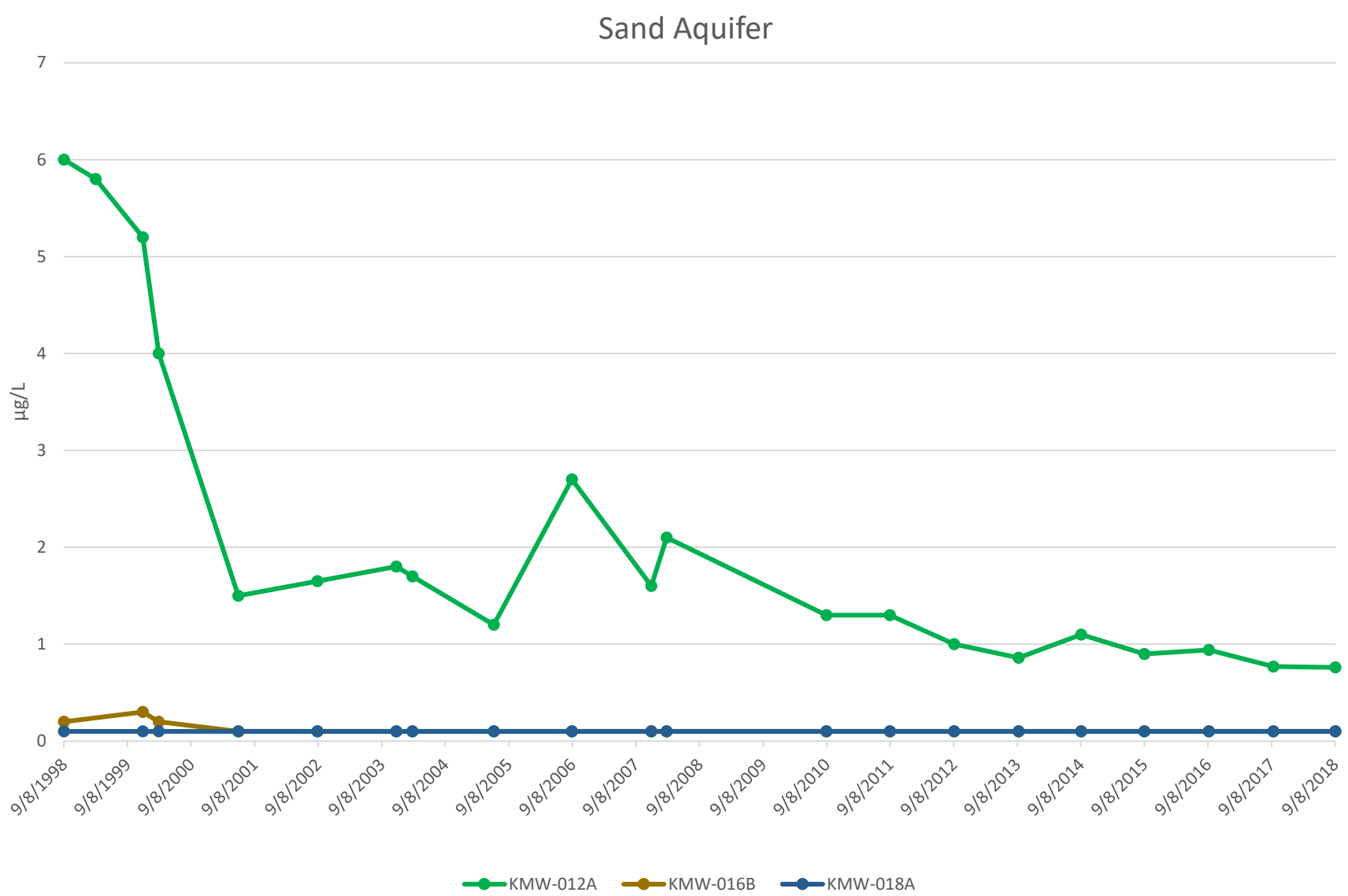


Figure 9
cis-1,2-Dichloroethene Results
Kent Highlands Landfill

Appendix A

Groundwater Quality Summary Tables



Table A-1. Vinyl Chloride Data Summary, 2014 through 2018, Kent Highlands Landfill

		Vinyl Chloride (µg/L)				
		Regulatory Value: 0.025 mg/L				
		2014	2015	2016	2017	2018
Recent Alluvium Aquifer						
KMW-010A	Compliance	0.036	0.034 M	0.0254	0.0283	0.0221 J
<i>Duplicate</i>		0.037				
KMW-015A	Background	0.020 U	0.020 U	0.02 U	0.020 U	0.02 U
KMW-016A	Indicator	0.020 U	0.020 U	0.02 U	0.0219	0.020 U
<i>Duplicate</i>			0.020 U			
KMW-017	Compliance	0.54	0.46 M	0.416	0.394	0.362 J
KMW-017Z	Indicator	0.11	0.18 M	0.0664	0.0687	0.0669 J
KMW-019A	Compliance	0.020 U	0.020 U	0.02 U	0.020 U	0.02 U
Sand Aquifer						
KMW-008A	Indicator	0.020 U	0.020 U	0.02 U	0.02 U	0.02 U
<i>Duplicate</i>						0.02 U
KMW-012A	Indicator	0.14	0.095 M	0.109	0.0806	0.0921
<i>Duplicate</i>					0.0786	
KMW-013	Background	0.020 U	0.020 U	0.02 U	0.020 U	0.020 U
KMW-016B	Indicator	0.020 U	0.020 U	0.02 U	0.020 U	0.020 U
<i>Duplicate</i>				0.02 U		
KMW-018A	Indicator	0.032	0.024 M	0.0239	0.0243	0.0207
Trip Blanks						
KMW-401		0.020 U	0.020 U	0.02 U	0.020 U	0.020 U
KMW-402		0.020 U	0.020 U	0.02 U	0.020 U	0.02 U
KMW-403		0.020 U	0.020 U			

Samples Dates:

2014: September 9-11
2015: September 8-10
2016: September 12-13
2017: September 18-19
2018: September 10-11

Table A-2. Iron and Manganese Data Summary, 2014 through 2018, Kent Highlands Landfill

	Dissolved Iron (mg/L) Regulatory Value: 0.3 mg/L					Dissolved Manganese (mg/L) Regulatory Value: 0.05 mg/L				
	2014	2015	2016	2017	2018	2014	2015	2016	2017	2018
Recent Alluvium Aquifer										
KMW-010A Compliance	5.7	4.65	5.21	5.96	4.92	1.69	1.22	1.35	1.55	1.21
Duplicate	5.6					1.71				
KMW-015A Background	9.4	8.55	7.77	10.2	9.22	0.42	0.39	0.4	0.46	0.43
KMW-016A Indicator	1.1	1.19	1.57	1.45	1.35	1.05	1.49	1.45	1.75	1.42
Duplicate		1.17					1.48			
KMW-017 Compliance	6.3	5.38	5.12	4.74	4.48	0.2	0.23	0.19	0.18	0.17
KMW-017Z Indicator	8	8.77	8.29	6.77	10.7	0.24	0.26	0.23	0.18	0.28
KMW-019A Compliance	14	14.3	13.7	14.6	14.8	1.31	1.24	1.45	1.36	1.39
Sand Aquifer										
KMW-008A Indicator	0.1 U	##### U	0.050 U	##### U	##### U	0.14	0.12	0.14	0.15	0.130
Duplicate					##### U					0.130
KMW-012A Indicator	0.2	0.11	0.2	0.141	0.212	1.61	1.61	1.59	1.45	1.46
Duplicate				0.169					1.45	
KMW-013 Background	1.00	1.01	0.92	1.07	1.03	0.630	0.63	0.59	0.65	0.64
KMW-016B Indicator	0.1 U	##### U	0.050 U	##### U	##### U	1.31	1.54	1.50	1.76	1.73
Duplicate			0.050 U					1.51		
KMW-018A Indicator	0.1 U	##### U	0.050 U	##### U	##### U	3.39	3.30	3.32	3.17	3.13

Samples Dates:

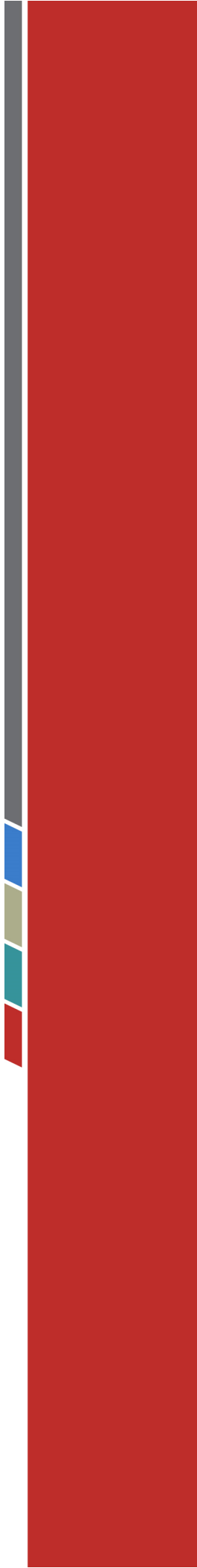
2014: September 9-11
2015: September 8-10
2016: September 12-13
2017: September 18-19
2018: September 10-11

Appendix B

BIOSCREEN and BIOCHLOR Modeling



Bioscreen 2018 Model Runs



BIOSCREEN Natural Attenuation Decision Support System

Air Force Center for Environmental Excellence

Version 1.4

Kent Highlands

KMW-17

Run Name

1. HYDROGEOLOGY

Seepage Velocity* Vs 64.4 (ft/yr)
or
Hydraulic Conductivity K 5.0E-03 (cm/sec)
Hydraulic Gradient i 0.00436 (ft/ft)
Porosity n 0.35 (-)

2. DISPERSION

Longitudinal Dispersivity* alpha x 13.3 (ft)
Transverse Dispersivity* alpha y 1.3 (ft)
Vertical Dispersivity* alpha z 0.0 (ft)
or
Estimated Plume Length Lp 280 (ft)

3. ADSORPTION

Retardation Factor* R 2.3 (-)
or
Soil Bulk Density rho 1.67 (kg/l)
Partition Coefficient Koc 56 (L/kg)
Fraction Organic Carbon foc 5.0E-3 (-)

4. BIODEGRADATION

1st Order Decay Coeff* lambda 3.6E-1 (per yr)
or
Solute Half-Life t-half 1.90 (year)
or Instantaneous Reaction Model
Delta Oxygen* DO 1.65 (mg/L)
Delta Nitrate* NO3 0.7 (mg/L)
Observed Ferrous Iron* Fe2+ 16.6 (mg/L)
Delta Sulfate* SO4 22.4 (mg/L)
Observed Methane* CH4 6.6 (mg/L)

5. GENERAL

Modeled Area Length* 200 (ft)
Modeled Area Width* 1000 (ft)
Simulation Time* 50 (yr)

6. SOURCE DATA

Source Thickness in Sat. Zone* 30 (ft)

Source Zones:

Width* (ft)	Conc. (mg/L)*
125	0.001
125	0.00221
500	0.362
125	0.00221
125	0.001

Source Halflife (see Help):

5 400 (yr)
Inst. React. 1st Order
Soluble Mass 2000 (Kg)
In Source NAPL, Soil

7. FIELD DATA FOR COMPARISON

Concentration (mg/L)								.067			
Dist. from Source (ft)	0	20	40	60	80	100	120	140	160	180	200

8. CHOOSE TYPE OF OUTPUT TO SEE:

RUN
CENTERLINE

View Output

RUN ARRAY

View Output

Help

Recalculate This

Paste Example Dataset

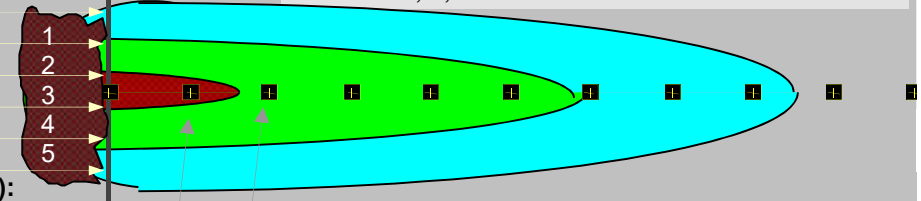
Restore Formulas for Vs,

Data Input Instructions:

115
or
0.02

1. Enter value directly....or
 2. Calculate by filling in grey cells below. (To restore formulas, hit button below).
- Variable* → Data used directly in model.
20 → Value calculated by model. (Don't enter any data).

Vertical Plane Source: Look at Plume Cross-Section and Input Concentrations & Widths for Zones 1, 2, and 3



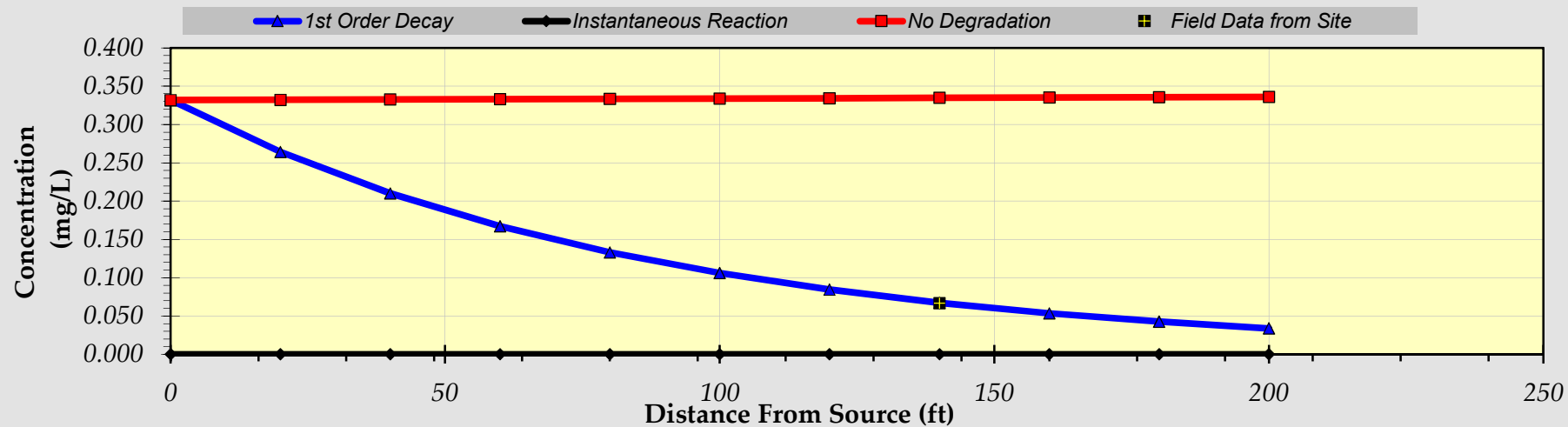
View of Plume Looking Down

Observed Centerline Concentrations at Monitoring Wells
If No Data Leave Blank or Enter "0"

DISSOLVED HYDROCARBON CONCENTRATION ALONG PLUME CENTERLINE (mg/L at Z=0)

Distance from Source (ft)

TYPE OF MODEL	0	20	40	60	80	100	120	140	160	180	200
No Degradation	0.332	0.332	0.333	0.333	0.334	0.334	0.334	0.335	0.335	0.336	0.336
1st Order Decay	0.332	0.264	0.210	0.167	0.133	0.106	0.084	0.067	0.053	0.043	0.034
Inst. Reaction	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Field Data from Site								0.067			



Calculate Animation

Time:

50 Years

Return to

Recalculate This

BIOSCREEN Natural Attenuation Decision Support System

Air Force Center for Environmental Excellence

Version 1.4

Kent Highlands

KMW-17

Run Name

1. HYDROGEOLOGY

Seepage Velocity* Vs 64.4 (ft/yr)
or
Hydraulic Conductivity K 5.0E-03 (cm/sec)
Hydraulic Gradient i 0.00436 (ft/ft)
Porosity n 0.35 (-)

2. DISPERSION

Longitudinal Dispersivity* alpha x 13.3 (ft)
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Vertical Dispersivity* alpha z 0.0 (ft)
or
Estimated Plume Length Lp 280 (ft)

3. ADSORPTION

Retardation Factor* R 2.3 (-)
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Soil Bulk Density rho 1.67 (kg/l)
Partition Coefficient Koc 56 (L/kg)
Fraction Organic Carbon foc 5.0E-3 (-)

4. BIODEGRADATION

1st Order Decay Coeff* lambda 3.6E-1 (per yr)
or
Solute Half-Life t-half 1.90 (year)
or Instantaneous Reaction Model
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Delta Nitrate* NO3 0.7 (mg/L)
Observed Ferrous Iron* Fe2+ 16.6 (mg/L)
Delta Sulfate* SO4 22.4 (mg/L)
Observed Methane* CH4 6.6 (mg/L)

5. GENERAL

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Modeled Area Width* 1000 (ft)
Simulation Time* 50 (yr)

6. SOURCE DATA

Source Thickness in Sat.Zone* 30 (ft)

Source Zones:

Width* (ft)	Conc. (mg/L)*
125	0.001
125	0.00221
500	0.26
125	0.00221
125	0.001

Source Halflife (see Help):

5 600 (yr)
Inst. React. 1st Order
Soluble Mass 2000 (Kg)
In Source NAPL, Soil

7. FIELD DATA FOR COMPARISON

Concentration (mg/L)

Dist. from Source (ft)

0	20	40	60	80	100	120	140	160	180	200
---	----	----	----	----	-----	-----	-----	-----	-----	-----

8. CHOOSE TYPE OF OUTPUT TO SEE:

RUN
CENTERLINE

View Output

RUN ARRAY

View Output

Help

Recalculate This

Paste Example Dataset

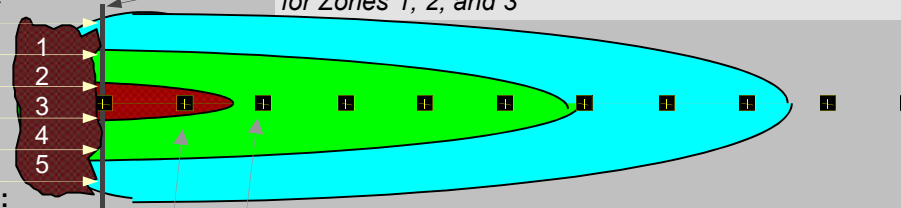
Restore Formulas for Vs,

Data Input Instructions:

115
or
0.02

1. Enter value directly....or
 2. Calculate by filling in grey cells below. (To restore formulas, hit button below).
- Variable* → Data used directly in model.
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Vertical Plane Source: Look at Plume Cross-Section and Input Concentrations & Widths for Zones 1, 2, and 3



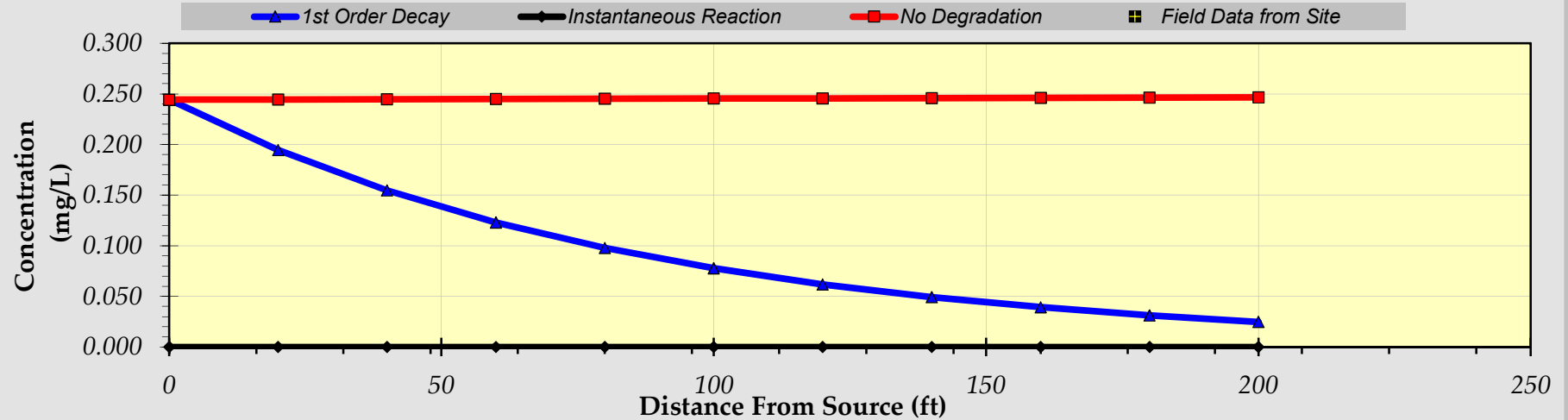
View of Plume Looking Down

Observed Centerline Concentrations at Monitoring Wells
If No Data Leave Blank or Enter "0"

DISSOLVED HYDROCARBON CONCENTRATION ALONG PLUME CENTERLINE (mg/L at Z=0)

Distance from Source (ft)

TYPE OF MODEL	0	20	40	60	80	100	120	140	160	180	200
No Degradation	0.244	0.244	0.245	0.245	0.245	0.245	0.246	0.246	0.246	0.246	0.246
1st Order Decay	0.244	0.194	0.155	0.123	0.098	0.078	0.062	0.049	0.039	0.031	0.025
Inst. Reaction	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Field Data from Site											



Calculate Animation

Time:

50 Years

Return to

Recalculate This

BIOSCREEN Natural Attenuation Decision Support System

Air Force Center for Environmental Excellence

Version 1.4

Kent Highlands

KMW-17

Run Name

1. HYDROGEOLOGY

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or
Hydraulic Conductivity K 5.0E-03 (cm/sec)
Hydraulic Gradient i 0.00436 (ft/ft)
Porosity n 0.35 (-)

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Longitudinal Dispersivity* alpha x 13.3 (ft)
Transverse Dispersivity* alpha y 1.3 (ft)
Vertical Dispersivity* alpha z 0.0 (ft)
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Delta Oxygen* DO 1.65 (mg/L)
Delta Nitrate* NO3 0.7 (mg/L)
Observed Ferrous Iron* Fe2+ 16.6 (mg/L)
Delta Sulfate* SO4 22.4 (mg/L)
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Width* (ft)	Conc. (mg/L)*
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125	0.00221
500	0.13
125	0.00221
125	0.001

Source Half-life (see Help):

5 >1000 (yr)

Inst. React. 1st Order

Soluble Mass 2000 (Kg)

In Source NAPL, Soil

7. FIELD DATA FOR COMPARISON

Concentration (mg/L)

Dist. from Source (ft)

0	20	40	60	80	100	120	140	160	180	200
---	----	----	----	----	-----	-----	-----	-----	-----	-----

8. CHOOSE TYPE OF OUTPUT TO SEE:

RUN
CENTERLINE

View Output

RUN ARRAY

View Output

Help

Recalculate This

Paste Example Dataset

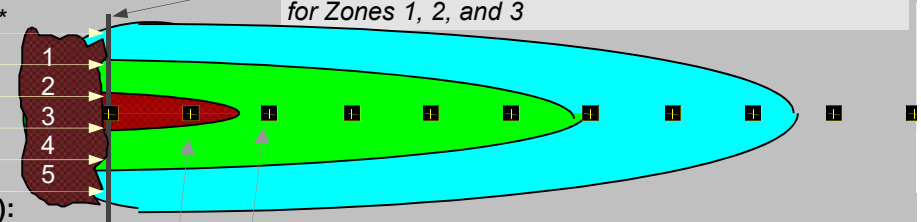
Restore Formulas for Vs,

Data Input Instructions:

115
or
0.02

1. Enter value directly....or
 2. Calculate by filling in grey cells below. (To restore formulas, hit button below).
- Variable* → Data used directly in model.
- 20 → Value calculated by model. (Don't enter any data).

Vertical Plane Source: Look at Plume Cross-Section and Input Concentrations & Widths for Zones 1, 2, and 3



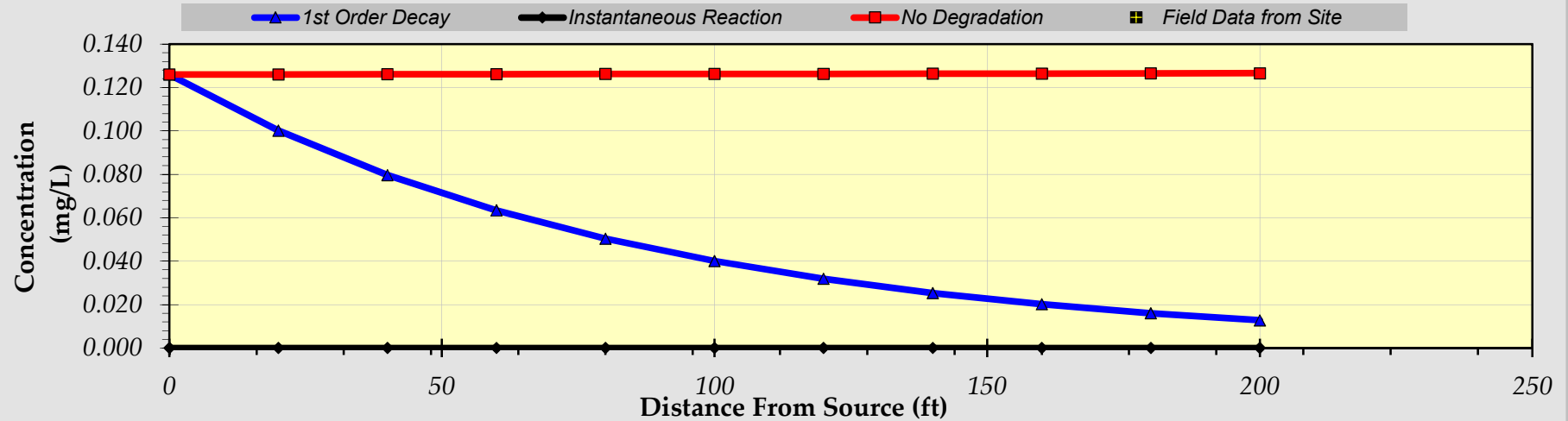
View of Plume Looking Down

Observed Centerline Concentrations at Monitoring Wells
If No Data Leave Blank or Enter "0"

DISSOLVED HYDROCARBON CONCENTRATION ALONG PLUME CENTERLINE (mg/L at Z=0)

Distance from Source (ft)

TYPE OF MODEL	0	20	40	60	80	100	120	140	160	180	200
No Degradation	0.126	0.126	0.126	0.126	0.126	0.126	0.126	0.126	0.126	0.126	0.127
1st Order Decay	0.126	0.100	0.080	0.063	0.050	0.040	0.032	0.025	0.020	0.016	0.013
Inst. Reaction	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Field Data from Site											



Calculate Animation

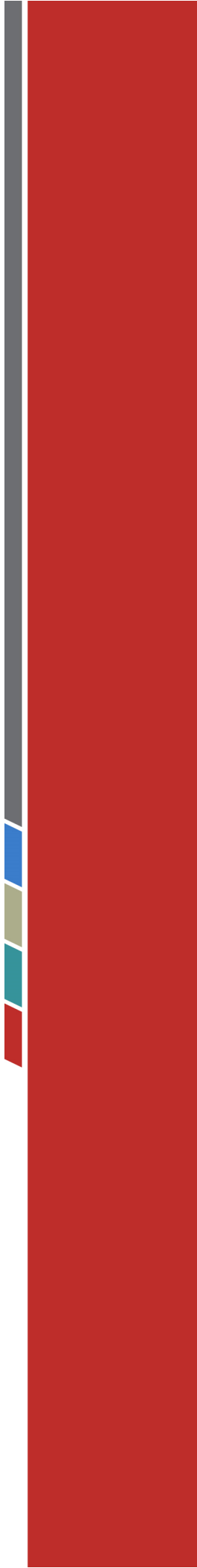
Time:

50 Years

Return to

Recalculate This

Biochlor CS 2018 Model Runs



BIOCHLOR Natural Attenuation Decision Support System

Version 2.2
Excel 2000

Kent Highlands

KMW-17

Run Name

TYPE OF CHLORINATED SOLVENT:

Ethenes ☒
Ethanes ☐

1. ADVECTION

Seepage Velocity* Vs (ft/yr)
or
Hydraulic Conductivity K (cm/sec)
Hydraulic Gradient i (ft/ft)
Effective Porosity n (-)

2. DISPERSION

Alpha x* (ft)
(Alpha y) / (Alpha x)* (-)
(Alpha z) / (Alpha x)* (-)

3. ADSORPTION

Retardation Factor*
or
Soil Bulk Density, rho (kg/L)
Fraction Organic Carbon, foc (-)
Partition Coefficient Koc (L/kg)
PCE (-)
TCE (-)
DCE (-)
VC (-)
ETH (-)

Common R (used in model)* =

4. BIOTRANSFORMATION

Zone 1
PCE (1/yr) half-life (yrs) Yield
TCE (1/yr) half-life (yrs)
DCE (1/yr) half-life (yrs)
VC (1/yr) half-life (yrs)
Zone 2
PCE (1/yr) half-life (yrs) Yield
TCE (1/yr) half-life (yrs)
DCE (1/yr) half-life (yrs)
VC (1/yr) half-life (yrs)

5. GENERAL

Simulation Time* (yr)
Modeled Area Width* (ft)
Modeled Area Length* (ft)
Zone 1 Length* (ft)
Zone 2 Length* (ft)
Zone 2 = L - Zone 1

6. SOURCE DATA

Source Options
Source Thickness in Sat. Zone* (ft)
Width* (ft)
Conc. (mg/L)* C1
PCE
TCE
DCE
VC
ETH

7. FIELD DATA FOR COMPARISON

PCE Conc. (mg/L)
TCE Conc. (mg/L)
DCE Conc. (mg/L)
VC Conc. (mg/L)
ETH Conc. (mg/L)
Distance from Source (ft)
Date Data Collected

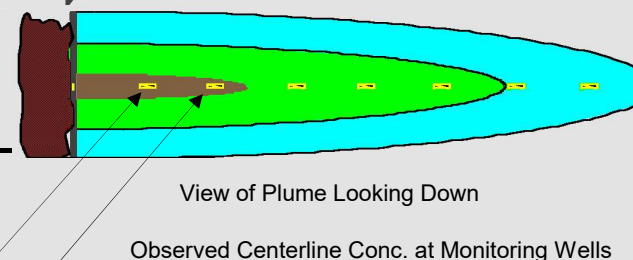
8. CHOOSE TYPE OF OUTPUT TO SEE:

Data Input Instructions:

115 → 1. Enter value directly....or
↑ or 0.02 → 2. Calculate by filling in gray cells. Press Enter, then
(To restore formulas, hit "Restore Formulas" button)
Variable* → Data used directly in model.

Test if Biotransformation is Occurring →

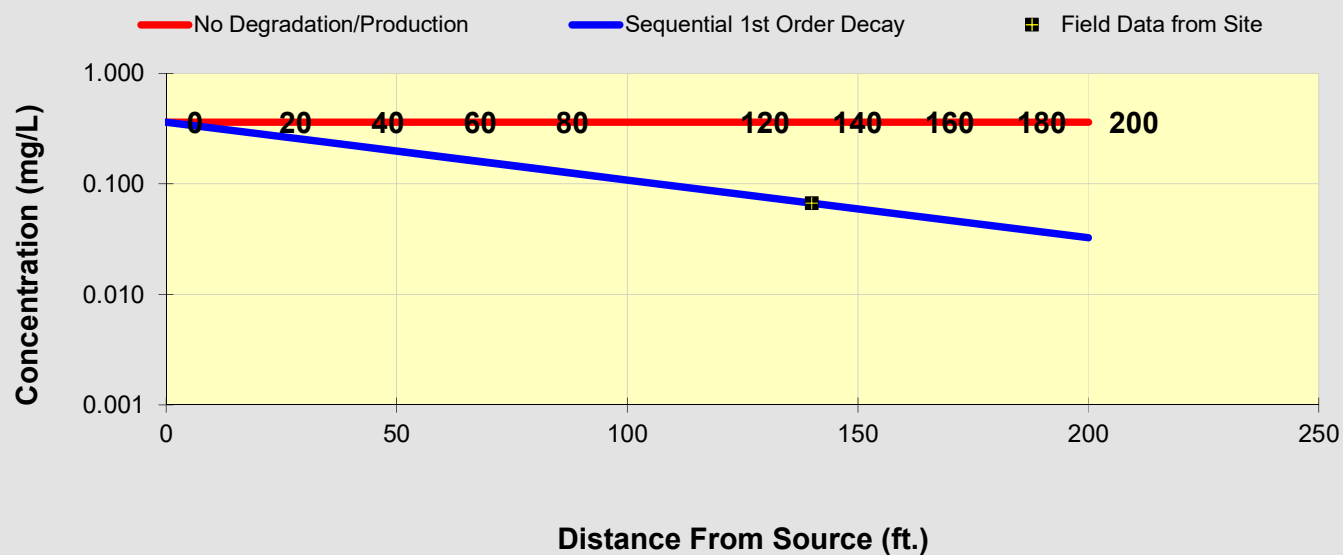
Vertical Plane Source: Determine Source Well Location and Input Solvent Concentrations



DISSOLVED CHLORINATED SOLVENT CONCENTRATIONS ALONG PLUME CENTERLINE (mg/L) at Z=0

VC	Distance from Source (ft)										
	0	20	40	60	80	100	120	140	160	180	200
No Degradation	0.362	0.362	0.362	0.362	0.362	0.362	0.362	0.362	0.362	0.362	0.362
Biotransformation	0.3620	0.285	0.224	0.176	0.138	0.109	0.086	0.067	0.053	0.042	0.033

Monitoring Well Locations (ft)										
140										
Field Data from Site	0.067									



See PCE

See TCE

See DCE

See VC

See ETH

Prepare Animation

Time:

50.0 Years

Log $\longleftrightarrow$ Linear

Return to
Input

To All

To Array

BIOCHLOR Natural Attenuation Decision Support System

Version 2.2
Excel 2000

Kent Highlands

KMW-17

Run Name

Data Input Instructions:

115

↑ or

0.02

1. Enter value directly....or
 2. Calculate by filling in gray cells. Press Enter, then **C**
- (To restore formulas, hit "Restore Formulas" button)

Variable* → Data used directly in model.

Test if
Biotransformation
is Occurring →

Natural Attenuation
Screening Protocol

TYPE OF CHLORINATED SOLVENT:

Ethenes



Ethanes



1. ADVECTION

Seepage Velocity* Vs 64.4 (ft/yr)

or

Hydraulic Conductivity K 5.0E-03 (cm/sec)

Hydraulic Gradient i 0.004357 (ft/ft)

Effective Porosity n 0.35 (-)

2. DISPERSION

Alpha x* 28 (ft) Calc. Alpha x

(Alpha y) / (Alpha x)* 0.1 (-)

(Alpha z) / (Alpha x)* 1.E-99 (-)

3. ADSORPTION

Retardation Factor* R

or

Soil Bulk Density, rho 1.67 (kg/L)

Fraction Organic Carbon, foc 5.0E-3 (-)

Partition Coefficient Koc

PCE 426 (L/kg) 11.16 (-)

TCE 130 (L/kg) 4.10 (-)

DCE 125 (L/kg) 3.98 (-)

VC 56 (L/kg) 2.34 (-)

ETH 302 (L/kg) 8.20 (-)

Common R (used in model)* = 2.34

4. BIOTRANSFORMATION

-1st Order Decay Coefficient*

Zone 1 λ (1/yr) half-life (yrs) Yield

PCE → TCE 0.000 ← 0.79

TCE → DCE 0.000 ← 0.74

DCE → VC 0.000 ← 0.64

VC → ETH 1.034 ← 0.45

Zone 2 λ (1/yr) half-life (yrs)

PCE → TCE 0.000 ←

TCE → DCE 0.000 ←

DCE → VC 0.000 ←

VC → ETH 0.000 ←

λ
HELP

5. GENERAL

Simulation Time* 50 (yr)

Modeled Area Width* 1000 (ft)

Modeled Area Length* 200 (ft)

Zone 1 Length* 200 (ft)

Zone 2 Length* 0 (ft)

L

W

Zone 2= L - Zone 1

6. SOURCE DATA

TYPE: Continuous
Single Planar

Source Options

Source Thickness in Sat. Zone* 30 (ft)

Width* (ft) 500

Conc. (mg/L)* C1

PCE 0

TCE 0

DCE 0

VC 0

ETH 0

k_s* (1/yr)

0

0

0

0

0

0

0

0

0

0

0

0

0

0

0

0

0

0

0

0

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0

0

0

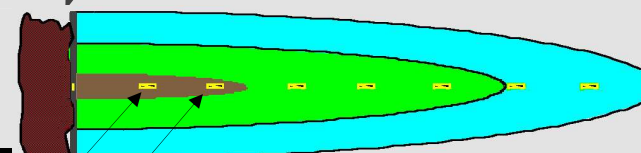
0

0

0

0

Vertical Plane Source: Determine Source Well
Location and Input Solvent Concentrations



View of Plume Looking Down

Observed Centerline Conc. at Monitoring Wells

7. FIELD DATA FOR COMPARISON

PCE Conc. (mg/L)

TCE Conc. (mg/L)

DCE Conc. (mg/L)

VC Conc. (mg/L)

ETH Conc. (mg/L)

Distance from Source (ft) 140

Date Data Collected 2018

8. CHOOSE TYPE OF OUTPUT TO SEE:

RUN CENTERLINE

RUN ARRAY

Help

Restore

RESET

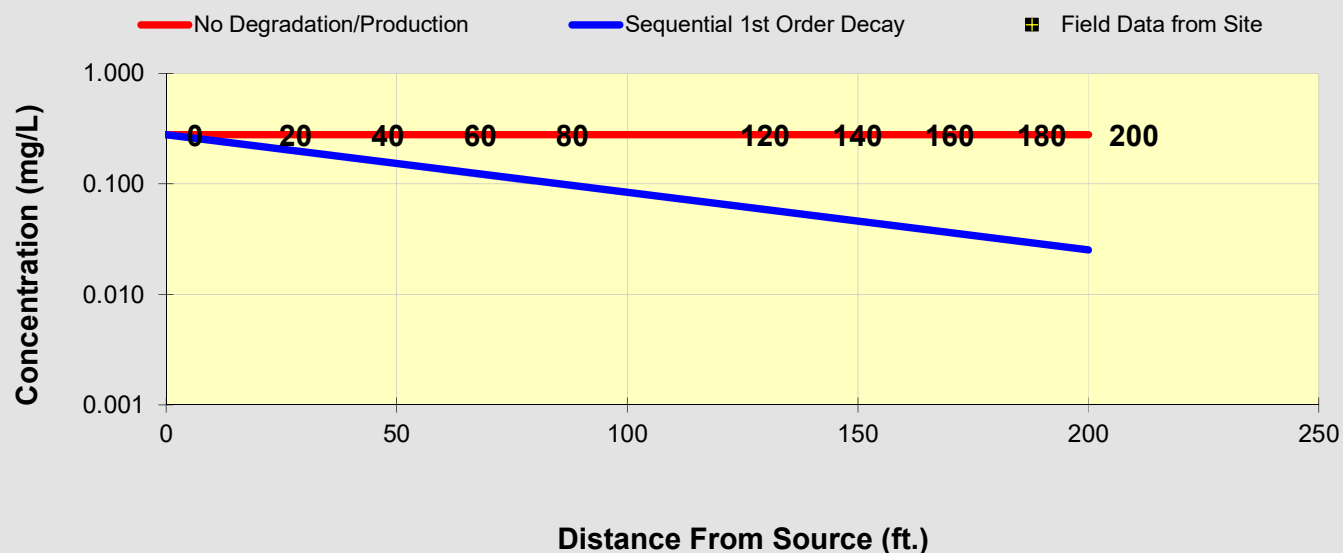
SEE OUTPUT

Paste

DISSOLVED CHLORINATED SOLVENT CONCENTRATIONS ALONG PLUME CENTERLINE (mg/L) at Z=0

VC	Distance from Source (ft)										
	0	20	40	60	80	100	120	140	160	180	200
No Degradation	0.280	0.280	0.280	0.280	0.280	0.280	0.280	0.280	0.280	0.280	0.280
Biotransformation	0.2800	0.220	0.173	0.136	0.107	0.084	0.066	0.052	0.041	0.032	0.025

Monitoring Well Locations (ft)										
140										
Field Data from Site										



See PCE

See TCE

See DCE

See VC

See ETH

Prepare Animation

Time:

50.0 Years

Log $\longleftrightarrow$ Linear

Return to
Input

To All

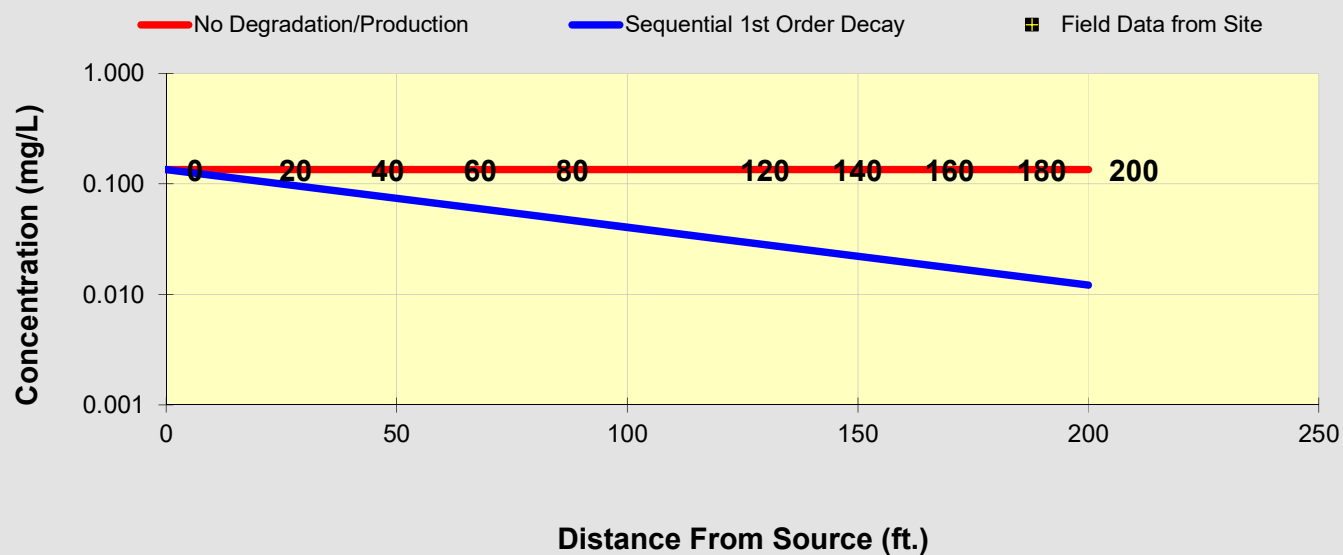
To Array

BIOCHLOR Natural Attenuation Decision Support System				Kent Highlands	
Version 2.2 Excel 2000				KMW-17	
Run Name					
TYPE OF CHLORINATED SOLVENT:		☒ Ethenes ☐ Ethanes			
1. ADVECTION					
Seepage Velocity*	Vs	64.4	(ft/yr)		
or					
Hydraulic Conductivity	K	5.0E-03	(cm/sec)		
Hydraulic Gradient	i	0.004357	(ft/ft)		
Effective Porosity	n	0.35	(-)		
2. DISPERSION					
Alpha x*		28	(ft)	Calc. Alpha x	
(Alpha y) / (Alpha x)*		0.1	(-)		
(Alpha z) / (Alpha x)*		1.E-99	(-)		
3. ADSORPTION					
Retardation Factor*		R			
or					
Soil Bulk Density, rho		1.67	(kg/L)		
Fraction Organic Carbon, foc		5.0E-3	(-)		
Partition Coefficient	Koc				
PCE		426	(L/kg)	11.16	(-)
TCE		130	(L/kg)	4.10	(-)
DCE		125	(L/kg)	3.98	(-)
VC		56	(L/kg)	2.34	(-)
ETH		302	(L/kg)	8.20	(-)
Common R (used in model)* =				2.34	
4. BIOTRANSFORMATION					
Zone 1		-1st Order Decay Coefficient*			
	λ (1/yr)	half-life (yrs)	Yield		
PCE → TCE	0.000	0.79	0.79		
TCE → DCE	0.000	0.74	0.74		
DCE → VC	0.000	0.64	0.64		
VC → ETH	1.034	0.45	0.45		
Zone 2					
	λ (1/yr)	half-life (yrs)			
PCE → TCE	0.000	0.79			
TCE → DCE	0.000	0.74			
DCE → VC	0.000	0.64			
VC → ETH	0.000	0.45			
5. GENERAL					
Simulation Time*		50	(yr)		
Modeled Area Width*		1000	(ft)		
Modeled Area Length*		200	(ft)		
Zone 1 Length*		200	(ft)		
Zone 2 Length*		0	(ft)		
				Zone 2 = L - Zone 1	
6. SOURCE DATA					
Source Options		TYPE: Continuous Single Planar			
Source Thickness in Sat. Zone*		30	(ft)		
Width* (ft)		500			
Conc. (mg/L)*		C1			
PCE		0			
TCE		0			
DCE		0			
VC		0.135			
ETH		0			
7. FIELD DATA FOR COMPARISON					
PCE Conc. (mg/L)					
TCE Conc. (mg/L)					
DCE Conc. (mg/L)					
VC Conc. (mg/L)					
ETH Conc. (mg/L)					
Distance from Source (ft)	140				
Date Data Collected	2018				
8. CHOOSE TYPE OF OUTPUT TO SEE:					
RUN CENTERLINE		RUN ARRAY		Help	
SEE OUTPUT		Restore		RESET	
Paste					

DISSOLVED CHLORINATED SOLVENT CONCENTRATIONS ALONG PLUME CENTERLINE (mg/L) at Z=0

VC	Distance from Source (ft)										
	0	20	40	60	80	100	120	140	160	180	200
No Degradation	0.135	0.135	0.135	0.135	0.135	0.135	0.135	0.135	0.135	0.135	0.135
Biotransformation	0.1350	0.106	0.083	0.066	0.052	0.041	0.032	0.025	0.020	0.016	0.012

Monitoring Well Locations (ft)										
140										
Field Data from Site										



See PCE

See TCE

See DCE

See VC

See ETH

Prepare Animation

Time:

50.0 Years

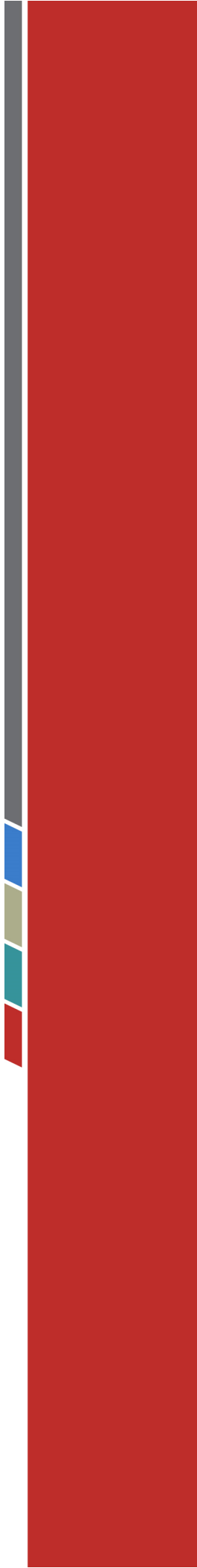
Log $\longleftrightarrow$ Linear

Return to
Input

To All

To Array

Biochlor DS 2018 Model Runs



BIOCHLOR Natural Attenuation Decision Support System

Version 2.2
Excel 2000

Kent Highlands

KMW-17

Run Name

TYPE OF CHLORINATED SOLVENT:

Ethenes ☒
Ethanes ☐

1. ADVECTION

Seepage Velocity* Vs (ft/yr)
or
Hydraulic Conductivity K (cm/sec)
Hydraulic Gradient i (ft/ft)
Effective Porosity n (-)

2. DISPERSION

Alpha x* (ft)
(Alpha y) / (Alpha x)* (-)
(Alpha z) / (Alpha x)* (-)

3. ADSORPTION

Retardation Factor*
or
Soil Bulk Density, rho (kg/L)
Fraction Organic Carbon, foc (-)
Partition Coefficient Koc (L/kg)
PCE (-)
TCE (-)
DCE (-)
VC (-)
ETH (-)

Common R (used in model)* =

4. BIOTRANSFORMATION

Zone 1
PCE (1/yr) half-life (yrs) Yield
TCE (1/yr) half-life (yrs)
DCE (1/yr) half-life (yrs)
VC (1/yr) half-life (yrs)
Zone 2
PCE (1/yr) half-life (yrs)
TCE (1/yr) half-life (yrs)
DCE (1/yr) half-life (yrs)
VC (1/yr) half-life (yrs)

5. GENERAL

Simulation Time* (yr)
Modeled Area Width* (ft)
Modeled Area Length* (ft)
Zone 1 Length* (ft)
Zone 2 Length* (ft)
Zone 2 = L - Zone 1

6. SOURCE DATA

Source Options
Source Thickness in Sat. Zone* (ft)
Width* (ft)
Conc. (mg/L)* C1
PCE
TCE
DCE
VC
ETH

7. FIELD DATA FOR COMPARISON

PCE Conc. (mg/L)
TCE Conc. (mg/L)
DCE Conc. (mg/L)
VC Conc. (mg/L)
ETH Conc. (mg/L)
Distance from Source (ft)
Date Data Collected

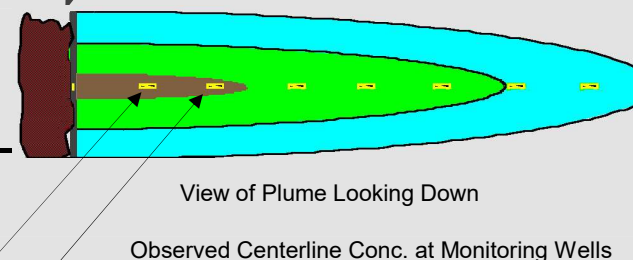
8. CHOOSE TYPE OF OUTPUT TO SEE:

Data Input Instructions:

115 → 1. Enter value directly....or
↑ or 0.02 → 2. Calculate by filling in gray cells. Press Enter, then
(To restore formulas, hit "Restore Formulas" button)
Variable* → Data used directly in model.

Test if Biotransformation is Occurring →

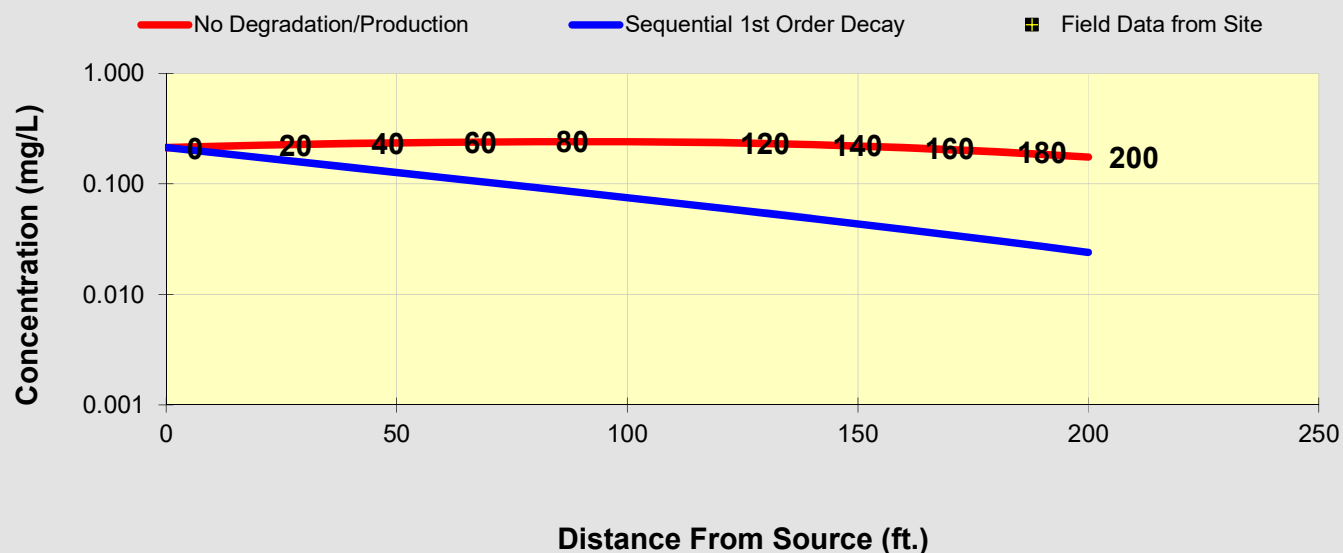
Vertical Plane Source: Determine Source Well Location and Input Solvent Concentrations



DISSOLVED CHLORINATED SOLVENT CONCENTRATIONS ALONG PLUME CENTERLINE (mg/L) at Z=0

VC	Distance from Source (ft)										
	0	20	40	60	80	100	120	140	160	180	200
No Degradation	0.214	0.224	0.233	0.239	0.242	0.242	0.237	0.228	0.214	0.196	0.175
Biotransformation	0.2138	0.174	0.141	0.115	0.093	0.075	0.061	0.049	0.039	0.031	0.024

Monitoring Well Locations (ft)										
140										
Field Data from Site										



See PCE

See TCE

See DCE

See VC

See ETH

Prepare Animation

Time:

7.0 Years

Log $\longleftrightarrow$ Linear

Return to
Input

To All

To Array

BIOCHLOR Natural Attenuation Decision Support System

Version 2.2
Excel 2000

Kent Highlands

KMW-17

Run Name

Data Input Instructions:

115

↑ or

0.02

1. Enter value directly....or
 2. Calculate by filling in gray cells. Press Enter, then **C**
- (To restore formulas, hit "Restore Formulas" button)

Variable* → Data used directly in model.

Test if
Biotransformation
is Occurring →

Natural Attenuation
Screening Protocol

TYPE OF CHLORINATED SOLVENT:

Ethenes



Ethanes



1. ADVECTION

Seepage Velocity* Vs 64.4 (ft/yr)

or

Hydraulic Conductivity K 5.0E-03 (cm/sec)

Hydraulic Gradient i 0.00436 (ft/ft)

Effective Porosity n 0.35 (-)

2. DISPERSION

Alpha x* 28 (ft) Calc. Alpha x

(Alpha y) / (Alpha x)* 0.1 (-)

(Alpha z) / (Alpha x)* 1.E-99 (-)

3. ADSORPTION

Retardation Factor* R

or

Soil Bulk Density, rho 1.67 (kg/L)

Fraction Organic Carbon, foc 5.0E-3 (-)

Partition Coefficient Koc

PCE 426 (L/kg) 11.16 (-)

TCE 130 (L/kg) 4.10 (-)

DCE 125 (L/kg) 3.98 (-)

VC 56 (L/kg) 2.34 (-)

ETH 302 (L/kg) 8.20 (-)

Common R (used in model)* = 2.34

4. BIOTRANSFORMATION

-1st Order Decay Coefficient*

Zone 1 λ (1/yr) half-life (yrs) Yield

PCE → TCE 0.000 ← 0.79

TCE → DCE 0.000 ← 0.74

DCE → VC 0.000 ← 0.64

VC → ETH 1.034 ← 0.45

Zone 2 λ (1/yr) half-life (yrs)

PCE → TCE 0.000 ←

TCE → DCE 0.000 ←

DCE → VC 0.000 ←

VC → ETH 0.000 ←

λ

HELP

5. GENERAL

Simulation Time* 17 (yr)

Modeled Area Width* 1000 (ft)

Modeled Area Length* 200 (ft)

Zone 1 Length* 200 (ft)

Zone 2 Length* 0 (ft)

L

W

Zone 2= L - Zone 1

6. SOURCE DATA

TYPE: Decaying

Source Options

Single Planar

Source Thickness in Sat. Zone* 30 (ft)

Width* (ft) 500

Conc. (mg/L)* C1

PCE 0.075

TCE 0.075

DCE 0.075

VC 0.075

ETH 0.075

k_s* (1/yr)

0.075

0.075

0.075

0.075

0.075

0.075

0.075

0.075

0.075

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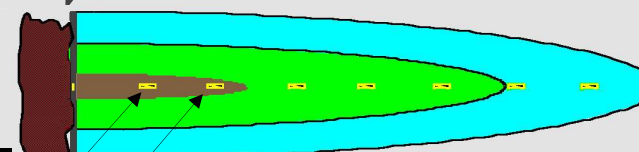
0.075

0.075

0.075

0.075

Vertical Plane Source: Determine Source Well Location and Input Solvent Concentrations



View of Plume Looking Down

Observed Centerline Conc. at Monitoring Wells

7. FIELD DATA FOR COMPARISON

PCE Conc. (mg/L)

TCE Conc. (mg/L)

DCE Conc. (mg/L)

VC Conc. (mg/L)

ETH Conc. (mg/L)

Distance from Source (ft) 140

Date Data Collected 1998

8. CHOOSE TYPE OF OUTPUT TO SEE:

RUN CENTERLINE

RUN ARRAY

Help

Restore

RESET

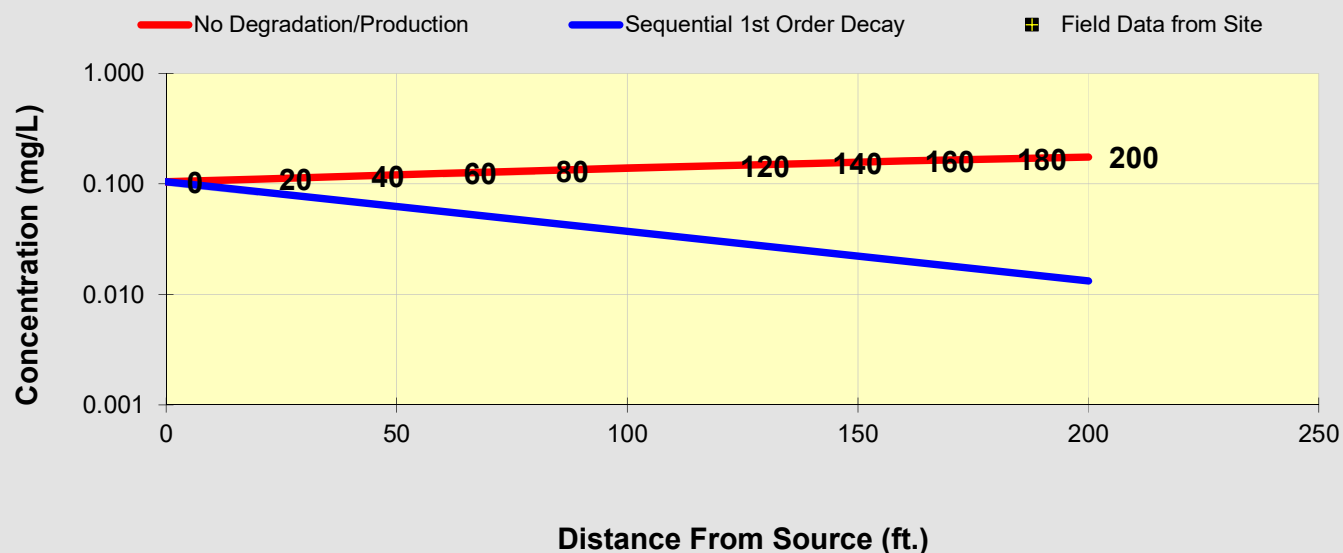
SEE OUTPUT

Paste

DISSOLVED CHLORINATED SOLVENT CONCENTRATIONS ALONG PLUME CENTERLINE (mg/L) at Z=0

VC	Distance from Source (ft)										
	0	20	40	60	80	100	120	140	160	180	200
No Degradation	0.105	0.111	0.118	0.125	0.132	0.139	0.147	0.154	0.161	0.169	0.175
Biotransformation	0.1047	0.085	0.069	0.056	0.046	0.037	0.030	0.025	0.020	0.016	0.013

Monitoring Well Locations (ft)										
140										
Field Data from Site										



See PCE

See TCE

See DCE

See VC

See ETH

Prepare Animation

Time:

16.5 Years

Log $\longleftrightarrow$ Linear

Return to
Input

To All

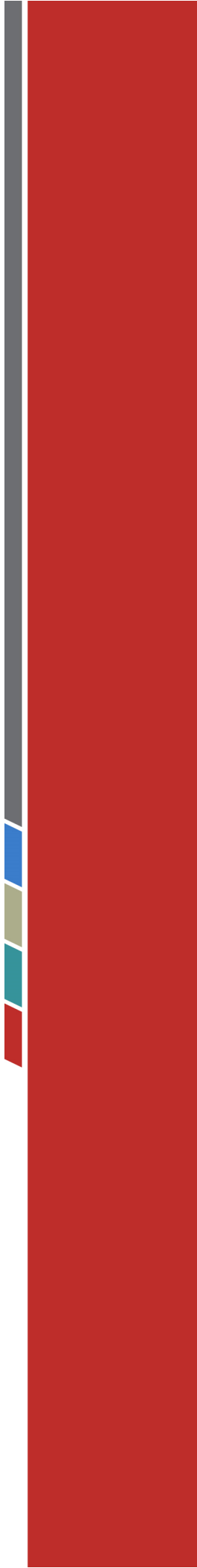
To Array

Appendix C

Information for Remediation Techniques



Air Stripping





Engineering Bulletin

Air Stripping of Aqueous Solutions

Purpose

Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants, and contaminants as a principal element." The Engineering Bulletins are a series of documents that summarize the latest information available on selected treatment and site remediation technologies and related issues. They provide summaries of and references for the latest information to help remedial project managers, on-scene coordinators, contractors, and other site cleanup managers understand the type of data and site characteristics needed to evaluate a technology for potential applicability to their Superfund or other hazardous waste site. Those documents that describe individual treatment technologies focus on remedial investigation scoping needs. Addenda will be issued periodically to update the original bulletins.

Abstract

Air stripping is a means to transfer contaminants from aqueous solutions to air. Contaminants are not destroyed by air stripping but are physically separated from the aqueous solutions. Contaminant vapors are transferred into the air stream and, if necessary, can be treated by incineration, adsorption, or oxidation. Most frequently, contaminants are collected in carbon adsorption systems and then treated or destroyed in this concentrated form. The concentrated contaminants may be recovered, incinerated for waste heat recovery, or destroyed by other treatment technologies. Generally, air stripping is used as one in a series of unit operations and can reduce the overall cost for managing a particular site. Air stripping is applicable to volatile and semivolatile organic compounds. It is not applicable for treating metals and inorganic compounds.

During 1988, air stripping was one of the selected remedies at 30 Superfund sites [1]*. In 1989, it was a component of the selected remedy at 38 Superfund sites [2]. An estimated

1,000 air-stripping units are presently in operation at sites throughout the United States [3]. Packed-tower systems typically provide the best removal efficiencies, but other equipment configurations exist, including diffused-air basins, surface aerators, and cross-flow towers [4, p. 2] [5, p. 10-48]. In packed-tower systems, there is no clear technology leader by virtue of the type of equipment used or mode of operation. The final determination of the lowest cost alternative will be more site specific than process equipment dominated.

This bulletin provides information on the technology applicability, the technology limitations, a description of the technology, the types of residuals produced, site requirements, the latest performance data, the status of the technology, and sources of further information.

Technology Applicability

Air stripping has been demonstrated in treating water contaminated with volatile organic compounds (VOCs) and semivolatile compounds. Removal efficiencies of greater than 98 percent for VOCs and greater than or equal to 80 percent for semivolatile compounds have been achieved. The technology is not effective in treating low-volatility compounds, metals, or inorganics [6, p. 5-3]. Air stripping has commonly been used with pump-and-treat methods for treating contaminated groundwater.

This technology has been used primarily for the treatment of VOCs in dilute aqueous waste streams. Effluent liquid quality is highly dependent on the influent contaminant concentration. Air stripping at specific design and operating conditions will yield a fixed, compound-specific percentage removal. Therefore, high influent contaminant concentrations may result in effluent concentrations above discharge standards. Enhancements, such as high temperature or rotary air stripping, will allow less-volatile organics, such as ketones, to be treated [6, p. 5-3].

Table 1 shows the effectiveness of air stripping on general contaminant groups present in aqueous solution. Examples of constituents within contaminant groups are provided in Reference 7, "Technology Screening Guide for Treatment of CERCLA Soils and Sludges." This table is based on the current available information or professional judgment

* [reference number, page number]

Table 1
Effectiveness of Air Stripping on General Contaminant Groups from Water

Contaminant Groups		Effectiveness
Organic	Halogenated volatiles	■
	Halogenated semivolatiles *	▼
	Nonhalogenated volatiles	■
	Nonhalogenated semivolatiles	□
	PCBs	□
	Pesticides	□
	Dioxins/Furans	□
	Organic cyanides	□
	Organic corrosives	□
Inorganic	Volatile metals	□
	Nonvolatile metals	□
	Asbestos	□
	Radioactive materials	□
	Inorganic corrosives	□
	Inorganic cyanides	□
Reactive	Oxidizers	□
	Reducers	□

■ Demonstrated Effectiveness: Successful treatability test at some scale completed
 ▼ Potential Effectiveness: Expert opinion that technology will work
 □ No Expected Effectiveness: Expert opinion that technology will not work
 * Only some compounds in this category are candidates for air stripping.

where no information was available. The proven effectiveness of the technology for a particular site or contaminant does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability testing demonstrated the technology was effective for that particular contaminant group. The ratings of potential effectiveness and no expected effectiveness are both based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular contaminant group, a no-expected-effectiveness rating is given.

Limitations

Because air stripping of aqueous solutions is a means of mass transfer of contaminants from the liquid to the air stream, air pollution control devices are typically required to capture or destroy contaminants in the offgas [8]. Even when offgas treatment is required, air stripping usually provides significant advantages over alternatives such as direct carbon adsorption from water because the contaminants are more favorably sorbed onto activated carbon from air than from water. Moreover,

contaminant destruction via catalytic oxidation or incineration may be feasible when applied to the offgas air stream.

Aqueous solutions with high turbidity or elevated levels of iron, manganese, or carbonate may reduce removal efficiencies due to scaling and the resultant channeling effects. Influent aqueous media with pHs greater than 11 or less than 5 may corrode system components and auxiliary equipment. The air stripper may also be subject to biological fouling. The aqueous solution being air stripped may need pretreatment to neutralize the liquid, control biological fouling, or prevent scaling [6][9].

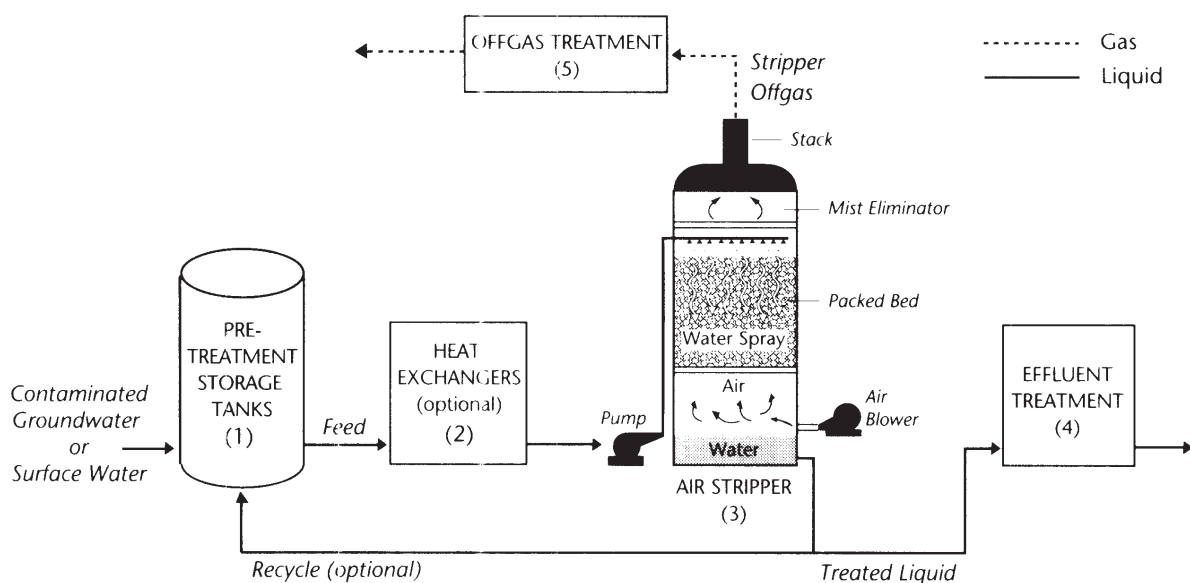
Contaminated water with VOC or semivolatile concentrations greater than 0.01 percent generally cannot be treated by air stripping. Even at lower influent concentrations, air stripping may not be able to achieve cleanup levels required at certain sites. For example, a 99 percent removal of trichloroethene (TCE) from groundwater containing 100 parts per million (ppm) would result in an effluent concentration of 1 ppm, well above drinking water standards. Without heating, only volatile organic contaminants with a dimensionless Henry's Law constant greater than 10^{-2} are amenable to continuous-flow air stripping in aqueous solutions [6][5]. In certain cases, where a high removal efficiency is not required, compounds with lower Henry's Law constants may be air stripped. Ashworth et al. published the Henry's Law constants for 45 chemicals [10, p. 25]. Nirmalakhandan and Speece published a method for predicting Henry's Law constants when published constants are unavailable [11]. Air strippers operated in a batch mode may be effective for treating water containing either high contaminant concentrations or contaminants with lower Henry's Law constants. However, batch systems are normally limited to relatively low average flow rates.

Several environmental impacts are associated with air stripping. Air emissions of volatile organics are produced and must be treated. The treated wastewater may need additional treatment to remove metals and nonvolatiles. Deposits, such as metal (e.g., iron) precipitates may occur, necessitating periodic cleaning of air-stripping towers [6, p. 5-5]. In cases where heavy metals are present and additional treatment will be required, it may be beneficial to precipitate those metals prior to air stripping.

Technology Description

Air stripping is a mass transfer process used to treat groundwater or surface water contaminated with volatile or semivolatile organic contaminants. At a given site, the system is designed based on the type of contaminant present, the contaminant concentration, the required effluent concentration, water temperature, and water flow rate. The major design variables are gas pressure drop, air-to-water ratio, and type of packing. Given those design variables, the gas and liquid loading (i.e., flows per cross-sectional area), tower diameter and packing height can be determined. Flexibility in the system design should allow for changes in contaminant concentration, air and water flow rates, and water temperature. Figure 1 is a schematic of a typical process for the air stripping of contaminated water.

Figure 1
Schematic Diagram of Air-Stripping System [8, p. 20][13, p. 43]



In an air-stripping process, the contaminated liquid is pumped from a groundwater or surface water source. Water to be processed is directed to a storage tank (1) along with any recycle from the air-stripping unit.

Air stripping is typically performed at ambient temperature. In some cases, the feed stream temperature is increased in a heat exchanger (2). Heating the influent liquid increases air-stripping efficiency and has been used to obtain a greater removal of semi-volatile organics such as ketones. At temperatures close to 100°C, steam stripping may be a more practical treatment technique [8, p. 3].

The feed stream (combination of the influent and recycle) is pumped to the air stripper (3). Three basic designs are used for air strippers: surface aeration, diffused-air systems, and specially designed liquid-gas contactors [4, p. 3]. The first two of these have limited application to the treatment of contaminated water due to their lower contaminant removal efficiency. In addition, air emissions from surface-aeration and diffused-air systems are frequently more difficult to capture and control. These two types of air strippers will not be discussed further. The air stripper in Figure 1 is an example of a liquid-gas contactor.

The most efficient type of liquid-gas contactor is the packed tower [4, p. 3]. Within the packed tower, structures called packing provide surface area on which the contaminated water can form a thin film and come in contact with a countercurrent flow of air. Air-to-water ratios may range from 10:1 to 300:1 on a volumetric basis [14, p. 8]. Selecting packing material that will maximize the wetted surface area will enhance air stripping. Packed towers are usually cylindrical and are filled with either random or structured packing. Random packing consists of pieces of packing dumped onto a support structure within the tower. Metal, plastic, or ceramic pieces come in standard sizes and a variety of shapes. Smaller packing sizes generally increase the interfacial area for stripping and improve the mass-

transfer kinetics. However, smaller packing sizes result in an increased pressure drop of the air stream and an increased potential for precipitate fouling. Tripacks*, saddles, and slotted rings are the shapes most commonly used for commercial applications. Structured packing consists of trays fitted to the inner diameter of the tower and placed at designated points along the height of the tower. These trays are made of metal gauze, sheet metal, or plastic. The choice of which type of packing to use depends on budget and design constraints. Random packing is generally less expensive. However, structured packing reportedly provides advantages such as lower pressure-drop and better liquid distribution characteristics [4, p. 5].

The processed liquid from the air-stripper tower may contain trace amounts of contaminants. If required, this effluent is treated (4) with carbon adsorption or other appropriate treatments.

The offgas can be treated (5) using carbon adsorption, thermal incineration, or catalytic oxidation. Carbon adsorption is used more frequently than the other control technologies because of its ability to remove hydrocarbons cost-effectively from dilute (< 1 percent) air streams [8, p. 5].

Process Residuals

The primary process residual streams created with air-stripping systems are the offgas and liquid effluent. The offgas is released to the atmosphere after treatment; activated carbon is the treatment most frequently applied to the offgas stream. Where activated carbon is used, it is recommended that the relative humidity of the air stream be reduced. Once spent, the carbon can be regenerated onsite or shipped to the original supplier for reactivation. If spent carbon is replaced, it may have to be handled as a hazardous waste. Catalytic oxidation and thermal incineration also may be used for offgas treatment [15, p. 10] [8, p. 5]. Sludges, such as iron precipitates, build up

within the tower and must be removed periodically [6, p. 5-5]. Spent carbon can also result if carbon filters are used to treat effluent water from the air-stripper system. Effluent water containing nonvolatile contaminants may need additional treatment. Such liquids are treated onsite or stored and removed to an appropriate facility. Biological, chemical, activated carbon, or other appropriate treatment technologies may be used to treat the effluent liquid. Once satisfactorily treated, the water is sent to a sewage treatment facility, discharged to surface water, or returned to the source, such as an underground aquifer.

Site Requirements

Air strippers are most frequently permanent installations, although mobile systems may be available for limited use. Permanent installations may be fabricated onsite or may be shipped in modular form and constructed onsite. Packing is installed after fabrication or construction of the tower. A concrete pad will be required to support the air-stripper tower in either case. Access roads or compacted soil will be needed to transport the necessary materials.

Standard 440V, three-phase electrical service is needed. Water should be available at the site to periodically clean scale or deposits from packing materials. The quantity of water needed is site specific. Typically, treated effluent can be used to wash scale from packing.

Contaminated liquids are hazardous, and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures. Spent activated carbon may be hazardous and require similar handling. Storage may be needed to hold the treated liquid until it has been tested to determine its acceptability for disposal or release. Depending upon the site, a method to store liquid that has been pretreated may be necessary. Storage capacity will depend on liquid volume.

Onsite analytical equipment for conducting various analyses, including gas chromatography capable of determining site-specific organic compounds for performance assessment, make the operation more efficient and provide better information for process control.

Performance Data

System performance is measured by comparing contaminant concentrations in the untreated liquid with those in the treated liquid. Performance data on air-stripping systems, ranging from pilot-scale to full-scale operation, have been reported by several sources, including equipment vendors. Data obtained on air strippers at Superfund sites also are discussed below. The data are presented as originally reported in the referenced documents. The quality of this information has not been determined. The key operating and design variables are provided when they were available in the reference.

An air-stripping system, which employed liquid-phase GAC to polish the effluent, was installed at the Sydney Mine site in Valrico, Florida. The air-stripping tower was 4 feet in diameter,

Table 2
Performance Data for the Groundwater Treatment System at the Sydney Mine Site, FL. [13, p. 42]

Contaminant	Concentration	
	Influent (µg/L)	Effluent (µg/L)
<i>Volatile organics</i>		
Benzene	11	ND ^a
Chlorobenzene	1	ND
1,1-dichloroethane	39	ND
Trans-1,2-dichloropropane	1	ND
Ethylbenzene	5	ND
Methylene chloride	503	ND
Toluene	10	ND
Trichlorofluoromethane	71	ND
Meta-xylene	3	ND
Ortho-xylene	2	ND
<i>Extractable organics</i>		
3-(1,1-dimethylethyl) phenol	32	ND
<i>Pesticides</i>		
2,4-D	4	ND
2,4,5-TP	1	ND
<i>Inorganics</i>		
Iron (mg/L)	11	< 0.03

^aND = Not detected at method detection limit of 1 µg/L for volatile organics and 10 µg/L for extractable organics and pesticides

42 feet tall, and contained a 24-foot bed of 3.5-inch diameter polyethylene packing. The average design water flow was 150 gallons per minute (gpm) with a hydraulic loading rate of 12 gpm/ft² and a volumetric air-to-water ratio of approximately 200:1. The air-stripping tower was oversized for use at future treatment sites. Effluent water from the air stripper was polished in a carbon adsorption unit. Table 2 summarizes the performance data for the complete system; it is unclear how much removal was accomplished by the air stripper and how much by the activated carbon. Influent concentrations of total organics varied from approximately 25 parts per billion (ppb) to 700 ppb [13, p. 41].

Air stripping was used at well 12A in the city of Tacoma, Washington. Well 12A had a capacity of 3,500 gpm and was contaminated with chlorinated hydrocarbons, including 1,1,2,2-tetrachloroethane; trans-1,2-dichloroethene (DCE); TCE; and perchloroethylene. The total VOC concentration was approximately 100 ppb. Five towers were installed and began operation on July 15, 1983. Each tower was 12 feet in diameter and was packed with 1-inch polypropylene saddles to a depth of 20 feet. The water flow rate was 700 gpm for each tower, and the volumetric air-to-water ratio was 310:1. The towers consistently removed 94 to 98 percent of the influent 1,1,2,2-tetrachloroethane with an overall average of 95.5 percent removal. For the other contaminants, removal efficiencies in excess of 98 percent were achieved [16, p. 112].

Another remedial action site was Wurtsmith Air Force Base in Oscoda, Michigan. The contamination at this site was the result of a leaking underground storage tank near a mainte-

Table 3
Air-Stripper Performance Summary
At Wurtsmith AFB
[17, p. 121]

G/L (vol)	Water Flow (L/min)	Single Tower (% Removed)	Series Operation (% Removed)
10	1,135	95	99.8
10	1,700	94	99.8
10	2,270	86	96.0
18	1,135	98	99.9
18	1,700	97	99.9
18	2,270	90	99.7
25	1,135	98	99.9
25 *	1,700	98	99.9
25	2,270	98	99.9

Influent TCE concentration: 50-8,000 µg/L Water temperature: 283°K

nance facility. Two packed-tower air strippers were installed to remove TCE. Each tower was 5 feet in diameter and 30 feet tall, with 18 feet of 16mm pall ring packing. The performance summary for the towers, presented in Table 3, is based on evaluations conducted in May and August 1982 and January 1983. Excessive biological growth decreased performance and required repeated removal and cleaning of the packing. Operation of the towers in series, with a volumetric air-to-water ratio of 25:1 and a water flow of 600 gpm (2,270 L/min), removed 99.9 percent of the contaminant [17, p. 119].

A 2,500 gpm air stripper was used to treat contaminated groundwater during the initial remedial action at the Verona Well field site in Battle Creek, Michigan. This well field is the major source of public potable water for the city of Battle Creek. The air stripper was a 10-foot diameter tower packed to a height of 40 feet with 3.5 inch pall rings. The air stripper was operated at 2,000 gpm with a 20:1 volumetric air-to-water ratio. Initial problems with iron oxide precipitating on the packed rings were solved by recirculating sodium hypochlorite through the stripper about four times per year [8, p. 8-9]. The total VOC concentration of 131 ppb was reduced by approximately 82.9 percent [15, p. 56]. The air stripper offgas was treated via vapor phase granular activated carbon beds. The offgas was heated prior to entering the carbon beds to reduce its humidity to 40 percent.

An air stripper is currently operating at the Hyde Park Superfund site in New York. Treatek, Inc., which operates the unit, reports the system is treating about 80,000 gallons per day (gpd) of landfill leachate. The contaminants are in the range of 4,000 ppm total organic carbon (TOC). The air stripper is reportedly able to remove about 90 percent of the TOCs [18]. A report describing the performance of the air stripper is expected to be published during 1991.

The primary VOCs at the Des Moines Superfund site were TCE; 1,2-DCE; and vinyl chloride. The TCE initial concentration was approximately 2,800 ppb and gradually declined to the 800 to 1,000 ppb range after 5 months. Initial groundwater

concentrations of 1,2-DCE were unreported while the concentration of vinyl chloride ranged from 38 ppb down to 1 ppb. The water flow rate to the air stripper ranged from 500 to 1,850 gpm and averaged approximately 1,300 gpm. No other design data were provided. TCE removal efficiencies were generally above 96 percent, while the removal efficiencies for 1,2-DCE were in the 85 to 96 percent range. No detectable levels of vinyl chloride were observed in the effluent water [12, p. B-1].

VOCs were detected in the Eau Claire municipal well field in Eau Claire, Wisconsin, as part of an EPA groundwater supply survey in 1981. An air stripper was placed on-line in 1987 to protect public health and welfare until completion of the remedial investigation/feasibility study (RI/FS) and final remedy selection. Data reported on the Eau Claire site were for the period beginning August 31, 1987 and ending February 15, 1989. During this period, the average removal efficiency was greater than

Table 4
Air-Stripper Performance at
Eau Claire Municipal Well Field [12, p. C-1]

Contaminant	Influent Concentration (ppb)	Removal Efficiency (%)
1,1-Dichloroethene	0.17-2.78	88
1,1-Dichloroethane	0.38-1.81	93
1,1,1-Trichloroethane	4.32-14.99	99
Trichloroethene	2.53-11.18	98

88 percent for the four chlorinated organic compounds studied. The average removal efficiencies are shown in Table 4. The air stripper had a 12-foot diameter and was 60 feet tall, with a packed bed of 26 feet. Water feed rates were approximately 5 to 6 million gallons per day (mgd). No other design parameters were reported [12, p. C-1].

In March 1990, an EPA study reviewed the performance data from a number of Superfund sites, including the Brewster Well Field, Hicksville MEK Spill, Rockaway Township, Western Processing, and Gilson Road Sites [15].

Reported removal efficiencies at the Brewster Well Field site in New York were 98.50 percent, 93.33 percent, and 95.59 percent for tetrachloroethene (PCE); TCE; and 1,2-DCE; respectively. Initial concentrations of the three contaminants were 200 ppb (PCE), 30 ppb (TCE) and 38 ppb (1,2-DCE) [15, p. 55]. The 300 gpm air stripper had a tower diameter of 4.75 feet, packing height of 17.75 feet, air-to-water ratio of 50:1, and used 1-inch saddles for packing material [15, p. 24].

A removal efficiency of 98.41 percent was reported for methyl ethyl ketone (MEK) at the Hicksville MEK spill site in New York. The reported influent MEK concentration was 15 ppm. The air stripper had a 100 gpm flowrate, an air-to-water ratio of 120:1, a tower diameter of 3.6 feet, a packing height of 15 feet, and used 2-inch Jaeger Tripack packing material. Water entering the air stripper was heated to approximately 180° to 195°F by heat exchangers [15, p. 38].

Table 5
Air Stripper Performance at Rockaway
Township, NJ [15, p. 53]

<i>Contaminant</i>	<i>Influent Concentration (ppb)</i>	<i>Removal Efficiency (%)</i>
Trichloroethylene	28.3	99.99
Methyl-tert-butyl ether	3.2	99.99
1,1-Dichloroethylene	4.0	99.99
cis-1,2-Dichloroethylene	6.4	99.99
Chloroform	1.3	99.99
1,1,1-Trichloroethane	20.0	99.99
1,1-Dichloroethane	2.0	99.99
Total VOC	65.2	99.99

The Rockaway Township air stripper had a flowrate of 1,400 gpm, tower diameter of 9 feet, packing height of 25 feet, air-to-water ratio of 200:1, and used 3-inch Tellerettes packing material. The performance data are shown in Table 5 [15, p. 18].

The Western Processing site had two air-stripping towers treating different wells in parallel. The first tower had a 100 gpm (initial) and 200 gpm (maximum) flowrate, a tower diameter of 40 feet, a packing height of 40.5 feet, an air-to-water ratio of 160:1 (initial) and 100:1 (maximum), and used 2-inch Jaeger Tripack packing material. The second tower had a 45

Table 6
Air-Stripper Performance at
Western Processing, WA [15, p. 61]

<i>Contaminant</i>	<i>Influent Concentration (ppb)</i>	<i>Removal Efficiency (%)</i>
Benzene	73	93.15
Carbon tetrachloride	5	—
Chloroform	781	99.36
1,2-Dichloroethane	22	77.27
1,1-Dichloroethylene	89	94.38
1,1,1-Trichloroethane	1,440	99.65
Trichloroethylene	8,220	99.94
Vinyl chloride	159	99.37
Dichloromethane	8,170	99.63
Tetrachloroethylene	378	98.68
Toluene	551	99.09
1,2-Dichlorobenzene	11	54.55
Hexachlorobutadiene	250	96.00
Hexachloroethane	250	96.00
Isobutanol	10	0.00
Methyl ethyl ketone	1,480	70.27

Table 7
Air-Stripper Performance at the
Gilson Road Site, NH [15, p. 65]

<i>Contaminant</i>	<i>Influent Concentration (ppb)</i>	<i>Average Removal Efficiency (%)</i>
Isopropyl alcohol	532	95.30
Acetone	473	91.93
Toluene	14,884	99.87
Dichloromethane	236	93.79
1,1,1-Trichloroethane	1,340	99.45
Trichloroethylene	1,017	99.71
Chloroform	469	99.06
Total VOC	18,951	99.41

gpm (initial) and 60 gpm (maximum) flowrate, a tower diameter of 2 feet, packing height of 22.5 feet, air-to-water ratio of 83.1:1 (initial) and 62.3:1 (maximum), and used 2-inch Jaeger Tripack packing material [15, p. 31]. The performance data are presented in Table 6.

The Gilson Road Site used a single column high-temperature air stripper (HTAS) which had a 300 gpm flowrate (heated influent), tower diameter of 4 feet, packing height of 16 feet, air-to-water ratio of 51.4:1, and used 16 Koch-type trays at 1-foot intervals [15, p. 42-45]. The performance data are provided in Table 7. Due to the relatively high influent concentration and the high (average) removal efficiency, this system required supplemental control of the volatiles in the offgas.

Another EPA study, completed in August 1987, analyzed performance data from 177 air-stripping systems in the United States. The study presented data on systems design, contaminant types, and loading rates, and reported removal efficiencies for 52 sites. Table 8 summarizes data from 46 of those sites, illustrating experiences with a wide range of contaminants [19]. Reported efficiencies should be interpreted with caution. Low efficiencies reported in some instances may not reflect the true potential of air stripping, but may instead reflect designs intended to achieve only modest removals from low-level contaminant sources. It is also important to recognize that, because different system designs were used for these sites, the results are not directly comparable from site to site.

Technology Status

Air stripping is a well-developed technology with wide application. During 1988, air stripping of aqueous solutions was a part of the selected remedy at 30 Superfund sites [1]. In 1989, air stripping was a part of the selected remedy at 38 Superfund Sites [2].

The factors determining the cost of an air stripper can be categorized as those affecting design, emission controls, and operation and maintenance (O&M). Design considerations such as the size and number of towers, the materials of construction, and the desired capacity influence the capital costs. Equipment cost components associated with a typical packed-tower air strip-

Table 8
Summary of Reported Air-Stripper Removal Efficiencies from 46 Sites [19]

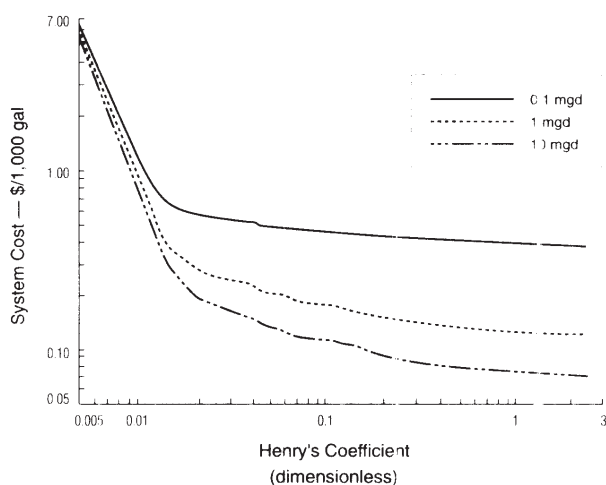
Contaminant	No. of Data Points	Influent Concentration ($\mu\text{g/L}$)		Reported Removal Efficiency ^a (%)	
		Average	Range	Average	Range
Aniline	1	226	NA ^b	58	NA
Benzene	3	3,730	200-10,000	99.6	99-100
Bromodichloromethane	1	36	NA	81	NA
Bromoform	1	8	NA	44	NA
Chloroform	1	530	1500	48	NA
Chlorobenzene	0	95	NA	ND ^c	ND
Dibromochloromethane	1	34	NA	60	NA
Dichloroethylene	7	409	2-3,000	98.6	96-100
Diisopropyl ether	2	35	20-50	97.0	95-99
Ethylbenzene	1	6,370	100-1,400	99.8	NA
Ethylene dichloride	7	173	5-1,000	99.3	79-100
Methylene chloride	1	15	9-20	100	NA
Methyl ethyl ketone	1	100	NA	99	NA
2-Methylphenol	1	160	NA	70	NA
Methyl tertiary butylether	2	90	50-130	97.0	95-99
Perchloroethylene	17	355	3-4,700	96.5	86-100
Phenol	1	198	NA	74	NA
1,1,2,2-Tetrachloroethane	1	300	NA	95	NA
Trichloroethane	8	81	5-300	95.4	70-100
Trichloroethylene	34	7,660	1-200,000	98.3	76-100
1,2,3-Trichloropropane	1	29,000	NA	99	NA
Toluene	2	6,710	30-23,000	98	96-100
Xylene	4	14,823	17-53,000	98.4	96-100
Volatile organic compounds	3	44,000	57-130,000	98.8	98-99.5
Total Volatile Organics	46	11,120	12-205,000	97.5	58.1-100

^aNote that the averages and ranges presented in this column represent more data points than are presented in the second column of this table because the removal efficiencies were not available for all air strippers.

^bNA = Not Applicable. Data available for only one stripper.

^cND = No Data. Insufficient data available.

Figure 2
Cost Estimates for Air Stripping without Air Emission Controls as a Function of the Henry's Law Coefficient



per include tower shell, packing support, water distributor, mist eliminator, packing, blower and motor, engineering, and contractor overhead and profit. The addition of an air treatment system roughly doubles the cost of an air-stripping system [3][6, p. 5-5]. Onsite regeneration or incineration of carbon may increase the cost associated with emission controls. The primary O&M cost components are operating labor, repair and upkeep, and energy requirements of blower motor and pumps [12].

Adams et al. made cost estimates based on flows from 0.1 to 10 mgd assuming a removal efficiency of 99 percent. The process was optimized for packed tower volume and energy consumption. Figure 2 presents general cost curves for three flow rates based on their work. Air emissions controls were not included in the costs. Within the range of Henry's Law Coefficients of 0.01 to 1.0, the cost ranged from \$0.07/1,000 gallons to \$0.70/1,000 gallons. As the Henry's Law Coefficient approached 0.005, the costs rapidly rose to \$7.00/1,000 gallons [20, p. 52].

According to Hydro Group, Inc., the cost of air stripping may range from \$0.04 to \$0.17 per 1,000 gallons [21, p. 7]. The Des Moines Superfund site unit cost for groundwater treatment is estimated to be about \$0.45/1,000 gallons based on a 1,250 gpm treatment rate and an average O&M cost of \$200,000/year for 10 years at 10 percent interest. The Eau Claire site had a unit cost of roughly \$0.14/1,000 gallons assuming a 5-year operation period and an average treatment rate of 7 million gpd [12, p. C-6].

Recent developments in this technology include high-temperature air stripping (HTAS) and rotary air stripping. A full-scale HTAS system was demonstrated at McClellan AFB to treat groundwater contaminated with fuel and solvents from spills and storage tank leaks. The combined recycle and makeup was heated to 65°C, and a removal efficiency of greater than 99 percent was achieved [8, p. 9]. The rotary design, marketed under the name HIGEE, was demonstrated at a U.S. Coast Guard air station in East Bay Township, Michigan. At a gas-to-liquid ratio of 30:1 and a rotor speed of 435 rpm, removal efficiencies for all contaminants, except 1, 2-DCE, exceeded 99 percent. The removal efficiency for 1,2-DCE was not reported [4, p. 19].

Raising influent liquid temperature increases mass-transfer rates and the Henry's Law Constants. This results in improved removal efficiencies for VOCs and the capability to remove contaminants that are less volatile. Table 9 illustrates the influence that changes in liquid temperature have on contaminant removal efficiencies. Note that steam stripping may be the preferred treatment technology at a feed temperature approaching 100°C, because the higher temperatures associated with steam stripping allow organics to be removed more efficiently than in HTAS systems. However, steam stripping uses more fuel and therefore will have higher operating costs. Additionally, the capital costs for steam stripping may be higher than for HTAS if higher-grade construction materials are needed at the elevated temperatures used in steam stripping [8, p. 3].

Table 9
Influence of Feed Temperature on Removal of Water Soluble Compounds from Groundwater [8, p. 15]

Compound	Percent Removed at Selected Temperature		
	12°C	35°C	73°C
2 - Propanol	10	23	70
Acetone	35	80	95
Tetrahydrofuran	50	92	>99

Rotary air strippers use centrifugal force rather than gravity to drive aqueous solutions through the specially designed packing. This packing, consisting of thin sheets of metal wound together tightly, was developed for rotary air strippers because of the strain of high centrifugal forces. The use of centrifugal force reportedly results in high removal efficiencies due to formation of a very thin liquid film on wetted surfaces. The rotary motion also causes a high degree of turbulence in the gas phase. The turbulence results in improved liquid distribution over conventional gravity-driven air strippers. The biggest advantage of rotary strippers is the high capacity for a relatively small device. Disadvantages include the potential for mechanical failures and additional energy requirements for the drive motor. Water carryover into the air effluent stream may cause problems with certain emission control devices used to treat the contaminated air. Cost and performance data on rotary air strippers are very limited [4, p. 16].

EPA Contact

Technology-specific questions regarding air stripping of liquids may be directed to:

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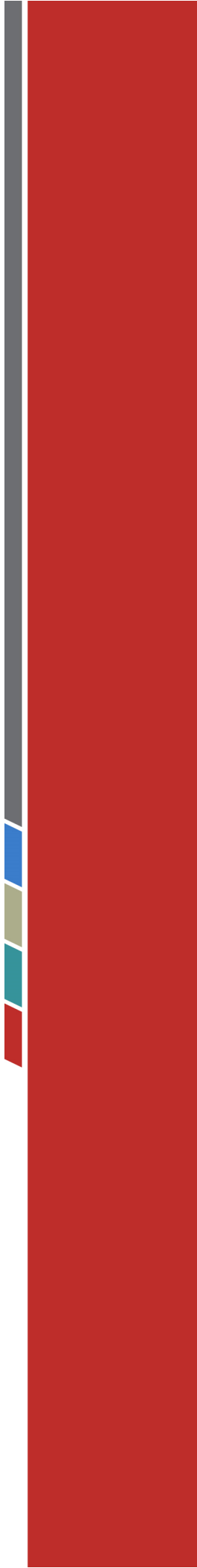
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In-situ Biodegradation





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Superfund

EPA/540/S-94/502

April 1994

Engineering Bulletin

In Situ Biodegradation Treatment

Purpose

Section 121(b) of the Comprehensive Environment Response, Compensation, and Liability Act (CERCLA) mandates the Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants and contaminants as a principal element." The Engineering Bulletins comprise a series of documents that summarize the latest information available on selected treatment and site remediation technologies and related issues. They provide summaries of and references for the latest information to help remedial project managers, on-scene coordinators, contractors, and other site cleanup managers understand the type of data and site characteristics needed to evaluate a technology for potential applicability to their Superfund or other hazardous waste site. Those documents that describe individual treatment technologies focus on remedial investigation scoping needs. Addenda will be issued periodically to update the original bulletins.

Abstract

In situ biodegradation may be used to treat low-to-intermediate concentrations of organic contaminants in place without disturbing or displacing the contaminated media. Although this technology has been used to degrade a limited number of inorganics, specifically cyanide and nitrate, in situ biodegradation is not generally employed to degrade inorganics or to treat media contaminated with heavy metals.

During in situ biodegradation, electron acceptors (e.g., oxygen and nitrate), nutrients, and other amendments may be introduced into the soil and groundwater to encourage the growth of an indigenous population capable of degrading the contaminants of concern. These supplements are used to control or modify site-specific conditions that

impede microbial activity and, thus, the rate and extent of contaminant degradation. Depending on site-specific cleanup goals, in situ biodegradation can be used as the sole treatment technology or in conjunction with other biological, chemical, and physical technologies in a treatment train. In the past, in situ biodegradation has often been used to enhance traditional pump and treat technologies by reducing the time needed to achieve aquifer cleanup standards.

One of the advantages of employing an in situ technology is that media transport and excavation requirements are minimized, resulting in both reduced potential for volatile releases and minimized material handling costs. Biological technologies that require the physical displacement of media during treatment (e.g., "land treatment" applications involving excavation for treatment in lined beds or tilling of non-excavated soils) assume many of the risks and costs associated with ex situ technologies and cannot strictly be considered in situ applications.

As of Fall 1993, in situ biodegradation was being considered or implemented as a component of the remedy at 21 Superfund sites and 38 Resource Conservation and Recovery Act (RCRA), Underground Storage Tank (UST), Toxic Substances Control Act (TSCA), and Federal sites with soil, sludge, sediment, or groundwater contamination [1, p. 13][2][3]. This bulletin provides information on the technology's applicability, the types of residuals produced, the latest performance data, the site requirements, the status of the technology, and sources for further information.

Technology Applicability

In situ biodegradation has been shown to be potentially effective at degrading or transforming a large number of organic compounds to environmentally-acceptable or less mobile compounds [4, p. 54][5, p. 103][6][7][8][9]. Soluble organic contaminants are particularly amenable to biodegradation; however, relatively insoluble contaminants may be degraded if they are accessible to microbial degrad-

* [reference number, page number]





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ers. Classes of compounds considered amenable to biodegradation include petroleum hydrocarbons (e.g., gasoline and diesel fuel), nonchlorinated solvents (e.g., acetone, ketones, and alcohols), wood-treating wastes (e.g., creosote and pentachlorophenol), some chlorinated aromatic compounds (e.g., chlorobenzenes and biphenyls with fewer than five chlorines per molecule), and some chlorinated aliphatic compounds (e.g., trichloroethene and dichloroethene). As advances in anaerobic biodegradation continue, many compounds traditionally considered resistant to aerobic biodegradation may eventually be degraded, either wholly or partially, under anaerobic conditions. Although not normally used to treat inorganics (e.g., acids, bases, salts, heavy metals, etc.), in situ biodegradation has been used to treat water contaminated with nitrate, phosphate, and other inorganic compounds.

Although in situ biodegradation may be used to remediate a specific site, this does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. The complex contaminant mixtures found at many Superfund sites frequently result in chemical interactions or inhibitory effects that limit contaminant biodegradability. Elevated concentrations of pesticides, highly chlorinated organics, and some inorganic salts have been known to inhibit microbial activity and thus system performance during in situ biodegradation. Treatability studies should be performed to determine the effectiveness of a given in situ biological technology at each site. Experts based out of EPA's Risk Reduction Engineering Laboratory (RREL) in Cincinnati, Ohio and the Robert S. Kerr Environmental Research Laboratory (RSKERL) in Ada, Oklahoma may be able to provide useful guidance during the treatability study and design phases. Other sources of general observations and average removal efficiencies for different treatability groups are contained in the Superfund Land Disposal Restrictions (LDR) Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS, September 1990) [10] and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," (OSWER Directive 9347.3-06BFS, September 1990) [11].

Limitations

Site- and contaminant-specific factors impacting contaminant availability, microbial activity, and chemical reaction rates may limit the application of in situ biodegradation. Variations in media composition and contaminant concentrations can lead to variations in biological activity and, ultimately, inconsistent degradation rates. Soil characteristics (e.g., non-uniform particle size, soil type, moisture content, hydraulic conductivity, and permeability) and the amount, location, and extent of contamination can also have a profound impact on bioremediation. The following text expands upon these factors.

The biological availability, or bioavailability, of a contaminant is a function of the contaminant's solubility in water and its tendency to sorb on the surface of the soil. Contaminants with low solubility are less likely to be distrib-

uted in an aqueous phase and may be more difficult to degrade biologically. Conversely, highly soluble compounds may leach from the soil before being degraded. In general, however, poor bioavailability can be attributed to contaminant sorption on the soil rather than a low or high contaminant solubility. The tendency of organic molecules to sorb on the soil is determined by the physical and chemical characteristics of the contaminant and soil. In general, the leaching potential of a chemical is proportional to the magnitude of its adsorption (partitioning) coefficient in the soil. Hydrophobic (i.e., "water fearing") contaminants, in particular, routinely partition from the soil water and concentrate in the soil organic matter, thus limiting bioavailability. Additionally, contaminant weathering may lead to binding in soil pores, which can limit availability even of soluble compounds. Important contaminant properties that affect sorption include: chemical structure, contaminant acidity or basicity (pKa or pKb), water solubility, permanent charge, polarity, and molecule size. In some situations surfactants (e.g., "surface acting agents") may be used to increase the bioavailability of "bound" or insoluble contaminants. However, it may be difficult to identify a surfactant that is both nontoxic and not a preferred substrate for microbial growth.

Soil solids, which are comprised of organic and inorganic components, may contain highly reactive charged surfaces that play an important role in immobilizing organic constituents, and thus limiting their bioavailability. Certain types of inorganic clays, possess especially high negative charges, thus exhibiting a high cation exchange capacity. Alternatively, clays may also contain positively charged surfaces, causing these particles to exhibit a high anion exchange capacity. Soil organic matter also has many highly reactive charged surfaces which can limit bioavailability [12].

Bioavailability is also a function of the biodegradability of the target chemical, i.e., whether it acts as a substrate, co-substrate, or is recalcitrant. When the target chemical cannot serve as a metabolic substrate (source of carbon and energy) for microorganisms, but is oxidized in the presence of a substrate already present or added to the subsurface, the process is referred to as co-oxidation and the target chemical is defined as the co-substrate [12][13, p.4]. Co-metabolism occurs when an enzyme produced by an organism to degrade a substrate that supports microbial growth also degrades another non-growth substrate that is neither essential for nor sufficient to support microbial growth. Co-oxidation processes are important for the biodegradation of high molecular weight polycyclic aromatic hydrocarbons (PAHs), and some chlorinated solvents, including trichloroethene (TCE). However, like surfactants, cometabolites (e.g., acetate and phenol) may be more readily mineralized by the indigenous microorganisms than the target organics [13, p. 4].

Microbial activity can be reduced by nutrient, moisture, and oxygen deficiencies, significantly decreasing biodegradation rates. Extreme soil temperatures, soil alkalinity, or soil acidity can limit the diversity of the microbial population and may suppress specific contaminant degrad-

ers. Spatial variation of soil conditions (e.g., moisture, oxygen availability, pH, and nutrient levels) may result in inconsistent biodegradation due to variations in biological activity. While these conditions may be controlled to favor biodegradation, the success of in situ biodegradation depends in a large part on whether required supplements can be delivered to areas where they are needed. Low hydraulic conductivity can hinder the movement of water, nutrients, aqueous-phase electron acceptors (e.g., hydrogen peroxide and nitrate), and, to a lesser extent, free oxygen through the contamination zone [14, p. 155]. Restrictive layers (e.g., clay lenses), although more resistant to contamination, are also more difficult to remediate due to poor permeability and low rates of diffusion [13, p. 4]. Low percolation rates may cause amendments to be assimilated by soils immediately surrounding application points, preventing them from reaching areas that are more remote, either vertically or horizontally. During the simultaneous addition of electron acceptors and donors through injection wells, excessive microbial growth or high iron or manganese concentrations may cause clogging in the well screen or in the soil pores near the well screen [15]. Variable hydraulic conductivities in different soil strata within a contaminated area can also complicate the design of flow control; minor heterogeneities in lithology can, in some cases, impede the transfer of supplements to specific subsurface locations.

Microbial activity may also be influenced by contaminant concentrations. Each contaminant has a range of concentrations at which the potential for biodegradation is maximized. Below this range microbial activity may not occur without the addition of co-substrate. Above this range microbial activity may be inhibited and, once toxic concentrations are reached, eventually arrested. During inhibition, contaminant degradation generally occurs at a reduced rate. In contrast, at toxic concentrations, contaminant degradation does not occur. The concentrations at which microbial growth is either supported, inhibited, or arrested vary with the contaminant, medium, and microbial species. Given long-term exposure, microbes have been known to acclimate to very high contaminant concentrations and other conditions inhibiting microbial activity. However, if prompt treatment is a primary goal, as is the case during most remedial activities, toxic conditions may need to be addressed by pH control, metals control (e.g., immobilization), sequential treatment, or by introducing microbial strains resistant to toxicants.

Numerous biological and non-biological mechanisms (e.g., volatilization, sorption, chemical degradation, migration, and photodecomposition) occur during biological treatment. Since some amendments may react with the soil, site geochemistry can limit both the form and concentration of any supplements added to the soil. Thus, care must be employed when using amendments to "enhance" biological degradation. For example, ozone and hydrogen peroxide, which can be added to enhance dissolved oxygen levels in soil or groundwater systems, may react violently with other compounds present in the soil, reduce the sorptive capacity of the soil being treated, produce gas bubbles that block the pores in the soil matrix, or damage

the bacterial population in the soil [4, p. 43]. Nitrogen and phosphorus (phosphate) must also be applied cautiously to avoid excessive nitrate formation [4, p.47] and the precipitation of calcium and iron phosphates, respectively. Excessive nitrate levels in the groundwater can cause health problems in humans, especially children. If calcium concentrations are high, the added phosphate can be tied up by the calcium and, therefore, may not be available to the microorganisms [16, p. 23]. Lime treatment for soil pH adjustment is dependent on several soil factors including soil texture, type of clay, organic matter content, and aluminum concentrations [4, p. 45]. Since changes in soil pH may also affect the dissolution or precipitation of materials within the soil and may increase the mobility of hazardous materials, pH amendments (acid or base) should be added cautiously and should be based on the soil's ability to resist changes in pH, otherwise known as the soil's "buffering capacity" [4, p. 46]. Since the buffering capacity varies between soils, lime and acidification requirements should be determined on a site-specific basis.

Finally, high concentrations of metals can have a detrimental effect on the biological treatment of organic contaminants in the same medium. A number of metals can be oxidized, reduced, methylated (i.e., mercury), demethylated, or otherwise transformed by various organisms to produce new contaminants. The solubility, volatility, and sorption potential of the original soil contaminants can be greatly changed in the process [17, p. 144], leading to potential significant toxicological effects, as is the case during the methylation of mercury. To avoid these complications, it is sometimes possible to pretreat or complex the metals into a less toxic or leachable form.

Technology Description

During in situ biodegradation, site-specific characteristics are modified to encourage the growth of a microbial population capable of biologically degrading the contaminants of concern. Presently, two major types of in situ systems are being employed to biodegrade organic compounds present in soils, sludges, sediments, and groundwater: bioventing systems and "traditional" in situ biodegradation systems, which usually employ infiltration galleries/wells and recovery wells to deliver required amendments to the subsurface. In general, bioventing has been used to treat contaminants present in the unsaturated zone. Traditional in situ biodegradation, on the other hand, has mostly been used to treat saturated soils and groundwater. The occasional treatment of unsaturated soil using traditional in situ biodegradation techniques has been generally limited to fairly shallow regions over groundwater that is already contaminated.

Traditional In Situ Biodegradation

Traditional in situ biodegradation is generally used in conjunction with groundwater-pumping and soil-flushing systems to circulate nutrients and oxygen through a contaminated aquifer and associated soil. The process usually

involves introducing aerated, nutrient-enriched water into the contaminated zone through a series of injection wells or infiltration trenches and recovering the water down-gradient. Depending upon local regulations and engineering concerns, the recovered water can then be treated and, if necessary, reintroduced to the soil onsite, discharged to the surface, or discharged to a publicly-owned treatment works (POTW). A permit may be required for the re-injection of treated water. Note that a variety of techniques can be used to introduce and distribute amendments in the subsurface. For example, a lower horizontal well is being used at the Savannah River Site near Aiken, North Carolina to deliver air and methane to the subsurface. A vacuum has been applied to an upper well (in the vadose zone) located at this site to encourage the distribution of air and methane within the upper saturated zone and lower vadose zone [18][19].

Figure 1 is a general schematic of a traditional in situ biodegradation system [20, p. 113][16, p. 13]. The first step in the treatment process involves pretreating the infiltration water, as needed, to remove metals (1). Treated or contaminated groundwater, drinking water, or alternative water sources (e.g., trucked water) may be used as the water source. If groundwater is used, iron dissolved in the groundwater may bind phosphates needed for biological growth. Excess phosphate may be added to the infiltration water at this point in the treatment process in order to complex the iron [20, p. 111]. The presence of iron will also cause a more rapid depletion of hydrogen peroxide, which is sometimes used as an oxygen source. Surface active agents may also be added at this point in the treatment process to increase the bioavailability of contaminants, especially hydrophobic or sorbed pollutants, while methane or other substances may be added to induce the cometabolic biodegradation of certain contaminants. In continuous recycle systems, toxic metals originally located in the contaminated medium may have to be removed from

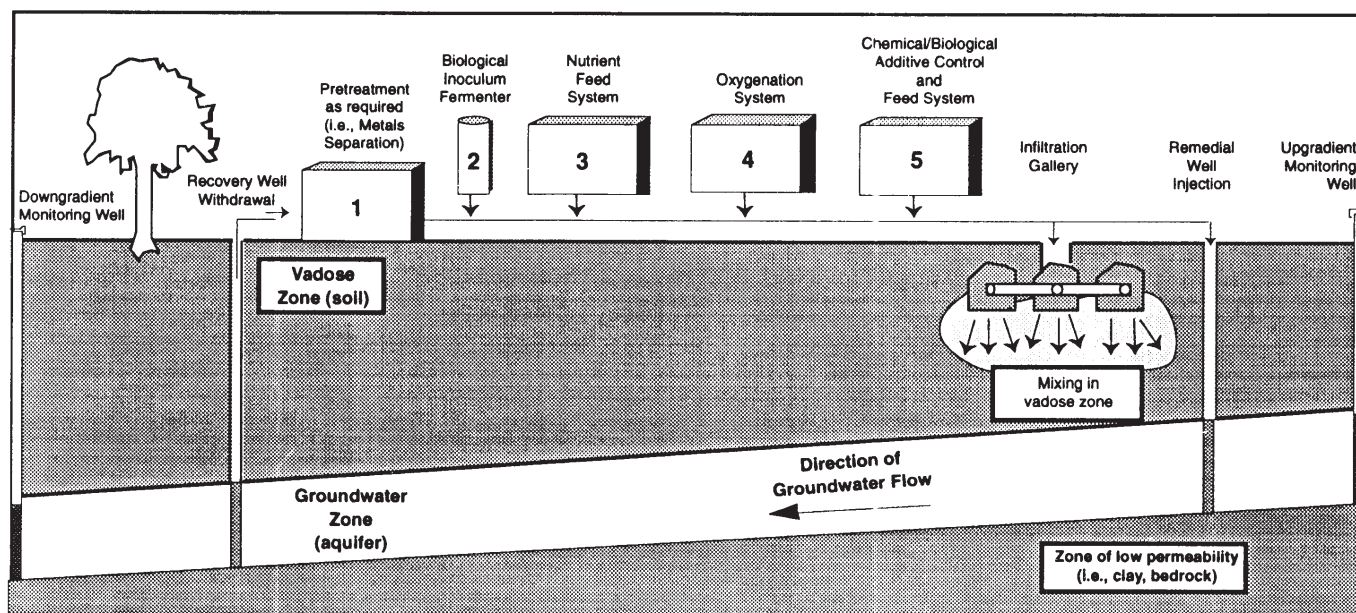
the recycled infiltration water to prevent inhibition of bacterial growth. The exact type of pretreatment will vary with the water source, contamination problem, and treatment system used.

Following infiltration water pretreatment, a biological inoculum can be added to the infiltration water to enhance the natural microbial population (2). A site-specific inoculum enriched from site samples may be used; commercially available cultures reported to degrade the contaminants of concern can also be used (e.g., during the remediation of "effectively sterile soils"). Project managers are cautioned against employing microbial supplements without first assessing the relative advantages associated with their use and potential competition that may occur between the indigenous and introduced organisms. The ability of microbes to survive in a foreign and possibly hostile (i.e., toxic) environment, as well as the ability to metabolize a wide range of substrates should be evaluated. The health effects of commercial inocula must also be carefully evaluated, since many products on the market are not carefully screened or processed for pathogens. It is essential that independently-reviewed data be examined before employing a commercially-marketed microbial supplement [21].

Nutrient addition can then be employed to provide nitrogen and phosphorus, two elements essential to the biological activity of both indigenous and introduced organisms (3). Optimum nutrient conditions are site-specific. Trace elements may be added at this stage, but are normally available in adequate supply in the soil or groundwater.

During contaminant oxidation, energy is released as electrons are removed. Since oxygen acts as the terminal electron acceptor during aerobic biodegradation, oxygen concentrations in the subsurface may become depleted. To avoid this complication, air, oxygen, and other oxygen

Figure 1.
Schematic Diagram of Traditional In Situ Biodegradation of Soil and Groundwater





sources (hydrogen peroxide and ozone) can be added to the infiltration water (4). To prevent gas binding in the subsurface, and a subsequent reduction in the effective soil permeability, oxygen amendment/supplementation methods must be carefully selected. During anaerobic degradation, alternative electron acceptors (nitrate, carbonate, or sulfate) may be added to the infiltration water in place of oxygen. Alternatively, during the co-oxidation of a target substrate, a co-substrate (methanol or acetate) may be added to the infiltration water [22].

Just before the water is added to the soil or groundwater, chemical additives may be used to adjust the pH (neutral is recommended for most systems) and other parameters that impact biodegradation (5). Care should be taken when making adjustments to the pH, since contaminant mobility (especially of metals) can be increased by changing the pH [4, p. 45]. Site managers are also cautioned against employing chemical additives that are persistent in the environment. The potential toxicity of additives and any synergistic effects on contaminant toxicity should also be evaluated.



During in situ bioremediation, amendment concentrations and application frequencies can be adjusted to compensate for physical/chemical depletion and high microbial demand. If these modifications fail to compensate for microbial demand, remediation may occur by a sequential deepening and widening of the active treatment layer (e.g., as the contaminant is degraded in areas near the amendment addition points, and microbial activity decreases due to the reduced substrate, the amendments move farther, increasing microbial activity in those areas). Additionally, hydraulic fracturing may be employed to improve amendment circulation within the subsurface.

The importance of using a well-designed hydraulic delivery system and thoroughly evaluating the compatibility of chemical supplements was demonstrated at sites in Park City, Kansas; Kelly AFB, Texas; and Eglin AFB, Florida. Air entrainment and iron precipitation resulted in a continued loss of injection capacity during treatment at the Park City site [23][24] and calcium phosphate and iron precipitation resulted in the failure of the two field tests at Kelly and Eglin AFBs, respectively [25].

Bioventing



Bioventing uses relatively low-flow soil aeration techniques to enhance the biodegradation of soils contaminated with organic contaminants. Although bioventing is predominantly used to treat unsaturated soils, applications involving the remediation of saturated soils and groundwater (e.g., using air sparging techniques) are becoming more common [26][27]. Aeration systems similar to those employed during soil vapor extraction are used to supply oxygen to the soil (Figure 2). Typically a vacuum extraction, air injection, or combination vacuum extraction and air injection system is employed [28]. An air pump, one or more air injection or vacuum extraction probes, and emissions monitors at the ground surface are commonly used. Although some systems utilize higher air flow rates, thereby

combining bioventing with soil vapor extraction, low air pressures and low air flow rates are generally used to maximize vapor retention times in the soil while minimizing contaminant volatilization. An interesting modification to traditional aeration techniques has been proposed at the Picatinny Arsenal in New Jersey. Here researchers and project managers have proposed collecting TCE vapors at the surface, amending them with degradable hydrocarbons (methane, propane, or natural gas) capable of stimulating the cometabolic degradation of vapor-phase TCE, and then re-injecting the amended vapors into the unsaturated zone in an attempt to encourage the in situ bioremediation of the TCE remaining in the subsurface [29][30][31][32][27].

Off-gas treatment (e.g., through biofiltration or carbon adsorption) will be needed during most bioventing applications to ensure compliance with emission standards and to control fugitive emissions. Off-gas treatment systems similar to those employed during soil vapor extraction may be used. These systems must be capable of effectively collecting and treating a vapor stream consisting of the original contaminants and/or any volatile degradation products generated during treatment. Although similar vapor treatment systems may be employed during soil vapor extraction and bioventing, less concentrated off-gases would be expected from a bioventing system than from a soil vapor extraction system employed at the same site. This difference in concentration is attributed to enhanced biological degradation within the subsurface.

Nutrient addition may be employed during bioventing to enhance biodegradation. Nutrient addition can be accomplished by surface application, incorporation by tilling into surface soil, and transport to deeper layers through applied irrigation water. However, in some field applications to date, nutrient additions have been found to provide no additional benefits [33]. Increasing the soil temperature may also enhance bioremediation, although in general high temperatures should be avoided since they can decrease microbial population and activity. Heated air, heated water, and low-level radio-frequency heating are some of the techniques which can be used to modify soil temperature. Soil core analyses can be performed periodically to assess system performance as determined by contaminant removal. A control plot located near the bioventing system, but not biovented, may also be used to obtain additional information to assess system performance.

Process Residuals

During in situ biodegradation, limited but potentially significant process residuals may be generated. Although the majority of wastes requiring disposal are generated as part of pre- and post-treatment activities, process residuals directly arising from in situ biological activities may also be generated. These process residuals may include: 1) partially degraded metabolic by-products, 2) residual contamination, 3) wastes produced during groundwater pre- and post-treatment activities, and 4) volatile contaminants that are either directly released into the atmosphere or

collected within add-on emission control/treatment systems. The following text expands upon the specific types of process residuals, their control, and their impact on disposal requirements.

Ultimately biological technologies seek to mineralize hazardous contaminants into relatively innocuous by-products, specifically carbon dioxide, water, and inorganic salts. However, a number of site- and contaminant-specific factors may cause the partial degradation or "biotransformation" of a contaminant and the generation of an intermediate by-product. These metabolic by-products may be located in either the saturated or unsaturated zones. The identity, toxicity, and mobility of these partially degraded compounds should be determined since intermediate degradation products can be as toxic or more toxic than the parent compound. Since metabolic by-products can accumulate in the soil and groundwater, future remedial actions may be necessary.

In addition to intermediate degradation by-products, residual contamination may persist in the soil following treatment. Microbes are capable of degrading only that fraction of the contamination that is readily available for microbial incorporation. As a result, biologically resistant contaminants and contaminants that remain sorbed to the soil and sediment during the remedial action cannot be degraded. Depending on the nature of the contaminants and media, the "bound" fraction may slowly desorb over long periods of times (months to years), potentially recontaminating "treated" media near the residual contamination [34][35]. Additionally, fluctuations in the water table may result in the recontamination of previously remediated soils if groundwater contamination, specifically

contamination associated with the presence of a light non-aqueous phase layer (LNAPL), has not been effectively addressed.

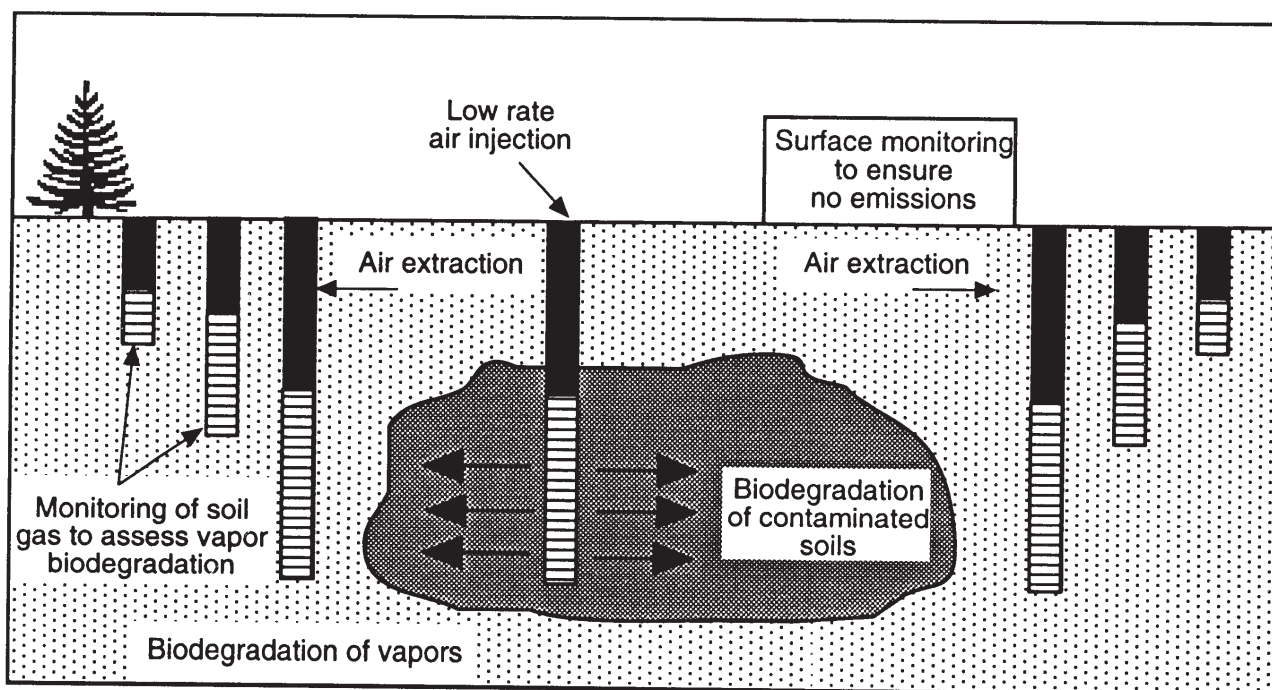
Above-ground activities taken to ensure that the remedial action complies with regulatory requirements and adequately guards against cross-contamination and uncontrolled releases may result in the generation of a significant volume of waste requiring disposal. For example, when groundwater is used to deliver amendments to the subsurface, it may be necessary to pre-treat the water before it can be re-introduced to the subsurface. Additionally, in order to protect water quality outside of the treatment zone from contaminant or amendment migration, a down-gradient groundwater recovery and treatment system designed to collect and treat amendment- and contaminant-laden groundwater may be needed. The residuals produced by these add-on treatment processes will eventually require disposal.

Significant volatile emissions may also be produced during in situ biodegradation (e.g., bioventing). Depending on their concentration, toxicity, and total volume, these emissions, which may consist of the original contaminant or any volatile degradation products produced during treatment, may need to be controlled, collected, or treated. Ultimately, the by-products of an emissions treatment/control system will require disposal.

Site Requirements

In situ biodegradation normally requires the installation of wells or infiltration trenches; therefore, adequate

Figure 2. Bioventing





access roads are required for heavy equipment such as well-drilling rigs and backhoes. Soil-bearing capacity, traction, and soil stickiness can limit vehicular traffic [17, p. 61].

In general, the area required to set up mixing equipment is not significant. However, space requirements increase as the complexity of the various pre- and post-treatment systems increases. During the installation of infiltration galleries and wells, several hundred up to several thousand square feet of clear surface area will be required. Climate can also influence site requirements. If periods of heavy rainfall or extremely cold conditions are expected, a cover may be required.

Electrical requirements will depend on the type of technology employed. Standard 220V, three-phase electrical service may be used to supply power to pumps and mixing equipment. Since water is used for a variety of purposes during biological treatment, a readily available water supply will be needed at most sites. Municipal water or clean groundwater may be used. Contaminated groundwater may be used if permitted by the appropriate regulatory agency. The quantity of water needed is site- and process-specific. Waste storage is not normally required for in situ biodegradation.

Onsite analytical equipment for conducting pH and nutrient analyses will help improve operation efficiency and provide better information for process control. During bioventing applications, air emissions monitors at the ground surface are commonly used.



Regulatory Considerations and Response Actions

Federal mandates can have a significant impact on the application of in situ biodegradation. RCRA LDRs that require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements (ARARs) for CERCLA response actions. The in situ biodegradation technology can produce a treated waste that meets treatment levels set by BDAT, but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where in situ biodegradation does not meet these levels, it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. Treatability variances are justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.06FS, September 1990) [10], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.06BFS, September 1990) [11]. Another approach could be to use other treatment techniques with in situ biodegradation to obtain desired treatment levels,

for example, carbon treatment of recovered groundwater prior to re-infiltration into the subsurface.

When determining performance relative to ARARs and BDATs, emphasis should be placed on assessing the risk presented by a bioremediation technology. As part of this effort, risk assessment schemes, major metabolic pathways of selected hazardous pollutants, human health protocols for metabolite and pathogenicity tests, and fate protocols and issues for microorganisms and metabolites must be assessed [36]. A detailed summary of the findings of the June 17-18, 1993 EPA/Environment Canada Workshop in Duluth, Minnesota addressing Bioremediation Risk Assessment should be available in early 1994.

Performance Data

Performance data for Superfund sites are limited. The first record of decision (ROD) selecting in situ biodegradation as a component of the remedy was in FY87. Since then, in situ biodegradation of soil or groundwater contaminants has either been considered or selected at 22 Superfund sites and 30 RCRA, UST, TSCA, and Federal sites [1][2][3]. The following two subsections address traditional in situ and bioventing applications, respectively; a third subsection has been included to briefly address information sources and data concerns related to remedial efforts performed in the private sector.

Traditional In Situ Bioremediation

Methane and phenol were employed during a series of stimulus-response studies investigating the co-metabolic degradation of TCE, cis-dichloroethene (c-DCE), trans-dichloroethene (t-DCE), and vinyl chloride (VC) at the Moffet Field site in California. Both sets of experiments used indigenous bacteria and were performed under the induced gradient conditions of injection and extraction. During the first set of experiments, methane, oxygen, and TCE (from 50 to 100 µg/L), c-DCE, t-DCE, and VC were added to the soil to stimulate methanotrophic degradation of the injected chlorinated aliphatic compounds. Approximately 20 percent of the TCE added to the system was degraded within the 2-meter hydraulically-controlled biostimulated zone. Approximately 50 percent of the c-DCE, 90 percent of the t-DCE, and 95 percent of the VC were also degraded. During the second set of tests, methane was replaced with phenol in order to stimulate growth of an indigenous phenol-utilizing population. During 4 weeks of testing, the concentration of TCE injected into the subsurface was raised from an initial concentration of 62 µg/L to a final concentration of 1000 µg/L. A bromide tracer was used to determine transformation extent. Up to 90 percent of the TCE in the 2-meter biostimulated zone was degraded, demonstrating that even at relatively high TCE concentrations significant removal efficiencies can be achieved in situ through phenol and dissolved oxygen (DO) addition. During the course of the project, transformation yields (i.e., grams of TCE per grams of phenol) ranging from 0.0044 to 0.062 were obtained for varying concentrations

of phenol and TCE. Future studies at the site will determine whether a compound more environmentally acceptable than methane or phenol can be used to induce an indigenous population that effectively degrades TCE [37][7][8].

A 40- by 120-foot test zone in an aquifer that receives leachate from an industrial landfill at the Du Pont Plant near Victoria, Texas was used to demonstrate the in situ biotransformation of tetrachloroethene (PCE), TCE, DCE, chloroethane, and VC to ethane and ethylene using microbial reductive dehalogenation under sulfate-reducing conditions. Groundwater from this zone was alternately amended with either benzoate or sulfate and circulated through the aquifer. Initially PCE and TCE concentrations were approximately 10 and 1 micro-mole (μM), respectively. After a year of treatment the halogenated compounds were reduced to concentrations near or below 0.1 μM . PCE and TCE degraded to DCE rapidly following the introduction of benzoate. A decrease in sulfate concentrations led to increases in the vinyl chloride concentrations. Therefore, sulfate concentrations were kept above 10 mg/L until the DCE was further biodegraded. After approximately 6 months of treatment, most of the DCE, chloroethane, and VC biodegraded to produce ethane and ethylene [38].

A field-scale in situ bioremediation system, consisting of down-gradient groundwater extraction wells and an up-gradient infiltration system, was installed at a gasoline-contaminated site owned by the San Diego Gas and Electric Company. [Note: extracted groundwater was amended with nutrients (nitrate and phosphate) prior to re-infiltration into the subsurface]. Due to the relatively low rate of groundwater extraction (approximately 800 to 900 gallons per day) and the low hydraulic gradient at the site (0.004), it took nearly 2 years (until June/July 1991) for the added nitrate to reach the down-gradient well and overtake the xylene (BTX) plume. BTX concentrations, which ranged from 25 to 50 mg/L for the preceding 2-year period, dropped markedly as nitrate levels in the groundwater increased. By late August 1991, benzene and toluene concentrations had dropped below the detection limit (0.01 mg/L), and total xylene concentrations had dropped to 0.02 mg/L. The coincident occurrence of nitrate appearance and BTX loss in the aquifer, as well as an eight-fold increase in the percentage of denitrifiers present in the groundwater (from 1 to 8 percent), points to a potential stimulatory effect nitrate may have on BTX loss in situ [5].

An in situ bioremediation system consisting of four injection and three recovery wells was employed to treat gasoline contamination present in the saturated zone at a former service station in Southern California. During treatment, recovered groundwater was amended with hydrogen peroxide (from 500 to 1,000 mg/L) and nutrients and re-injected into the aquifer. Prior to treatment, total fuel hydrocarbons in the saturated clay soils ranged from below detection limits to 32 mg/kg as BTX. Maximum groundwater concentrations were 2,700 $\mu\text{g/L}$ for benzene; 6,600 $\mu\text{g/L}$ for toluene; 4,100 $\mu\text{g/L}$ for xylene; and 45,000 $\mu\text{g/L}$ for TPH [4]. After 10 months, BTX and TPH levels in the groundwater and saturated soils had dropped below the

detection limits. Roughly 1,350 kilograms of hydrogen peroxide were introduced to the aquifer over 10 months, roughly two times the estimated requirements based on the estimated mass of hydrocarbon in the saturated zone (i.e., 110 kg of fuel hydrocarbon and 2 to 3 kg of dissolved hydrocarbons). After 34 months of treatment, soil hydrocarbon concentrations ranged from below the detection limit to 321 ppm as TPH; benzene was not detected in any samples [39].

Following successful laboratory treatability testing, General Electric performed a 10¹/₂-week field study to investigate the biodegradation of polychlorinated biphenyls (PCBs) in the Hudson River sediment. Initial PCB concentrations in the sediment ranged between 20 and 40 ppm. The study attempted to enhance the aerobic bacteria native to the upper Hudson River. Six caissons were installed at the Hudson River Research Station (HRRS) to isolate sections of the river bottom for this field study. Because of extensive, naturally occurring dechlorination, approximately 80 percent of the total PCBs encountered in the sediments were mono-, di-, and trichlorobiphenyls. Biodegradation was stimulated using oxygen and nutrient addition. Mixing was employed to enhance the dispersal of oxygen and nutrients within the sediment. Between 38 and 55 percent of the PCBs present in the sediment were removed by aerobic degradation during the study. This corresponds to the percentage biologically available PCBs [9].

Bioventing

In May 1992, the U.S. Air Force began a Bioventing Initiative to examine bioventing as a remedial technique at contaminated sites across the country. The Air Force's decision to examine bioventing on such a large scale was prompted by a successful demonstration of the technology at Tyndall AFB, Florida, where bioventing coupled with moisture addition removed one-third of the TPH and nearly all of the BTEX in JP-4 contaminated soils during 7 months of treatment. The Bioventing Initiative targets 138 sites with diesel fuel, jet fuel, or fuel oil in soil. In selecting sites for the initiative, the Air Force looked for characteristics appropriate for bioventing, such as deep vadose soil, heavy hydrocarbon contamination, and high air permeability. The chosen sites represent a wide range of depths to groundwater, hydrocarbon concentrations, and soil textures. Preliminary testing has been completed and 33 systems have been installed at Battle Creek Air National Guard Base and the following AFBs: Beale, Eglin, Eielson, F.E. Warren, Galena, Hanscom, Hill, K.I. Sawyer, McGuire, Newark, Offutt, Plattsburgh, Robins, Vandenberg, and Westover. According to the Air Force, initial results are very promising with degradation rates measured as high as 5,000 mg/kg per year [40][41].

The EPA RREL, in collaboration with the U.S. Air Force, initiated two 3-year pilot-scale bioventing field studies in mid-1991 at JP-4 contaminated fuel sites located at Eielson AFB near Fairbanks, Alaska and at Hill AFB near Salt Lake City, Utah. Four soil plots are being used to evaluate passive, active, and buried heat tape soil-warming methods

during the Eielson study. The fourth plot was vented with injected air but not artificially heated. Roughly 1 acre of soil is contaminated from a depth of 2 feet to the water table at 6 to 7 feet. At the Hill site, a series of soil gas cluster wells capable of obtaining samples up to 90 feet deep is being used with a single air injection well and two groundwater wells to remediate JP-4 contamination found at depths ranging from 35 feet to perched water at approximately 95 feet. Inert gas tracer studies, regular soil gas measurements at several locations and depths, and periodic in situ respirometry tests to measure in situ oxygen uptake rates are being performed. Final soil hydrocarbon analyses will be conducted at both sites in mid-1994 and compared with the initial soil data. In situ respirometry data from the Hill site (Table 1) indicate that petroleum hydrocarbons are being removed at a significant rate. Intermediate respirometry data from the test and control plots at the Eielson site indicate that higher biodegradation rates are being obtained at higher soil temperatures.[42][43].

Table 1.
Rates of Biodegradation, Averaged Over Depth, at
Three Wells at Hill AFB

Well	Depths (ft)	Rate (mg/kg/day)	
		September 1991	September 1992 ¹
CW-1	20-90	0.97	0.30
CW-2	60-90	0.59	0.36
CW-3	10-90	0.56	0.32

1 Since bioventing is being performed on a sandy soil, with little to no naturally occurring organic matter, a biodegradation rate approaching zero would indicate that biodegradation had finished.

In November 1991, a pilot-scale bioventing system originally used to treat gasoline-contaminated vadose soils at the U.S. Coast Guard Air Station in Traverse City, Michigan was converted into a groundwater biosparging process. Eight 2-inch diameter sparge wells were installed to a depth of 10 feet below the water table. A control plot located in the vicinity of the contaminated plume, but not biosparged, was established to help assess the system's performance. After 12 months of biosparging, one-third of the oily phase residue below the water table, as well as almost all the BTEX initially present within the groundwater plume, was removed. (See Table 2 for groundwater quality data after 7 months of biosparging.) The globular nature of the oily residue limited the surface area in contact with the introduced air, thus restricting the biodegradation and vaporization of the oily-phase contaminants [44][45].

Non-Superfund Sites

In situ biodegradation has been applied at many sites in the private sector. Those interested in accessing informa-

Table 2.
Groundwater Quality After Seven Months of
Biosparging at the U.S. Coast Guard Air Station in
Traverse City, Michigan

Well Depth (ft)	Benzene (µg/L)	Xylenes (µg/L)	Total Fuel Carbon(µg/L)
Control			
16	9.9	19	2,880
17.5	228	992	4,490
20.5	70	38	956
22	57	7.7	783
Sparge Plot			
15	1.9	5.3	559
18	<1	5.0	<6
19.5	<1	<1	<6
21	<1	<1	<6

tion generated in the private sector may want to refer to the following EPA Publications:

- U.S. Environmental Protection Agency. Bioremediation Case Studies: Abstracts. EPA/600/R-92/044, March 1992.
- U.S. Environmental Protection Agency. Bioremediation Case Studies: An Analysis of Vendor Supplied Data. EPA/600/9-92/043, March 1992.

Most of the data contained in these resources were directly supplied by the vendor and have not been technically reviewed by EPA. Since independently-reviewed data are not always available from privately sponsored remedial efforts, in part due to proprietary issues [46, p. 1-1], readers should use these data cautiously. Often the quality of the data used to determine system effectiveness has not been substantiated by the scientific community. Thus, many vendor claims of effectiveness, specifically regarding introduced organisms and surface-active agents, are not supported within the scientific literature. Furthermore, many bioremediation firms have only limited experience working with the complex wastes normally associated with Superfund sites. Typically these firms deal only with gasoline and petroleum product leaks and spills. Additionally, many of the systems currently on the market involve the use of in situ biodegradation in combination with other above-ground treatment technologies such as carbon adsorption, air stripping, and biological reactors. In situ biodegradation is believed to enhance the total removal efficiency of the system. However, in many cases, it is unclear how much of the degradation occurred as a result of biological or non-biological mechanisms (volatilization, chemical destruction, etc.). How much biodegradation actually takes place in the soil or groundwater, in contrast to ex situ biodegradation, is not always clear.

Technology Status

In situ biodegradation either has been considered or selected as the remedial technology at 21 Superfund sites, as well as 38 RCRA, UST, TSCA, and Federal sites[1][2][3]. Table 3 lists the location, primary contaminants, treatment employed, and status of these sites. Information has also been included on three in situ biotechnology demonstrations presently being performed under the U.S. EPA Superfund Innovative Technology Evaluation (SITE) Program and seven sites selected for performance evaluations under the U.S. EPA Bioremediation Field Initiative. The data obtained during the SITE demonstrations and Bioremediation Field Initiative performance evaluations will be used to develop reliable cost and performance information on biotreatment technologies and applications.

The majority of the information found in Table 3 was obtained from the August 1993 version of "Bioremediation in the Field" [1]. These sites have been sorted numerically by Region and then alphabetically by site name. Sites employing "in situ land treatment" were not included in this list since these applications typically involve a significant amount of material handling. Additionally, some of the information was modified based on phone calls made to the various site project managers. This resulted in the removal of the American Creosote Works site in Florida and four pesticides sites (i.e., the Joliet Weed Control District site in the Joliet, Montana; the Lake County Weed Control site in Ronan, Montana; the Miles Airport site in Miles City, Montana; and the Richey Airport site in Richey, Montana) [47], which are no longer considering in situ treatment. Quarterly updates of this information can be obtained from subsequent versions of "Bioremediation in the Field".

Most of the hardware components of in situ biodegradation systems are available off-the-shelf and present no significant availability problems. Selected cultures, nutrients, and chemical/biological additives are also readily obtainable.

Bioremediation, particularly in situ applications, which avoid excavation and emissions control costs, are generally considered cost effective. This can be attributed in part to low operation and maintenance requirements. During set up and operation, material handling requirements are minimal, resulting in lowered worker exposures and reduced health impacts. Although in situ technologies are generally slow and somewhat difficult to control, a large volume of soil may be treated at one time.

It is difficult to generalize about treatment costs since site-specific characteristics can significantly impact costs. Typically, the greater the number of variables requiring control during biological treatment, the more problematic the implementation and the higher the cost. For example, it is less problematic to implement a technology in which only one parameter (e.g., oxygen availability) requires modification than to implement a remedy that requires modification of multiple factors (e.g., pH, oxygen levels, nutrients, microbes, buffering agents, etc.). Initial concentrations and volumes, pre- and post-treatment requirements, and air emissions and control systems will impact

final treatment costs. The types of amendments employed (e.g., hydrogen peroxide) can also impact capital cost and costs associated with equipment and manpower required during their application.

In general, however, in situ bioremediation is considered to be a relatively low-cost technology, with costs as low as 10 percent of excavation or pump and treat costs [7, p. 6-16]. The cost of soil venting using a field-scale system has been reported to be approximately \$50 per ton as compared to incineration, which was estimated to be more than ten times this amount. A cost estimate of about \$15 per cubic yard for bioventing sandy soil at a JP-4 jet fuel contaminated site has been reported by Vogel [48]. Exclusive of site characterization, the biological remediation of JP-4 contaminated soils at the Kelly Air Force Base site was estimated to be \$160 to \$230 per gallon of residual fuel removed from the aquifer [9]. At the French Limited site in Texas, the cost of bioremediation is projected to be almost three times less expensive than incineration. Because of the large amount of material requiring treatment at this site, it has been projected that cleanup goals will be achieved in less time by using bioremediation rather than incineration.

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Table 3. Superfund, RCRA, UST, TSCA, and Federal Sites

Site Location (Regions)	Primary Contaminants	Status/Cost	Treatment
Charlestown Navy Yard Boston, MA (1)	Sediments: wood preserving (PAHs).	Design: pilot scale TS underway.	In situ treatment. Ex situ treatment. Aerobic and anaerobic.
General Electric - Woods Pond Pittsfield, MA (1)	Sediments: PCBs. Volume: 250 gallons.	Design: lab scale TS underway.	Anaerobic treatment, confined treatment facility, nutrient addition.
FAA Technical Center - Area D Atlanta County, NJ (2)	Soil (saturated sand)/groundwater: petroleum (jet fuel, NAPLs). Volume: 33K cubic yards.	Design: pilot scale TS completed 8/92. Expected cost: capital, \$286K; O&M, \$200K	Nutrient addition (soil, water). Groundwater re-injection.
General Electric - Hudson River, NY (2)	Sediments: PCBs, cadmium, chromium, lead. Volume: 150 cubic feet.	Predesign: lab scale TS completed. Incurred cost: \$2.6M.	Aerobic treatment. Less than 1% of site underwent bioremediation.
Knispel Construction Site Horsehead, NJ (2)	Soil/groundwater: petroleum.	Completed: full scale 10/89 Start date: 01/89. Incurred cost: O&M, \$25K.	Aerobic treatment, hydrogen peroxide, nutrient addition (water). 100% of site underwent bioremediation [25].
Picatinny Arsenal NJ (2)	Soil (vadose)/soil vapors: solvents (TCE).	Design: lab scale studies completed.	Aerobic treatment, bioventing. Co-metabolic degradation (methane, propane, or natural gas) [27].
Plattsburgh AFB Plattsburgh, NY (2)	Groundwater: petroleum.	Design: pilot scale. Start date (est.): 3/94.	Aerobic treatment, bioventing.
ARC Gainesville, VA (3)	Soil: solvent (chlorobenzene). Volume: 2,000 cubic yards.	Completed: full scale 6/91. Start date: 10/89.	Aerobic treatment, bioventing. Exogenous organisms. 5% of the site underwent bioremediation.
Dover AFB Dover, DE (3)	Soil (vadose sand and silt)/groundwater: petroleum, PAHs, TCE, solvents, metals (lead, iron, manganese). Volume: 365K cubic yards.	Four separate processes are planned. Field and lab TS results are expected 2/94 and 11/94.	Aerobic treatment, bioventing, air sparging. Ex situ land treatment.
L.A. Clarke & Son Fredericksburg, VA (3)	Sediments/soil: wood preserving. Volume: 119K cubic yards.	Design: pilot scale TS started 7/92. Expected cost: \$23M.	In situ treatment, creosote recovery. 25% of site will undergo bioremediation.
Charleston AFB Charleston, SC (4)	Soil (vadose sand): petroleum (jet fuel), solvents (1,1-DCE; 1,1,1-TCA; TCE; VC; trans-1,2-DCE; PCE; and dichloromethane), lead. Volume: 25 cubic yards.	Pilot scale TS started 11/92. Expected completion 12/93.	Aerobic treatment, bioventing. Less than 10% of the site under bioremediation.
Eglin AFB FL (4)	Soil (vadose): petroleum (jet fuel).	Completed field scale study.	Aerobic treatment, bioventing. Nutrient and hydrogen peroxide addition [27].
Savannah River Site Aiken, NC (4)	Soil (vadose)/groundwater/sediments: chlorinated solvents (TCE and PCE).	Operational: pilot scale research study.	Aerobic treatment, horizontal wells, methane addition [18][19].
Stallworth Timber Beatrice, AL (4)	Soil (sand, silt)/groundwater: wood preserving (PCP).	Predesign.	In situ aerobic treatment, nutrient addition. Ex situ treatment, activated sludge, continuous flow. Exogenous and indigenous organisms. 100% of site will undergo bioremediation.
Allied Chemical Ironton, OH (5)	Sediments (coal and coke fines): PAHs, arsenic. Volume: 500K cubic yards.	Design: pilot scale TS study completed. Expected cost: \$26M	Aerobic treatment. 50% of site will undergo bioremediation.
Amoco Production Co. Kalaska, MI (5)	Soil (saturated)/groundwater: BTEX.	Pilot scale TS completed.	Aerobic treatment, air sparging [49].
B&F Trucking Company Rochester, MN (5)	Soil (vadose and saturated)/groundwater: petroleum (lube oil). Volume: 700 cubic yards.	Operational: full scale. Start Date: 4/91. Incurred cost: \$341K.	In situ treatment. Ex situ treatment, sequencing batch reactor, continuous flow. Aerobic conditions. 75% of site under bioremediation.
BendixCorp./Allied ¹ Automotive Site St. Joseph, MI (5)	Groundwater: solvents (TCE, DCE, DCA, VC).	Predesign: lab scale TS underway.	Aerobic and anaerobic treatment.

Table 3. Superfund, RCRA, UST, TSCA, and Federal Sites (continued)

Site Location (Regions)	Primary Contaminants	Status/Cost	Treatment
Un-named site ² Buchanan, MI (5)	Groundwater: BTEX, PCE, TCE, DCE.	Pilot field study started 3/93. Expected completion 3/94.	Aerobic treatment.
Galesburg/Kopper Galesburg, IL (5)	Soil: phenols, chlorophenol, PNAs, PCP, PAHs.	Pre-design. Start date (est): 12/92.	Nutrient addition. 100% of site under bioremediation.
Hentchells Traverse City, MI (5)	Soil/groundwater: petroleum.	Operational: full scale. Start date: 9/85.	Aerobic treatment, biosparging.
Kenworth Truck Company Chillicothe, OH (5)	Soil (vadose)/groundwater: solvents (BTEX, acetone, TPH).	Design: lab scale TS completed. Full scale system being installed.	In situ aerobic treatment, hydrogen peroxide, nutrient addition (nitrogen, phosphorus). Ex situ treatment, GAC bioreactor. 100% of site will undergo bioremediation.
K.I. Sawyer AFB Marquette, MI (5)	Soil (vadose sand): petroleum.	Field TS report expected 10/93.	Aerobic treatment, bioventing.
Mayville Fire Department Mayville, MI (5)	Groundwater: petroleum.	Operational: full scale since 5/90. Completion date (est): 1/94.	Aerobic treatment, air sparging. 100% of site will undergo bioremediation.
Michigan Air National Guard Battle Creek, MI (5)	Soil (vadose: sand, silt): petroleum, heavy metals.	Design: pilot scale TS started 9/92. Start date (est): 9/93 Expected cost: capital, \$3,000; O&M, \$1,268.	Aerobic treatment, bioventing. 100% of site will undergo bioremediation.
Newark AFB Newark, OH (5)	Soil (vadose: silt, clay): petroleum (gasoline). Volume: 60 cubic yards.	Design: pilot scale TS started 8/92. Expected completion 8/94. Expected cost: capital, \$35K; O&M, \$2K.	Aerobic treatment, bioventing. 40% of site under bioremediation.
Onalaska Municipal Landfill Lacrosse County, WI (5)	Soil (vadose and saturated sand): solvents (TCE), petroleum (total hydro-carbons), wood preserving (naphthalene). Volume: 5,000 cubic yards.	Design: lab scale TS completed 3/92. Expected cost: capital, \$400K; O&M, \$20K.	Aerobic treatment, bioventing. 20% of site will undergo bioremediation.
Parke-Davis Holland, MI (5)	Soil/groundwater: petroleum, solvents, arsenic, chloride, zinc.	Pre-design.	In situ treatment. Ex situ treatment, fixed film.
Reilly Tar & Chemical ^{1,2} St. Louis Park, MN (5)	Soil (vadose loam): wood preserving (PAHs).	Design: pilot scale TS started 11/92. Expected completion 11/95. Incurred cost: \$25K. Expected cost: \$70K.	Aerobic treatment, bioventing, nutrient addition [50].
Sheboygan River and Harbor Sheboygan, IL (5)	Sediments (sand, silt, clay): PCBs. Volume: 2,500 cubic yards.	Lab and pilot scale TS are being conducted.	In situ treatment, capping of sediments. Ex situ treatment, confined treatment facility (tank). Aerobic and anaerobic conditions.
West K&L Avenue e Landfill ¹ Kalamazoo, MI (5)	Groundwater: solvents (acetone; TCE; trans-1,2-DCE; 1,2-DCA; 1,1-DCA; BTEX; VC; methyl isobutyl ketone; MEK.	Design: pilot and lab scale TS ongoing.	Anaerobic treatment under sulfate reducing conditions.
Wright-Patterson AFB Dayton, Ohio (5)	Soil (vadose: sand, silt, clay): petroleum (jet fuel). Volume: 7.5K cubic yards.	Pre-design: pilot scale studies planned. Expected completion 3/94.	Aerobic treatment, bioventing. 100% of site will undergo bioremediation.
Dow Chemical Company Plaquemine, LA (6)	Groundwater: solvents (1,1-DCA; 1,2-DCA; 1,1,1-TCA; 1,1-DCE, chloroethane). Volume: 90K cubic yards.	Design: pilot scale started 3/93. Expected cost: capital, \$1M; O&M, \$50K. Incurred cost: capital, \$250K; O&M, \$10K.	Anaerobic treatment, nutrient addition. Less than 1% of site under bioremediation. Experiencing nutrient dispersion problems [46].
French Limited Crosby, TX (6)	Sediments (sand, silt)/sludge/soil (sand, silt, clay)/groundwater: PCBs, arsenic, rolexum (BAP, VOCs), arsenic.	Operational: full scale since 1/92. Expected cost: \$90M.	Aerobic treatment, pure oxygen dissolution system, nutrient addition (soil, water, sediments). 100% of site under bioremediation.
Kelly AFB San Antonio, TX (6)	Soil (vadose clay): petroleum (jet fuel), solvents (PCE, TCE, VC, DCE).	Operational: full scale since 2/93. Completion data (est): 9/94.	Aerobic treatment, bioventing.

Table 3. Superfund, RCRA, UST, TSCA, and Federal Sites (continued)

Site Location (Regions)	Primary Contaminants	Status/Cost	Treatment
Fairfield Coal & Gas Fairfield, IA (7)	Soil (saturated: sand, silt, clay)/groundwater: coal tar (BTEX, PAHs).	Design: pilot scale TS started 12/91. Expected completion 12/93. Expected cost: \$1.6M.	Aerobic treatment, injection and extraction wells, hydrogen peroxide, nitrate addition.
Offutt AFB LaPlatte, NE (7)	Soil (vadose: sand, silt): petroleum (TRPH), arsenic, barium, lead, zinc. Volume: 700 cubic yards.	Design: pilot scale TS started 8/92.	Aerobic treatment, bioventing. 10% of site under bioremediation.
Park City ¹ Park City, KS (7)	Groundwater: petroleum (lube oil), benzene. Volume: 700K cubic feet.	Design: pilot scale TS completed. Incurred cost: \$275K. Expected cost: \$650K.	Groundwater: in situ treatment. Possible bioventing for soils. Anaerobic and aerobic conditions [23][24].
Burlington Northern Tie Plant Somers, MT (8)	Soil/groundwater: wood preserving (PAHs). Volume: 82K cubic yards.	Installed: full scale. Start date (est.): 7/92. Expected cost: \$11M.	In situ treatment. Ex situ land treatment. Aerobic conditions. 80% of site will undergo bioremediation.
Geraldine Airport Geraldine, MT (8)	Soil (vadose: sand, silt, loam, clay): pesticides (aldrin; dieldrin; endrin; chlordane; toxaphene; b-BHC; 4,4'-DDE; 4,4'-DDT; 4,4'-DDD); herbicides (2,4-D).	Predesign.	In situ treatment. Ex situ treatment. Aerobic and anaerobic conditions.
Idaho Pole Company Bozeman, MT (8)	Sediments/soils/groundwater: PCP, PAHs, dioxins/furans.	Predesign.	In situ treatment, oxygen enhancement, nutrient addition. Ex situ treatment, fixed film, slurry reactor. Aerobic conditions.
Hill AFB ¹ Salt Lake City, UT (8)	Soil: petroleum (JP-4 jet fuel).	Operational: full scale since 9/91. Completion date (est): 9/94.	Aerobic treatment, bioventing. 100% of site under bioremediation [40].
Libby Groundwater Site ¹ Libby, MT (8)	Soil (vadose and saturated)/groundwater: wood preserving (PAHs, pyrene, PCP, dioxin, naphthalene, phenanthrene, benzene, arsenic). Volume: 45K cubic yards.	Operational: three pilot scale efforts ongoing. Incurred cost: \$4M. TS results available (est): 8/93 and 4/94.	In situ treatment (groundwater), ex situ land treatment (soil), nutrient addition (soil, water). Also, treatment of groundwater in bioreactor. Aerobic conditions. 75% of site under bioremediation.
Public Service Company ¹ Denver, CO (8)	Groundwater: petroleum. Volume: 12M gallon.	Completed: full scale 3/92. Start date: 06/89. Incurred cost: \$500K.	Aerobic treatment, hydrogen peroxide, nutrient addition, combined bioprocess.
Beale AFB Marysville, CA (9)	Soil (vadose silty clay): petroleum (gasoline, diesel), solvents (TCE), lead. Volume: 163K cubic yards.	Seven processes are planned. 4 are in design (pilot scale), 2 are in predesign (full scale), and 1 is presently operating (completion date 7/95). Expected cost: capital \$500K; O&M, 136K.	In situ aerobic treatment, bioventing. Ex situ aerobic treatment, pile. Results of 4 bioventing TS expected 2/94.
Converse/Montabello Corporation Yard Montabello, CA (9)	Soil (vadose silt): petroleum (gas, diesel).	Design: pilot scale TS started 5/93. Expected completion 12/93.	Aerobic treatment, bioventing, nutrient addition. 10% of site under bioremediation.
Former Service Station Los Angeles, CA (9)	Soil/groundwater: petroleum. Volume: 3,000 cubic yards.	Completed: full scale 3/91 Start date: 11/88. Incurred cost: \$1.6M.	Aerobic treatment, hydrogen peroxide, nutrient addition (water), closed loop system. 65% of site underwent bioremediation.
Koppers Company, Inc. Orville, CA (9)	Soil (vadose: sand, clay, gravel, cobbles): wood preserving (PCP, PAHs, dioxins/furans), arsenic, chromium. Volume: 110K cubic yards.	Predesign: pilot scale TS planned. Expected completion 11/94. Expected cost: capital, \$4.5M; O&M, \$7.7M.	Aerobic treatment, nutrient addition. 30% of site will undergo bioremediation. (20 year remedial effort)
Marine Corps Air/ Ground Combat Center Twenty-Nine Palms, CA (9)	Soil: petroleum (jet fuel, gasoline, diesel, aviation fluid, transmission fluid).	Design: full scale.	Aerobic treatment, bioventing.
Naval Air Station Fallon Fallon, NV (9)	Soil (vadose and saturated silt)/groundwater: petroleum (jet fuel, p-xylene, naphthalene, 1-methyl naphthalene, n-butylbenzene), arsenic.	Design: pilot scale TS started 10/92.	Aerobic treatment, bioventing, nutrient addition (soil), oil/water separation.
Naval Weapons Station Seal Beach, CA (9)	Groundwater: petroleum.	TS conducted or in progress: laboratory scale.	Aerobic and anaerobic treatment.
Oakland Chinatown Oakland, CA (9)	Soil (saturated sand): groundwater: petroleum.	Volume: 10K cubic yards. Completed: full scale 8/90. Start date: 3/89.	Aerobic treatment, hydrogen peroxide and nutrient addition.

Table 3. Superfund, RCRA, UST, TSCA, and Federal Sites (continued)

Site Location (Regions)	Primary Contaminants	Status/Cost	Treatment
San Diego Gas and Electric San Diego, CA (9)	Soil (sand): petroleum (gasoline). Volume: 1,200 cubic yards.	Completed: full scale 4/93. Start date: 10/89.	Aerobic treatment. 100% of site underwent bioremediation [5].
Williams AFB. ² Phoenix, AZ (9)	Soil (vadose): petroleum (JP-4 jet fuel).	Pilot field testing started 5/92. Test completed 6/93.	In situ treatment, bacterial supplementation (non-indigenous micro aerophilic bacteria).
East 15th Street Service Station Anchorage, AK (10)	Soil: petroleum (TPH diesel). Volume: 1,500 cubic yards.	Operational: full scale since 6/92. Incurred cost: \$75K. Expected cost: \$200K.	Aerobic treatment, bioventing. 20% of site under bioremediation.
Eielson AFB. ¹ Fairbanks, Alaska (10)	Soil (sand/silt): petroleum (JP-4 jet fuel).	Operational: pilot full scale. Start date: 9/91. Completion date (est): 9/94.	Aerobic treatment, bioventing, soil warming [42]
Fairchild AFB Spokane, WA (10)	Soil (vadose and saturated silt)/groundwater: petroleum, solvents (TCE).	3 separate processes are planned. The first process is in pre-design; a pilot scale TS should start 1/95. The remaining two started pilot scale TSs in 4/93.	Aerobic treatment, bioventing, nutrient addition.

TS - Treatability Study

1 Bioremediation Field Initiative

2 Superfund Innovative Technology Evaluation (SITE) Demonstration

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In-situ Carbon



Remedial Technology Fact Sheet – Activated Carbon-Based Technology for In Situ Remediation



Introduction

At a Glance

- ❖ An emerging remedial technology combining adsorption by activated carbon (AC) and degradation by reactive amendments.
- ❖ Several commercial products of various AC particle size and different amendments.
- ❖ Synergy between adsorption and degradation for treating chlorinated solvents and petroleum hydrocarbons.
- ❖ Applied to treat plumes but also residual source in low-permeability zones.
- ❖ Primarily uses direct push injection, including high-pressure in low-permeability zones for granular AC- and powdered AC-based products and low pressure for colloidal AC-based products in high-permeability zones. Injection well has also been used for delivering colloidal AC-based products.
- ❖ Requires adequate characterization (i.e., a high-resolution conceptual site model (CSM)) for effective remedial design.
- ❖ Adsorption to AC results in rapid concentration reduction in aqueous phase after injection.
- ❖ Rebound may occur due to greater contaminant influx than the rate of adsorption and degradation, poor site characterization, or lack of effective distribution.
- ❖ Performance assessment may be subject to bias if AC is present in monitoring wells. Other lines of evidence are important.
- ❖ Field evidence of degradation is limited but promising. However, persistence and contribution of degradation need further validation.

This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Office of Superfund Remediation and Technology Innovation, concerns an emerging remedial technology that applies a combination of activated carbon (AC) and chemical and/or biological amendments for in situ remediation of soil and groundwater contaminated by organic contaminants, primarily petroleum hydrocarbons and chlorinated solvents. The technology typically is designed to carry out two contaminant removal processes: adsorption by AC and destruction by chemical and/or biological amendments.

With the development of several commercially available AC-based products, this remedial technology has been applied with increasing frequency at contaminated sites across the country, including numerous leaking underground storage tank (LUST) and dry cleaner sites (Simon 2015). It also has been recently applied at several Superfund sites, and federal facility sites that are not on the National Priorities List.

This fact sheet provides information to practitioners and regulators for a better understanding of the science and current practice of AC-based remedial technologies for in situ applications. The uncertainties associated with the applications and performance of the technology also are discussed.

What is AC-based technology?

- ❖ AC-based technology applies a composite or mixture of AC and chemical and/or biological amendments that commonly are used in a range of in situ treatment technologies.
- ❖ Presently, five commercial AC-based products have been applied for in situ subsurface remediation in the U.S.: BOS-100® & 200® (RPI), COGAC® (Remington Technologies), and PlumeStop® (Regenesys) are the four most commonly used commercial products. CAT-100® from RPI is the most recent product, developed based on BOS-100®. One research group in Germany also developed a product called Carbo-Iron®. Detailed properties and compositions of these products are shown in Exhibit 1.
- ❖ The AC components of these products typically are acquired from specialized AC manufacturers. These types of AC have desired adsorption properties for chlorinated solvents and petroleum hydrocarbons. Different products also have different AC particle sizes, which determine the suitable injection approach and the applicable range of geological settings.

How are contaminants treated by AC-based technology?

- ❖ AC-based technology involves two contaminant removal processes: adsorption and degradation. AC is responsible for adsorption and reactive amendments are responsible for degradation.
- ❖ AC is composed of randomly oriented graphite stacks. The random orientation results in a highly porous matrix having a wide range of pore sizes. Adsorption of typical groundwater organic contaminants (e.g., benzene, trichloroethylene) primarily occurs in micropores (<2 nm in diameter). Large pores, mesopores and macropores, mainly serve as transport conduits for contaminants to reach adsorption sites via intraparticle diffusion (Bansal and Goyal 2005).
- ❖ Under typical subsurface temperatures, physical adsorption is the dominant adsorption mechanism, which is a reversible process governed by the van Der Waals force (Karanfil and Kilduff 1999). Contaminant desorption can occur when equilibrium conditions (e.g., pH, plume composition) change, but AC applications in sediment remediation showed that the desorption rate from AC is much slower than that from indigenous sediment materials (Sun and Ghosh 2008).
- ❖ Chemical or biological amendments determine the contaminant groups treated and degradation pathways supported. BOS-100® treats chlorinated solvents via zero-valent iron (ZVI)-mediated abiotic dechlorination; BOS-200® treats petroleum hydrocarbons by bioaugmentation. COGAC® treats either group by chemical oxidation and likely subsequent biostimulation; and PlumeStop® treats either group by biostimulation or bioaugmentation depending on the specific amendments applied (Exhibit 1).
- ❖ Solid amendments (e.g., ZVI) or bacteria often have much larger size than micropores, the major adsorption sites of AC (Exhibit 2). Therefore, sorbed contaminants must be desorbed and diffuse out of micropores to be degraded. This process is driven by the concentration gradient between sorption sites and bulk liquid phase (Spetel Jr et al. 1989; Tseng et al. 2011).
- ❖ Contaminant removal is controlled by the dynamic equilibrium between contaminant influx, adsorption and degradation. This has been suggested to occur in biological activated carbon reactors for wastewater treatment, where the relative contribution of adsorption and biodegradation to contaminant removal varies at different operational stages (Voice et al. 1992; Zhao et al. 1999). Contaminants stay within the treatment zone when combined rates of adsorption and degradation exceed the incoming mass flux.

Exhibit 1: Properties of six AC-based products that have been used for in situ applications

Product	Property	Target Contaminant	Degradation Pathway
BOS-100®	Granular AC (GAC) impregnated by ZVI	Chlorinated solvents	Abiotic reductive dechlorination
BOS-200®	Powder AC (PAC) mixed with nutrients, electron acceptors, and facultative bacteria mix	Petroleum Hydrocarbons	Aerobic and anaerobic bioaugmentation
CAT-100®	BOS-100® and reductive dechlorination bacterial strains	Chlorinated solvents	Abiotic and biotic reductive dechlorination
COGAC®	GAC or PAC mixed with calcium peroxide, and sodium persulfate	Chlorinated solvents or petroleum hydrocarbons	Chemical oxidation, aerobic and anaerobic biostimulation
PlumeStop®	Colloidal AC suspension with an organic stabilizer, co-applied with hydrogen or oxygen release compounds, and/or corresponding bacterial strains	Chlorinated solvents or petroleum hydrocarbons	Enhanced biotic reductive dechlorination for chlorinated solvents and aerobic biodegradation for petroleum hydrocarbons
Carbo-Iron®	Colloidal AC impregnated with ZVI	Chlorinated solvents	Abiotic reductive dechlorination

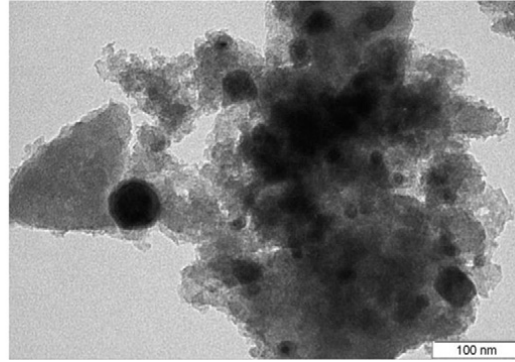
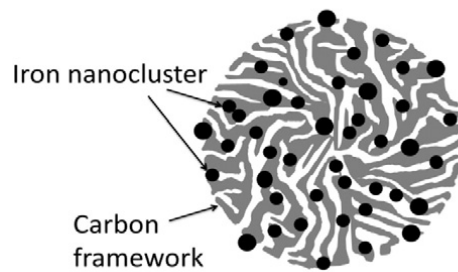


Exhibit 2. (Left) Conceptual structure and (Right) transmission electron micrograph (TEM) of Carbo-Iron® (Adopted from Mackenzie et al. 2016)

What are the potential benefits of using AC-based remedial technology?

- ❖ Adsorption can significantly retard contaminant migration and decrease dissolved phase concentrations. Retaining contaminants in the AC matrix allows longer residence time for contaminants to be degraded by reactive amendments. The coupling of adsorption and degradation reduces the potential for contaminant rebound that frequently is encountered with conventional treatment technologies (e.g., pump and treat (P&T) or in situ chemical oxidation (ISCO)).
- ❖ AC impregnated with nano zerovalent iron (nZVI) is shown to have more persistent reactivity than suspended nZVI particles (Choi et al. 2009). It was suggested that AC may protect nZVI from undesired side reactions with dissolved oxygen and water, which often outcompete contaminant degradation for nZVI because of their greater abundance.
- ❖ Adsorption may enrich chemicals (including both contaminants and nutrients) over time to facilitate formation of active biofilm and biodegradation (Voice et al. 1992). The combined effects may significantly reduce the time frame to reach remedial objectives.
- ❖ For high concentration of chlorinated VOCs, adsorption onto AC decreases the initial high aqueous contaminant concentration that inhibits biological dechlorination and shortens the lag phase for biodegradation (Aktas et al. 2012).

How is AC-based remedial technology implemented in field?

- ❖ Grid injection that targets a well-defined contaminated area commonly is used if the footprint of treatment areas is relatively small, such as some LUST sites or localized hotspots.
- ❖ For plume, barrier applications commonly are used. AC-based amendments typically are emplaced in transects to form a series of permeable reactive zones that are perpendicular to the direction of plumes. An external water supply typically is needed to mix and dilute amendments in these barrier wall configurations.
- ❖ High-pressure injection (typically 300 to 1000 psi), (i.e., hydraulic fracturing), is used for emplacing Granular AC(GAC)- or Powder AC(PAC)-based amendments due to the need to open up the formation for emplacement of the large particles. As fracturing is more effective in low-permeability formations, GAC or PAC-based amendments typically are injected in tight formations, such as clays and silts (Winner and Fox 2016).
- ❖ Less frequently, soil mixing or trenching has also been used for emplacement of GAC or PAC-based amendments provided suitable hydrogeological conditions. For example, BOS-100, a GAC-based product, was emplaced by deep soil mixing in a sandy aquifer during a pilot test at the Vandenberg Air Force Base, after high-pressure injection showed poor amendment distribution (ITRC 2011).
- ❖ Colloidal AC-based amendments are emplaced by low-pressure injection (e.g., 30–50 psi) using direct push or permanent injection wells without creating artificial fractures. As a result, the amendment primarily is applied to more permeable formations such as sands and gravels. However, even a low-permeability aquifer may contain permeable (flux) zones that permit application of colloidal AC-based amendment.

How is AC-based amendment distributed in the subsurface?

- ❖ For GAC- and PAC-based amendments, high-pressure injection typically produces thin seams or lenses of AC in seemingly random directions. In tight geologies, fractures typically have higher permeability than surrounding formations. This difference may allow contaminant desorption and diffusion from the low-permeability formations into the fractures. The conceptual model is shown on the left in Exhibit 3. Tight injection spacing in both horizontal and vertical directions is recommended to obtain sufficient coverage as it is difficult to control the formation and growth of fractures (Murdoch, 1995). Some recent improvements have been made to better control the direction and
- development of fractures (i.e., direct push jet injection), but these approaches have not been applied to injecting AC-based amendments.
- ❖ For colloidal AC, the particles infiltrate into the permeable zone or formation upon low-pressure injection and eventually deposit onto the surface of soil grains due to surface-surface interactions. The presence of an organic polymer improves the colloidal stability and transport in the subsurface. Therefore, the distribution of amendments in flux zones is expected to be more uniform than induced fracturing of AC-based amendments of larger particle size (Exhibit 3, on right).

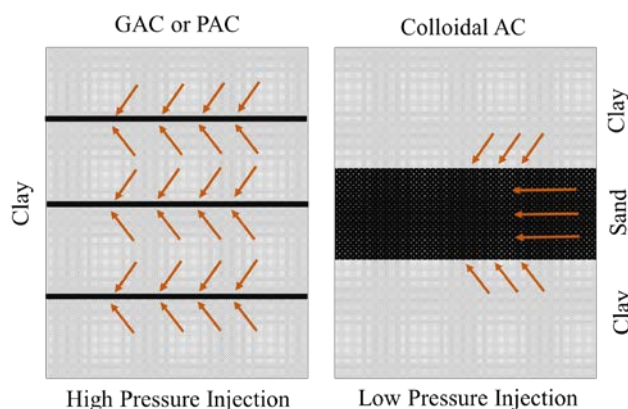


Exhibit 3. Different conceptual distribution patterns between GAC- or PAC-based amendment (left) and colloidal AC-based amendment (right). Dark regions represent the forms of amendment distribution and arrows represent the directions of contaminant flux entering the AC zone. (Adapted from Fan et al. 2017).

What are the key factors to consider during remedial design?

- ❖ Design of AC-based remedies primarily focuses on defining optimal injection locations and loadings, which are affected by the treatment approach and objective (e.g., area treatment to reduce mass flux or barrier application to intercept plume). The key to effective remedial design of AC-based technology (or any in situ remedial technology), is to conduct adequate site characterization to create a sufficiently detailed CSM.
- ❖ Subsurface geology and contaminant mass distribution are the two major aspects to characterize during remedial design investigation (Winner and Fox 2016). Subsurface hydrogeology can be characterized by grain size distribution analysis, clear water injection, or hydraulic profiling (Birnstingl et al. 2014). Contaminant distribution can be qualitatively determined by various in situ rapid screening tools, such as the membrane interface probe (MIP) (Winner and Fox 2016; EPA 2016); laser induced fluorescence (LIF) technique for non-aqueous phase liquid (NAPL); or a photo ionization detector (PID) for soil screening on-site. Selected samples can be subject to more rigorous laboratory analysis if needed.
- ❖ For GAC- and PAC- based amendments, it is important to profile the vertical distribution of contaminant mass as it determines the vertical injection interval and injection loading at each interval, especially when the remedy is designed to treat a residual source area with heterogeneous lithology. At a former manufacturing site in Denver, the initial injection of BOS-100® near the source area did not achieve performance objectives. Further high-resolution site characterization

revealed highly heterogeneous contaminant distribution in the vertical direction. Subsequent injection loading and approach were adjusted to the contaminant distribution pattern, which significantly improved the remedy performance (Noland et al. 2012; Harp 2014).

- ❖ For colloidal AC-based amendments, it is important to locate the high-permeability zones and estimate the mass flux across those zones to determine where to apply the amendments, and how much is needed.
- ❖ Contaminants associated with soil (e.g., sorbed) and residual NAPL phase represent the majority of the contaminant mass stored in low-permeability zones, and can serve as a long-term source for groundwater contamination. The calculation of contaminant loading needs to consider the rates of back diffusion of source material or the total mass of contamination.
- ❖ Laboratory-measured adsorption capacity often serves as a benchmark value to calculate

amendment loading. However, the actual adsorption capacity varies with contaminant concentration and can be further complicated by competitive adsorption and potential growth of biofilm.

- ❖ Vendors often are willing to actively participate in the remedial investigation and design phases to ensure successful implementation and desired performance of their products. Spreadsheets are available from the vendors to calculate the loading rates of amendments based on estimated contaminant mass (or mass flux), adsorption capacity, remedial objectives, and the designed lifetime of the remedy. However, the calculation is largely empirical due to various uncertainties caused by subsurface heterogeneity. Based on discussion with the vendors, a safety factor of 5 to 20 is recommended for estimating amendment loading.

How does the AC-based remedial technology perform in the field?

- ❖ The four commercial AC-based products combined have accumulated more than 1500 applications in North America and Europe as of 2015 (Simon 2015). To date, this technology has been used or selected at four NPL sites and one RCRA corrective action site.
- ❖ Field data generally show rapid decrease of aqueous contaminant concentration after emplacement of the amendments when initial contaminant concentration is high. The decrease is more gradual when initial contaminant concentration is low (e.g., <100 ppb). Temporary rebound shortly after injection is common, and may occur when equilibrium is reestablished after enhanced contaminant desorption from aquifer solids, or when plume is temporarily displaced by injection of amendments in large volumes.
- ❖ Regenesi evaluated the performance of PlumeStop[®] applied at 24 sites between 2014 and 2016 by pooling contaminant concentrations from 34 monitoring wells (Davis 2016). Regenesi found more than 65% of wells achieved >95% reduction within 1–3 months after injection. The initial rapid response is most likely due to rapid adsorption process.
- ❖ Rebound of contamination has been observed at some sites that applied AC-based amendments. The same study by Regenesi (Davis 2016) found that 15% of the wells examined showed some rebound over an average of 6-month time frame but the rebound is generally <10% of pre-treatment concentrations. Early applications of

PAC-based products at LUST sites in Colorado also identified frequent rebound (Fox 2015). Possible reasons cited for rebound include underestimation of contaminant mass due to poor site characterization (Fox 2015); insufficient amendment distribution due to large injection spacing or poor implementation (Fox 2015); or contaminant mass influx exceeding the combination of adsorption and degradation (Mackenzie et al. 2016).

- ❖ AC frequently is observed in monitoring wells post injection. Given amendment distribution is likely not uniform, especially when high-pressure injection is used, caution needs to be taken when using impacted monitoring wells for performance evaluation. Concentrations measured in those wells may not accurately represent the aquifer concentrations. In addition, impacted wells also typically should not be used for attainment monitoring because post remediation conditions may not be reached (EPA 2013; EPA 2014)¹. Other lines of evidence are recommended for confirming the treatment performance achieved in the treatment zone.
- ❖ Several measures have been taken to improve confidence in performance assessment using monitoring wells. Examples include preventing or

¹ “The attainment monitoring phase typically occurs after EPA makes a determination that the remediation monitoring phase is complete. When the attainment phase begins, data typically are collected to evaluate if the well has reached post remediation conditions (i.e., steady state conditions) where remediation activities, if employed, are no longer influencing the groundwater in the well.” (EPA 2013)

minimizing well impact using geochemical parameters as early indicators for breakthrough of AC; installing new wells near the existing impacted wells to demonstrate that either amendment distribution is not localized or AC-free wells exhibit similar treatment effects as AC-impacted wells; and monitoring downgradient wells adjacent to the

treatment zone to observe for decreasing contaminant trend (Winner and Fox, 2016). Removing AC from impacted wells prior to sampling could be another solution. It has been shown to be moderately successful for colloidal AC but not work for AC with large particle sizes, according to vendors and practitioners.

What is the evidence for degradation?

- ❖ Degradation is generally an indispensable component of contaminant removal processes by AC-based amendments. Without degradation, AC-based remedial technology may serve only to stabilize the contaminants, and contaminants may break through once adsorption capacity is exhausted or when desorption occurs. Throughout the development of the technology, the uncertainty regarding the importance and persistence of degradation has been a major hurdle for wide acceptance of the technology.
- ❖ Bench-scale tests have demonstrated the effectiveness of degradation processes involved in AC-based remedial products (Birnstingl et al. 2014). However, controlled laboratory results may not guarantee field effectiveness, especially for biodegradation that is more variable because of field heterogeneities.
- ❖ It is difficult to confirm contaminant degradation in the field. Both adsorption and degradation can result in decreasing contaminant concentrations without the appearance of daughter products, which may also be adsorbed by AC. Use of contaminant data from monitoring wells does not distinguish contaminant removal by adsorption from that by degradation.
- ❖ To date, field evidence of degradation has been limited and largely qualitative. For petroleum hydrocarbons, depletion of nitrate or sulfate, and production of volatile fatty acids, have been suggested as evidence of biodegradation.
- ❖ For chlorinated solvents, production of chloride has been used to indicate dechlorination, but this line of evidence only applies when background chloride concentration is low or contaminant concentration is very high (i.e., near the source area). In one pilot test of Carbo-Iron, significant elevation of ethene and ethane was used as evidence for abiotic reductive dechlorination (Mackenzie et al. 2016).
- ❖ More recently, environmental molecular diagnostic (EMD) tools have shown promise for assessing biodegradation of petroleum hydrocarbons and chlorinated solvents (ITRC 2013). The following recent data was provided to EPA by three vendors of AC-based products to demonstrate degradation:
 - o At one chlorinated solvent site where PlumeStop[®] was injected with a hydrogen release compound (HRC[®]) and *Dehalococcoides* cultures, the combination significantly increased the abundance of degraders and functional genes in the aqueous phase after injection. The high abundance was sustained for over 500 days, even though the dissolved tetrachloroethene (PCE) remained below the detection limit. This pattern suggests that enhanced concentrations of microbial indicators resulted from enhanced microbial activity in the up-gradient AC barrier.
 - o At one petroleum site where COGAC[®] was injected, groundwater samples were collected one year after injection. In these samples, the abundance of six anaerobic BTEX (benzene, toluene, ethylbenzene and xylenes) and PAH (polycyclic aromatic hydrocarbon) degraders was found to be 2 to 4 orders of magnitude higher in samples collected from wells within the injection influence zone than in samples collected from a well outside the injection influence zone.
 - o At one petroleum site where BOS-200[®] was injected to form a permeable reactive zone, compound specific isotope analysis (CSIA) was conducted on samples collected from wells up- and downgradient of the PRB two years after injection. Compared to the upgradient well, the downgradient wells consistently show small but evident enrichment of C¹³ for several BTEX compounds, indicating occurrence of biodegradation of these compounds.
- ❖ Applications of AC in other contaminant removal processes such as wastewater and sediment treatment have suggested that AC enhances biodegradation by promoting the formation of biofilms, which can be attributed to increasing nutrient retention, enhanced resistance to environmental shocks, and increased microbial diversity (Simpson 2008; Kjellerup et al. 2014).

What is the long-term effectiveness of AC-based remedial technology?

- ❖ The longevity of AC-based remedial technology is of particular interest because the long-term effectiveness to counter slow and persistent contaminant flux (from diffusion, desorption, and dissolution) is one of the major benefits claimed for this technology.
- ❖ Currently, there is lack of sufficient monitoring data to assess the long-term performance due to either recent implementation or the lack of long-term monitoring requirements at many small sites. Thus, the long-term effectiveness of this technology remains to be further evaluated when data become available.
- ❖ The relative contribution of contaminant adsorption versus degradation is a critical parameter for evaluating the long-term performance. As contaminant can eventually break through when adsorption capacity becomes exhausted, degradation is the main driver in maintaining the long-term effectiveness of the technology. This aspect remains to be further investigated.
- ❖ Competitive adsorption may affect long-term effectiveness. Competitive adsorption refers to a process where strongly sorbed compounds may displace weakly sorbed compounds, resulting in release of the latter. Competitive adsorption should be evaluated for treating comingled plumes or plumes where degradation intermediates are expected to form if degradation stalls or does not proceed to completion. For example, sorbed benzene may be displaced by xylene in a BTEX plume. For a chlorinated solvent plume, daughter products such as *cis*-dichloroethene (DCE) or vinyl chloride may be displaced by PCE or trichloroethene (TCE). This potential desorption behavior again highlights the importance of supporting degradation activity and including (bio)degradation assessment in a long-term monitoring plan.

Where and when should AC-based remedial technology be considered?

- ❖ AC-based remedial technology provides an effective approach to address persistent plumes emanating from low-permeability sources, desorption, or dissolution of residual NAPL phase.
- ❖ AC-based remedial technology could be considered when other remedial options at a site have demonstrated limited effectiveness. For example, applications of AC-based remediation at LUST sites in Colorado and Kentucky (primarily PAC-based amendments) mainly occurred at sites dominated by low-permeability formations, including fractured bedrock, where soil vapor extraction or bioremediation was not successful (Winner and Fox 2016).
- ❖ AC-based remedial technology can serve as a cost-saving alternative to active P&T to prevent plume migration. It may also complement an existing P&T system to contain a plume by reducing the rate or area for pumping.
- ❖ Several recent Superfund AC applications used AC only without adding reactive amendments for treating low-concentration chlorinated solvent plumes. The approach was selected to avoid potential generation of poorly sorbed daughter products or avoid secondary groundwater quality issues resulted from changes in subsurface redox conditions due to application of reactive amendments. At one site, the effectiveness of the adsorption mechanism alone is proposed to last sufficiently long to allow time for source treatment. However, long-term monitoring data are required to confirm long-term performance.
- ❖ While emplacement of AC-based amendments typically is not considered as a source treatment technology due to concerns of exhausting the adsorption capacity quickly, emplacements of AC in sources or around source areas as a barrier have been applied in the field. The goal is to significantly reduce contaminant mass flux out of the sources to reduce downgradient impacts. The technology can be coupled with source zone treatment technologies, such as in situ thermal treatment, or with excavation when not all contaminated material can be removed.
- ❖ In scenarios where fast groundwater flow velocity might limit the effectiveness of soluble amendments due to dilution, colloidal AC-based amendments may be considered since they more rapidly adsorb to aquifer materials and are more likely to remain in the target treatment area.

Where can I find more information?

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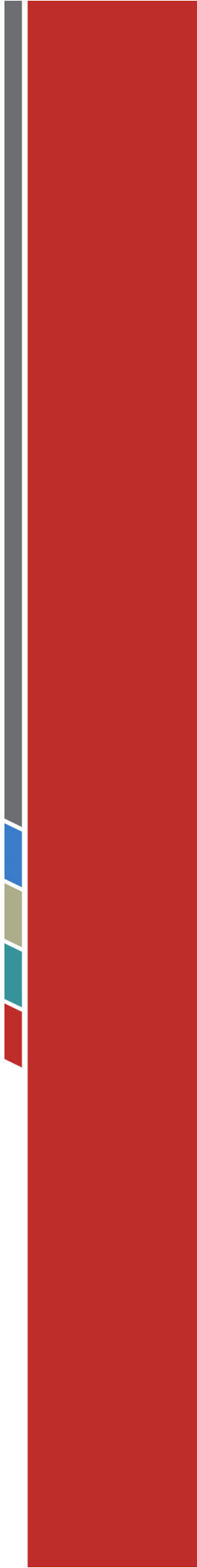
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For further information, contact Technology Assessment Branch, Office of Superfund Remediation and Technology Innovation, Office of Land and Emergency Management.

MNA





Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water



Access here: <https://archive.epa.gov/epawaste/hazard/web/pdf/protocol.pdf>

TECHNICAL PROTOCOL FOR EVALUATING NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUND WATER

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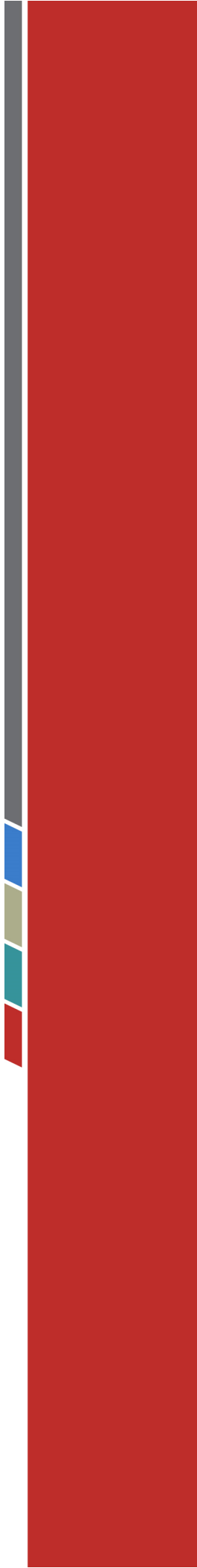
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ORC-Advanced Specification Sheet





**OXYGEN
RELEASE
COMPOUND**

ORC Advanced® Technical Description

ORC Advanced® is an engineered, oxygen release compound designed specifically for enhanced, *in situ* aerobic bioremediation of petroleum hydrocarbons in groundwater and saturated soils. Upon contact with groundwater, this calcium oxyhydroxide-based material becomes hydrated producing a controlled release of molecular oxygen (17% by weight) for periods of up to 12 months on a single application.

ORC Advanced decreases time to site closure and accelerates degradation rates up to 100 times faster than natural degradation rates. A single ORC Advanced application can support aerobic biodegradation for up to 12 months with minimal site disturbance, no permanent or emplaced above ground equipment, piping, tanks, power sources, etc are needed. There is no operation or maintenance required. ORC Advanced provides lower costs, greater efficiency and reliability compared to engineered mechanical systems, oxygen emitters and bubblers.



Example of ORC Advanced

ORC Advanced provides remediation practitioners with a significantly faster and highly effective means of treating petroleum contaminated sites. Petroleum hydrocarbon contamination is often associated with retail petroleum service stations resulting from leaking underground storage tanks, piping and dispensers. As a result, ORC Advanced technology and applications have been tailored around the remediation needs of the retail petroleum industry and include: tank pit excavations, amending and mixing with backfill, direct-injection, bore-hole backfill, ORC Advanced Pellets for waterless and dustless application, combined ISCO and bioremediation applications, etc.

For a list of treatable contaminants with the use of ORC Advanced, view the [Range of Treatable Contaminants Guide](#)

Chemical Composition

- Calcium hydroxide oxide
- Calcium hydroxide
- Monopotassium phosphate
- Dipotassium phosphate

Properties

- Physical state: Solid
- Form: Powder
- Odor: Odorless
- Color: White to pale yellow
- pH: 12.5 (3% suspension/water)



**OXYGEN
RELEASE
COMPOUND**

ORC Advanced® Technical Description

Storage and Handling Guidelines

Storage

- Store in a cool, dry place out of direct sunlight
- Store in original tightly closed container
- Store in a well-ventilated place
- Do not store near combustible materials
- Store away from incompatible materials
- Provide appropriate exhaust ventilation in places where dust is formed

Handling

- Minimize dust generation and accumulation
- Keep away from heat
- Routine housekeeping should be instituted to ensure that dust does not accumulate on surfaces
- Observe good industrial hygiene practices
- Take precaution to avoid mixing with combustibles
- Keep away from clothing and other combustible materials
- Avoid contact with water and moisture
- Avoid contact with eyes, skin, and clothing
- Avoid prolonged exposure
- Wear appropriate personal protective equipment

Applications

- Slurry mixture direct-push injection through hollow rods or direct-placement into boreholes
- *In situ* or *ex situ* slurry mixture into contaminated backfill or contaminated soils in general
- Slurry mixture injections in conjunction with chemical oxidants like RegenOx or PersulfOx
- Filter sock applications in groundwater for highly localized treatment
- *Ex situ* biopiles

Health and Safety

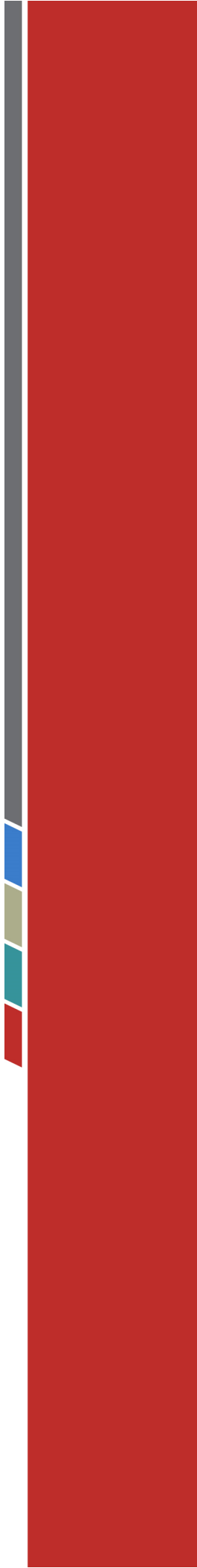
Wash thoroughly after handling. Wear protective gloves, eye protection, and face protection. Please review the [ORC Advanced Safety Data Sheet](#) for additional storage, usage, and handling requirements.



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Plume Stop White Paper





White Paper

Securing Rapid Contaminant Reduction and Enhanced Bioremediation Using a Dispersive Injectable Reagent

Jeremy Birnstingl, PhD; Craig Sandefur, MS; Kristen Thoreson, PhD;
Stephanie Rittenhouse, BS; Ben Mork, PhD

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PlumeStop® Liquid Activated Carbon™ represents a new technology innovation designed to address the challenges of excessive time and end-point uncertainty in groundwater bioremediation. The technology secures rapid groundwater contaminant concentration reduction (days), coupled with enhanced bio-destruction.

It is effective on most organic groundwater contaminants including hydrocarbons, halogenated compounds, and a wide variety of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). The technical innovation allows for wide dispersion of a sorptive medium in the aqueous subsurface. The product has a dual function; it sorbs contaminants, quickly removing them from the mobile phase ('PlumeStop'), and provides a high surface area matrix favorable for microbial colonization and growth. Contaminant availability within a risk pathway is therefore reduced while at the same time contaminant destruction is enhanced.

The product can be applied in combination with compatible controlled release electron donors/acceptors. Upon reagent injection, target contaminants partition out of the aqueous phase and into the reagent matrix, thereby removing mobile contaminants from the immediate risk pathway. Concentration of the contaminants in this manner, in a matrix conducive to degrader colonization and activity, results in results in an enhanced efficiency of contaminant destruction of contaminant destruction, given the quasi first-order biodegradation kinetics characteristic of environmental systems.

This phenomenon can be especially important at low contaminant concentrations, which may otherwise prove insufficient to support appreciable growth and activity of a degrading microflora.

The technology can be applied to inhibit spreading of contaminant plumes, to protect sensitive receptors, or to prevent contaminant migration across property boundaries. PlumeStop is also a very effective tool for treating sites with very low contaminant concentrations, and for control and treatment of groundwater contamination associated with low-permeability porous formations and matrix back-diffusion, promoting diffusion out of the immobile porosity while preventing groundwater impact.

Field studies confirm wide-area dispersion, with an order of magnitude (>90%) reduction in dissolved-phase concentrations at the test sites post-application sampling, and a further increase to two orders of magnitude (>99%) within two months for both chlorinated solvent and hydrocarbon species alike. Laboratory data provide confirmation of post-sorption degradation enhancement, describing a significant increase in efficiency of contaminant destruction in biotic matrix systems compared to abiotic matrix and biotic non-matrix controls.



1 Introduction

This paper provides an introduction and technical overview of PlumeStop® Liquid Activated Carbon™, designed to combine a rapid step-change reduction in groundwater contaminant concentrations with enhanced bio-destruction of the same. At the basis of the technology are the core features of:

- Dispersibility of a highly sorptive medium; and,
- Enhanced biodegradation of the sorbed contamination.

These features will be addressed respectively in individual sections of this paper. Laboratory demonstration of the principles of dispersion, retained sorptive capacity, and biodegradation enhancement of the product are provided. Field performance examples of the technology are shown and finally, typical product usage scenarios are discussed.

2 Securing Sorbent Dispersibility

2.1 Material Composition

PlumeStop is an aqueous liquid wherein a colloidal solid sorbent (carbon-based) is suspended. Incorporated into this, is an anti-clumping, distribution-supporting surface treatment and low-solubility/controlled availability matrix nutrients. Distribution limitation is overcome by altering the surface charge of the colloidal particles, thereby reducing interaction between particles, the soil matrix, and the particles themselves. As a consequence, the resulting material can be dispersed widely, and gradually coats the aquifer matrix rather than accumulating in localized clumps in or close to the point of application, as is common with activated carbon products.

2.2 Dispersibility – Benefits to Application

The sorptive characteristics of granular activated carbon (GAC) are well understood in the remediation industry (1). Sorption may be coupled with biodegradation (2, 3), with ‘bio-GAC’ a familiar term in common industry parlance. However, the solid nature of activated carbon has restricted its use in remediation principally to the *ex situ* treatment of extracted media, such as in pump-and treat (P&T) installations. The attraction of its use as a passive means of *in situ* groundwater treatment has been restricted to date by the challenge of distributing solid activated carbon through the charged, granular medium of soil. Solutions to this problem have included auger-based soil-mixing, trench-application, injection on tight centers, and fracture-based emplacement. These come at a cost; not only are the engineering requirements significant compared to those of fluid-injection, but good access to the contaminated area is required both above ground (e.g. absence of buildings, structures) and below ground (e.g. absence of services, structures). Limitations of depth may also be encountered, whether imposed by expense alone (e.g. mounting costs of tight injection spacing in large, deep applications) or in combination with physical constraints (e.g. trench or soil-mixing applications).

In addition to the physical challenge of application, another limiting factor for *in situ* application of GAC is the uncertainty of the subsurface distribution. The distribution of injected powdered GAC, irrespective of particle size, carrier volume, and dilution, will typically be restricted to the injection point; for example, the well-pack or near surround, or to the fractures themselves. This presents a risk of incomplete or variable clean-up. There may also be a potential for mistaking ‘monitoring-well clean-up’ for aquifer clean-up. This would not only be restricted to the obvious circumstance of using the same well for application and monitoring, but may also arise from a fracture-emplaced injection ‘fingering’ into a monitoring well and giving the appearance of remediation, yet leaving the bulk of the aquifer untreated.

The development of an injectable, dispersive form of activated carbon overcomes the majority of the limitations outlined above. In addition to improving confidence of reagent delivery and addressing certain access challenges, the cost-reduction in application may also be significant. With dispersible activated carbon, fracture-emplacement or augered soil mixing become unnecessary, and simpler injection-well or direct-push application approaches suffice.

Increasing the spacing of an injection grid will itself produce benefits, not only through minimization of obstacles, but also through savings of cost, disturbance, and time on site. For example, increasing the spacing of an injection grid from 2 m to 3 m will reduce the required number injection points by more than 50%, while increasing the spacing to 5 m presents a reduction in required points of over 80% (Figure 1).

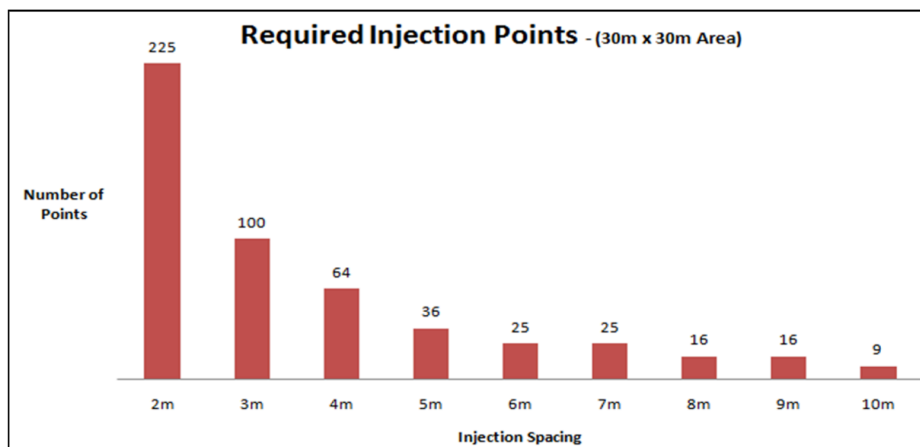


Figure 1. Impact of injection spacing on injection point requirement for a fixed area

3 Securing Bio-Enhancement

3.1 Introduction

The sorptive capacity of PlumeStop in itself is beneficial to remediation projects, as it is able to secure reductions in groundwater contamination and risk very efficiently, with the potential to achieve low clean-up targets in weeks or even days. The additional effect of PlumeStop to promote bio-destruction of the sorbed contaminants results in the permanent removal of the contaminant from the aquifer setting. To explore this feature, it may first be helpful to review some of the wider principles of bioremediation that are relevant to the process.

3.2 The Central Importance of Biological Processes

For groundwater remediation and aquifer restoration, biodegradation represents the principal destruction mechanism of organic species within the subsurface; this process may occur naturally without additional remediation efforts, or may be initiated by outside means. Biological processes are indeed recognized as the principal destruction mechanism among natural attenuation processes (4, 5), and as a means of completing contaminant destruction/mineralization following mass reduction technologies such as **in situ** chemical oxidation (ISCO) (6).

The potential of bioremediation is perhaps not surprising given that the biodegradation of organic compounds is of central importance to carbon cycling and thus to life on earth (7). The sheer potency of the degradative capacity of microorganisms given appropriate conditions has long been recognized (8). Moreover, an understanding of the range, diversity, resilience, and apparent ubiquity of their distribution continues to grow, (9).

3.3 Bioremediation – Potential and Challenges

In situ groundwater bioremediation is now itself an established remediation approach widely used around the world. However, since its early adoption as a contemporary remediation technology in the 1970s and 80s, there have been relatively few significant innovations within the sector beyond the increasing sophistication of electron donors and acceptors, and beyond ancillary developments such as improved measurement technologies. The technology of *in situ* groundwater remediation remains challenged by a number of factors, including two perennial, core issues:

- **Bioremediation takes time** – despite advances in bioremediation techniques over the years, it remains a relatively slow remediation approach;
- **End-points remain uncertain** – while bioremediation may be employed with confidence to efficiently and inexpensively reduce contamination by one or two orders of magnitude, the (linear) rate of destruction characteristically decreases with time, leading to unpredictable performance against very low clean-up targets.

In situ bioremediation nevertheless offers important benefits as a relatively low-cost, low-energy (green), minimally intrusive, destructive technology (i.e. contaminants destroyed, not simply relocated or bound), with applicability to most organic contaminants in a broad range of geological settings. These benefits would be enjoyed by a wider range of projects should the above limitations be overcome.

3.4 Analysis of the Problem

3.4.1 Biodegradation Takes Time

The basis of the time requirement of bioremediation cannot be reduced to a single factor. Some compounds simply degrade faster than others, microbial populations can take time to establish and/or acclimate, and conditions for microbial growth and activity are seldom uniformly optimal despite the skillful and earnest endeavors of environmental engineers.

Beyond this, complex biological processes themselves are not instant. With respect to end-point uncertainty, the above factors are joined by others related to varied mass-transfer limitations and to the fact that microbial populations may simply require a minimum amount of substrate to maintain appreciable activity (10). Within the varied factors that can limit biodegradation, however, certain principles are seen to recur.

3.4.2 Biodegradation Kinetics

The biodegradation rates of given compounds are commonly cited in terms of first-order kinetics – typically as half-lives (11, 12). The rates may vary from compound to compound and from setting to setting, but the principle of a quasi first-order kinetic approximation remains consistent across nearly all conditions. As illustrated in Figure 2, the result of this first-order approximation is that the rate of instantaneous mass destruction (mass removed per unit time) consistently decreases over time. Similar decays of instantaneous destruction rates (mass removed per unit time) are observed for other technologies, for example, *in situ* chemical oxidation ISCO.

At the basis of the first-order approximation is the principle of decreasing bioavailability. As the concentration of a contaminant in groundwater is reduced, the frequency of contact between contaminants and microorganisms is also reduced. The microorganisms that perform bioremediation are predominantly attached to particle surfaces rather than suspended or free-swimming in the aqueous phase, or as large immobile bundles of organisms living

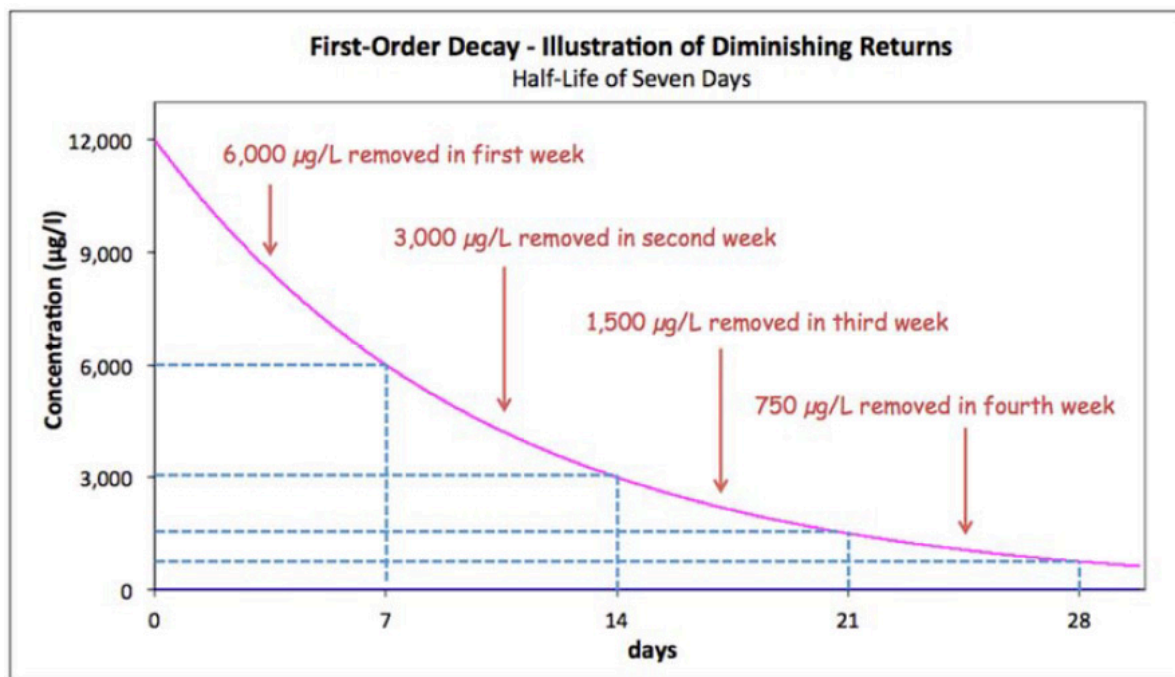


Figure 2. First-order decay – illustration of decreasing instantaneous mass destruction rates

in the interstitial spaces between aquifer mineral particles (biofilms) (7, 13). The contaminant must therefore approach and make contact with the microorganism if it is to be degraded – a separation of even a few microns between the microorganism and the substrate can be enough to prevent degradation (14). The degradation rate will therefore decrease naturally over time, albeit counteracted to an extent by increasing microbial numbers and proficiency, especially in the early treatment stages.

As the groundwater clean-up proceeds beyond the early stages of treatment, mass-transfer constraints begin to dominate the rate of contaminant destruction. At this advanced stage, the microorganisms have depleted their immediate environment of substrate (i.e. on the micro-scale), and the concentrations of contaminant within the bulk groundwater have also been reduced. As a result, the rate of contaminant bio-destruction becomes increasingly influenced by the rate of contaminant desorption into the groundwater and hence its availability to the microorganism (15, 16, 17).

3.4.3 Bioremediation End-Point Uncertainty

The uncertainty of end-point relates to the practical challenge of predicting the point at which the preceding factors will reach equilibrium and establish a performance asymptote. Beyond this asymptote, declining microbial activity may be expected due to depletion of the substrate, which is known as ‘starvation’ in familiar terms. The environmental conditions of bioremediation are generally favorable for copiotrophic microbial species, which are those that thrive on a high-concentration of substrate and are sometimes considered ‘opportunists’ (18, 19). For these microbes, sufficient contamination / substrate is required to initiate and maintain remediation. As degradation proceeds, oligotrophic conditions become prevalent, meaning substrate availability may be insufficient to support a viable, high-activity microbial population. This decrease in microbial activity contributes to the rate-limitation principles that were discussed earlier. Substrate concentration thresholds for microbial activity have been reported elsewhere (20, 21, 10, 22).

3.5 Addressing the Problem

The challenges outlined in the two preceding sections ultimately have bioavailability at their core. Given the fact that the mass of contamination in the system to be treated is fixed, the above rate limitations may be overcome through either of two approaches:

- Increasing the solution concentration – for example, using surfactants to desorb contaminants from the soil and other matrices (23, 24, 25). While this may be effective in overcoming the bioavailability constraint, uncontrolled contaminant concentration spikes in the dissolved-phase are not welcome. Furthermore, surfactants may present additional problems such as clogging of the formation or the introduction of a competing biological oxygen demand (BOD) (26, 27).
- Concentrating the contaminants and the bacteria together – for example, using a common sorptive surface.

This approach of concentrating the contaminant and bacteria on a surface reduces dissolved phase contaminant concentrations, benefits bioavailability, and ultimately enhances degradation.

3.6 Benefits of Liquid Activated Carbon

The principles of increasing contaminant-microbe contact and overcoming oligotrophic limitations are addressed directly by PlumeStop. The novelty of PlumeStop as a technology lies in the ability to widely distribute a sorptive medium using simple injection equipment and without compromise to sorptive capacity. PlumeStop injected into the aqueous subsurface quickly sorbs organic contaminants. Partitioning of contaminants out of the dissolved-phase and onto PlumeStop results in a fast and striking reduction in groundwater contaminant concentration. Thereafter, the sorptive PlumeStop medium provides a high surface-area, virgin matrix for fresh microbial colonization, thereby achieving the objective of concentrating the bacteria and the contaminants together.

3.7 Core Hypothesis

The core hypothesis of the PlumeStop technology may thus be summarized as follows: PlumeStop is injected into the subsurface as a colloidal suspension using simple liquid-injection equipment, securing wide-area dispersion on the order of meters. Dissolved-phase contamination then partitions out of the groundwater and onto the PlumeStop matrix, resulting in a rapid drop in groundwater contamination on the timescale of days. The net rate of sorptive partitioning is considerable owing to the extremely high relative surface area of the colloidal (1-2 μm) particles. The PlumeStop biomatrix itself becomes impregnated with the contaminants, concentrating them within its structure. Under favorable growth conditions of optimal electron donor acceptor nutrient concentrations, which can be artificially engineered as necessary through combined application of compatible reagents, microbial colonization of the PlumeStop follows. The colonizing microflora will predominantly comprise degrader species given that the contaminants impregnating the matrix act as the principle available substrate. Contaminants and microbes are thereby concentrated together, enhancing bioavailability and maintaining adequate substrate-availability (copiotrophic status) locally, irrespective of possible substrate-limited (oligotrophic) conditions in the wider aquifer. In this manner, the PlumeStop provides both a growth-medium and a substrate reservoir to support suitable microbial growth, while keeping the contaminants out of the groundwater. This results in:

- A rapid drop in groundwater contamination
- An increased rate of enhanced contaminant destruction
- An ability to pursue bioremediation effectively even at very low contaminant levels

Degradation of substrate within the matrix regenerates the sorption sites (28), extending and replenishing the reagent's sorptive capacity. The PlumeStop itself is not consumed; thus providing long-term management solutions for back-diffusion and ongoing low-level sources.

4 Reagent Development

4.1 Background

A variety of sorptive media could establish the desired dispersive biomatrix concept, and a spectrum of media was therefore evaluated through the course of the product development research. Once a medium was selected, its dispersibility was optimized through a series of over one hundred soil-packed column tests intended to identify and refine a proprietary treatment that would provide the desired step-change in dispersibility. The resulting PlumeStop composition exhibits striking performance improvements over conventional slurries and dispersed forms of carbon particles previously reported in the scientific literature (29).

The medium selected for initial commercialization as PlumeStop is liquid activated (micron-scale) carbon, which therefore represents the focus of the present paper. Mixed with this carbon medium is an anti-clumping distribution supporting surface treatment of non-toxic polymeric and molecular additives plus low-solubility controlled availability matrix nutrients. The inherent limitation in the dispersibility of colloidal carbon is overcome by cloaking the surface charge of the colloidal particles, thereby reducing interaction between the particles and the soil matrix and between the particles themselves. As a consequence, the resulting material can be dispersed widely, and gradually coats the aquifer matrix rather than clumping in, or close to, the point of application. The stabilized colloidal composition is therefore able to achieve unprecedented subsurface distribution and site remediation performance. A visual illustration of the dispersed PlumeStop distributed among and coating sand particles is given in the scanning electron microscope (SEM) photomicrograph images in Figure 3-Figure 5.

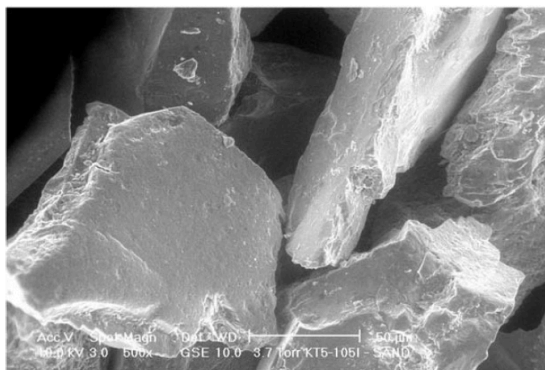


Figure 3. SEM image of sand particles without PlumeStop

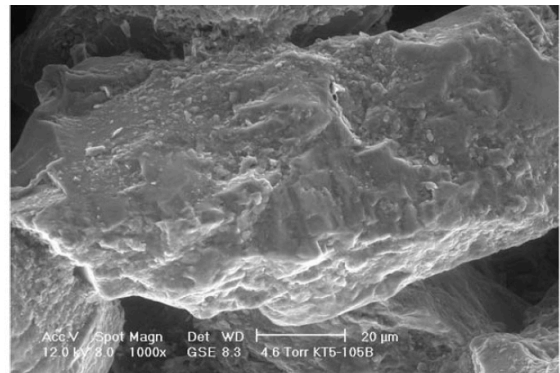


Figure 5. SEM image of sand particle coated with PlumeStop

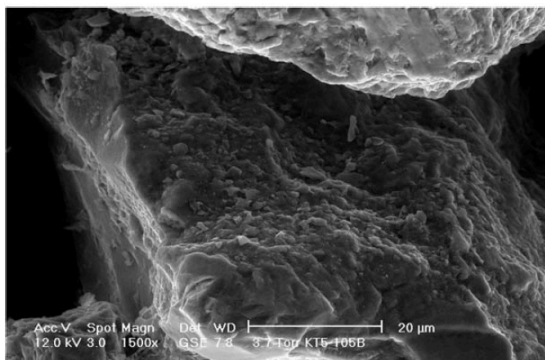


Figure 4. SEM image of sand particle coated with PlumeStop

4.2 Hypothesis Testing – Laboratory

The following sections of this paper describe laboratory-scale testing of the principles underpinning the core hypothesis of the PlumeStop technology. The following questions are addressed in sequence:

1. Can the liquid activated carbon be effectively distributed through a saturated soil medium?
2. Does the treatment to enhance distribution negatively affect sorption capacity?
3. Does biodegradation proceed within the biomatrix?
4. Is net contaminant degradation enhanced, inhibited, or unaffected by sorption into the biomatrix?

4.3 Test 1. Reagent Distribution

4.3.1 Introduction

Powdered solid materials are, by nature, difficult to apply and distribute through a soil matrix by injection. Poor distribution and clumping in or close to the point of application or fracture are typically observed.

Q: Can the matrix be effectively distributed through a saturated soil medium?

4.3.2 Test Description

The test set-up comprised two 25 mm (1") internal diameter columns 600 mm (2') in length, packed with a loamy coarse sand² and tap water. 25 g of 0.6% PlumeStop colloid was placed at the head of the test column, with an equivalent mass and concentration of powdered activated carbon in aqueous suspension placed at the head of the control column. The columns were allowed to drain by gravity upon opening a tap at their base. A head of water was maintained by manual addition of water to each column, pausing the flow as necessary in either column to maintain net volume / flux consistency. A total of three pore volumes of water were applied to each column.

4.3.3 Test Results

The comparative distribution of PlumeStop and powdered activated carbon is visually illustrated in the following figures.

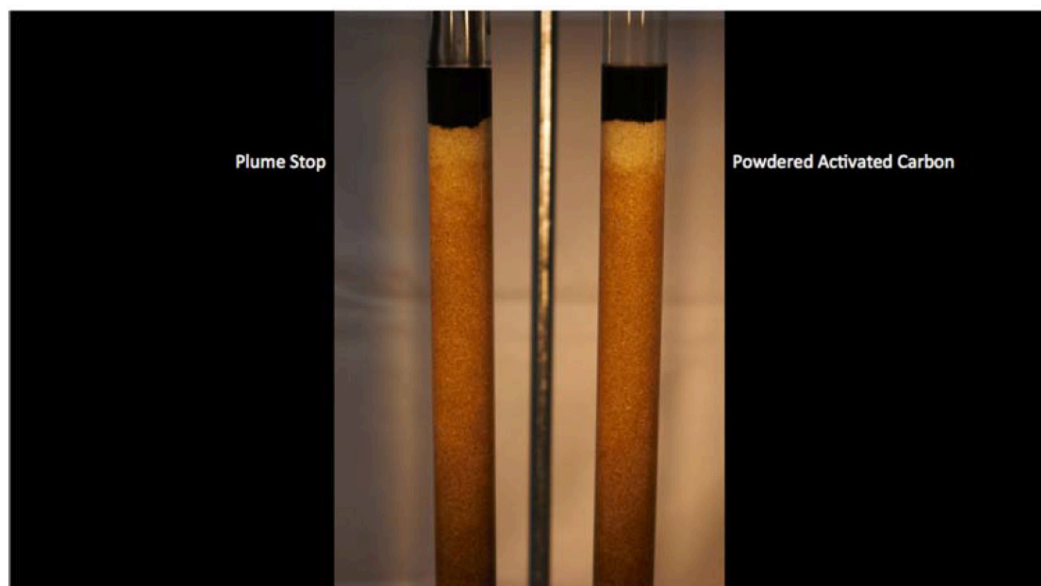


Figure 6. Soil columns (initial)

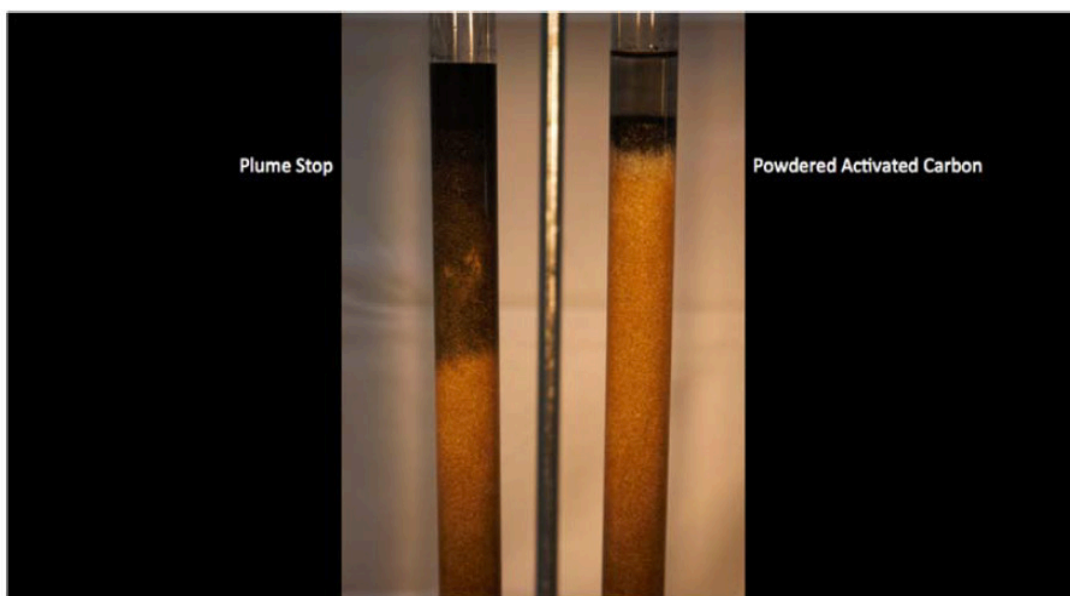


Figure 7. Soil columns after approximately 0.3 pore volumes.

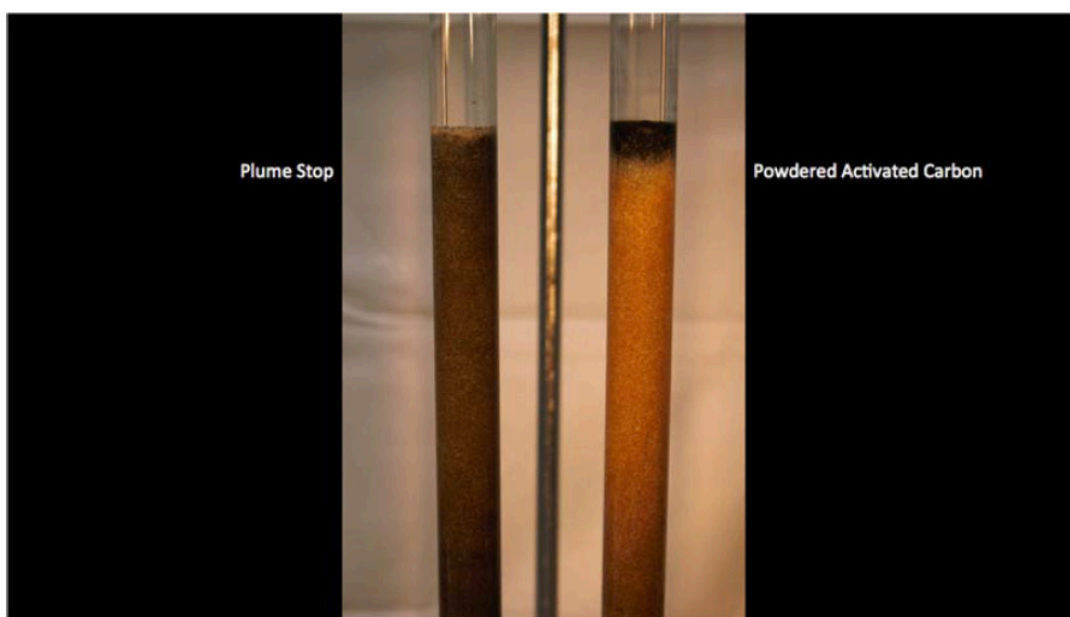


Figure 8. Soil columns on completion of test at three pore volumes.

4.3.4 Test Conclusion

The test confirmed that PlumeStop transports through 600 mm (2') of loamy coarse sand columns easily, whereas the distribution of the powdered activated carbon control was limited to approximately the top 25 mm (1") of the column. This represents a distribution difference in excess of a factor of 20 (the test being limited by the maximum length of the column).

PlumeStop material remained visually apparent throughout the column during the course of the study and showed no apparent decline/wash-out upon flushing of three pore volumes. The dispersibility assertion of the PlumeStop technology hypothesis was therefore supported by this study.

4.4 Test 2. Sorption Capacity

4.4.1 Introduction

Securing an effective distribution of PlumeStop through a saturated soil system is a core component of its function as a practical technology. However, a second functional question is if the treatment to effect dispersibility negatively impacts the sorptive capability of the PlumeStop material.

Q: Does the treatment to enhance distribution negatively affect sorption capacity?

4.4.2 Test Description

The test set-up for evaluation of the sorptive capacity of PlumeStop comprised:

1. A column study with o-xylene; and,
2. The determination of the sorption isotherm of PlumeStop with respect to benzene

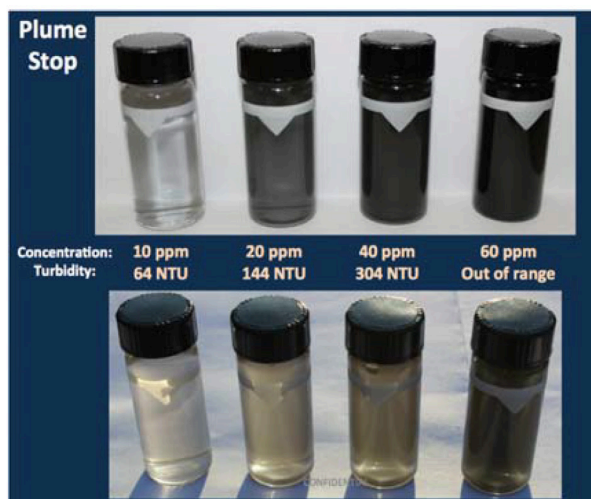
The column study comprised two columns, through which an aqueous solution of approximately 10,000 µg/L of o-xylene in tap water was passed (Figure 9). The columns were set up identically and packed with loamy coarse sand, as per Test 1 (Section 4.3). An equal flux of aqueous xylene solution was passed in parallel through each column in order to establish the natural equilibrium between aqueous phase and soil-sorbed xylene. The systems were run in this manner until the baseline conditions stabilized (approximately four weeks). 327 g of 0.2% Colloidal carbon suspension were then added to the head of the test column followed by continued elution with the o-xylene solution. For the control column, the o-Xylene solution was eluted without interruption. o-Xylene concentrations in the effluent of each column were recorded at intervals of 1–3 days over the course of six weeks.

The sorption isotherm of benzene on PlumeStop was determined through measurement of sorbed and dissolved benzene concentrations at equilibrium in multiple test systems. Benzene was applied to each system at a concentration of 50,000 µg/L. PlumeStop concentrations in each system were varied over a range of 63 – 4,000 mg/L (Figure 10)

Figure 9. o-Xylene column study set-up.



Figure 10. Serial dilution of PlumeStop for the isotherm study.



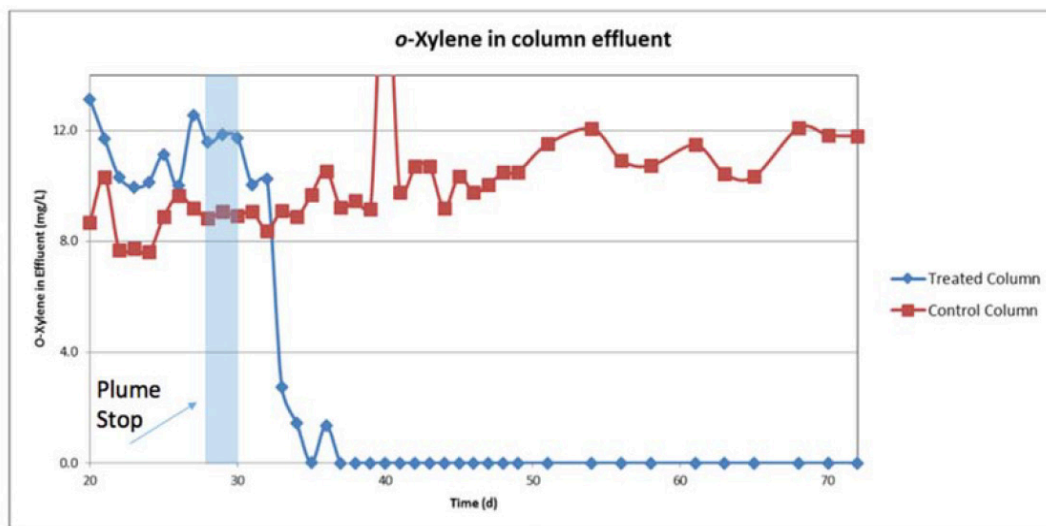


Figure 11. Comparative o-xylene concentrations in column effluent. The application of PlumeStop to the test column at 28- 30 days is shown by the blue box.

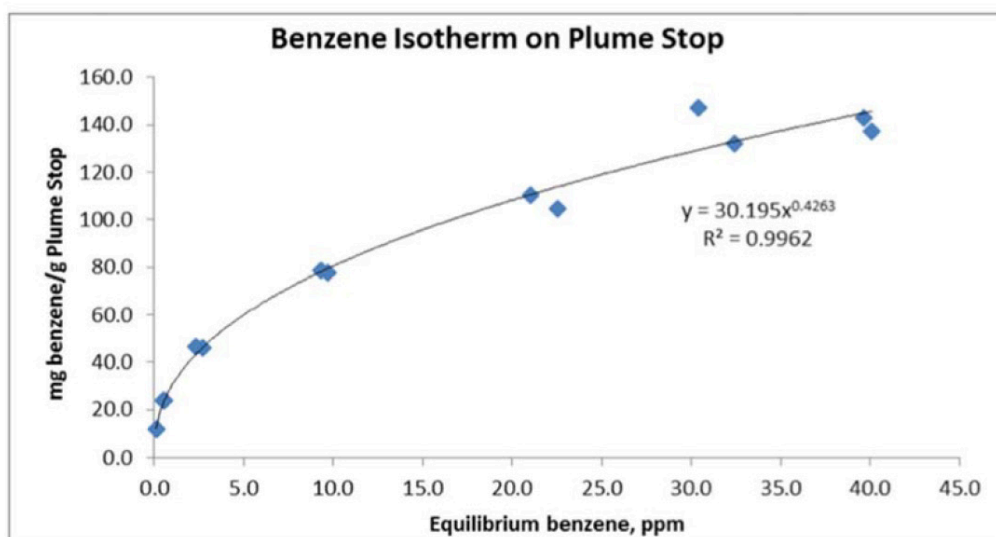


Figure 12. Sorption isotherm of benzene with PlumeStop.

4.4.4 Test conclusion

The column study provides confirmation that the distribution treatment of PlumeStop does not inhibit contaminant sorption – the PlumeStop in the test system was able to sorb 10,000 µg/L o-Xylene for well over ten pore volumes. The study additionally confirms that the PlumeStop was sufficiently retained within the soil to effect this result – the treatment not only did not inhibit sorption, but also did not result in excessive mobility leading to wash-out. The Freundlich sorption isotherms of PlumeStop with respect to benzene provide further illustration of the retained sorptive capacity and its relationship to concentration, which remains similar to unmodified powdered activated carbon. The retained sorptive capacity assertion of the PlumeStop technology hypothesis is therefore supported by this study.

4.5 Test 3. Post-Sorption Biodegradation

4.5.1 Introduction

The ability of PlumeStop to be readily dispersed into and then retained by a formation while maintaining its sorptive capacity provides a means of rapidly reducing or eliminating risk posed by organic groundwater contamination. The reduction of mobile contaminants from groundwater is sufficient in itself for securing common remedial objectives. The fate of the sorbed contaminant, however, continues to be a topic of interest, given that while sorption may indeed address risk, it does not in itself destroy the contaminant. Other questions that arise from a scenario in which contaminants are trapped but not destroyed include:

- How reliable is the sorption?
- Will the sorption be temporary?
- What long-term performance can be expected?

Such questions are commonly asked in relation to the remediation of inorganic contaminants, which cannot be destroyed. However, for organic species, the requirement for permanent binding is negated by the fact that they may be destroyed through biological processes post-sorption. The present test therefore evaluates the propensity for contaminants sorbed into the PlumeStop biomatrix to biodegrade.

Q: Does biodegradation proceed within the biomatrix?

4.5.2 Test Outline

The test comprises a batch-equilibrium study consisting of 227 mL (8 oz.) soil-water systems that are spiked with benzene, both with and without PlumeStop (Figure 13). Each system contained 70 mL of water and 10 g of soil, thereby filling approximately one third of the container volume. This allowed sufficient remaining capacity for headspace analysis and the provision of adequate oxygen to maintain aerobic status throughout the study. Three treatment profiles were completed (Table 1).

Table 1. Batch-Equilibrium Study – Test and Control Treatments

Treatment	Description
Sterile control	Autoclaved soil and sodium azide (abiotic control)
PlumeStop Treated	Soil and PlumeStop (test)
Sterile PlumeStop Treated (abiotic control)	Autoclaved soil, PlumeStop and sodium azide

The tests were conducted in parallel and run over a period of 21 days. Microcosms were sampled destructively in triplicate on days 1, 7, 14, and 21. Benzene was quantified in the aqueous phase and also as a mass-balance extract of the total soil-water system (i.e. the aqueous and solid-phase microcosm contents together).



Figure 13. Batch-Equilibrium Study – Experimental Set-up

4.5.3 Test Results

Aqueous-phase concentrations of benzene are presented graphically in Figure 14. Data from the total system mass extractions are presented in Figure 15.

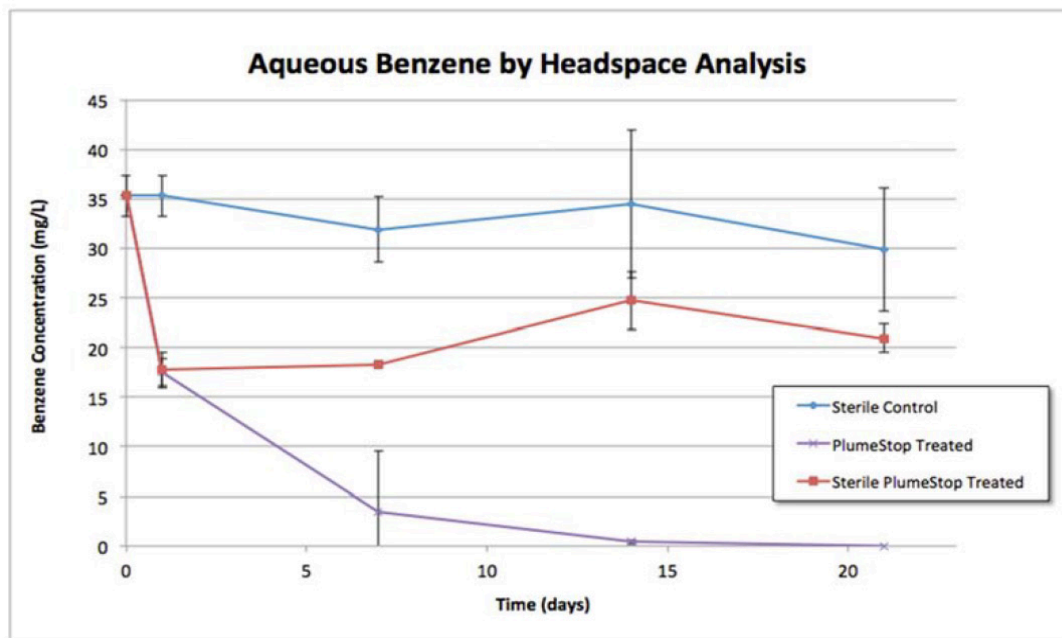


Figure 14. Batch-Equilibrium Study– Aqueous-Phase Results

Figure 14 illustrates a rapid and equal reduction in dissolved-phase benzene concentration in both the biotic and abiotic PlumeStop systems within the first sampling period. Thereafter, the aqueous benzene concentration in the biotic PlumeStop system continues to fall, whereas that in the abiotic PlumeStop control remains broadly static. Benzene concentrations in the soil-only sterile control did not change significantly throughout the study.

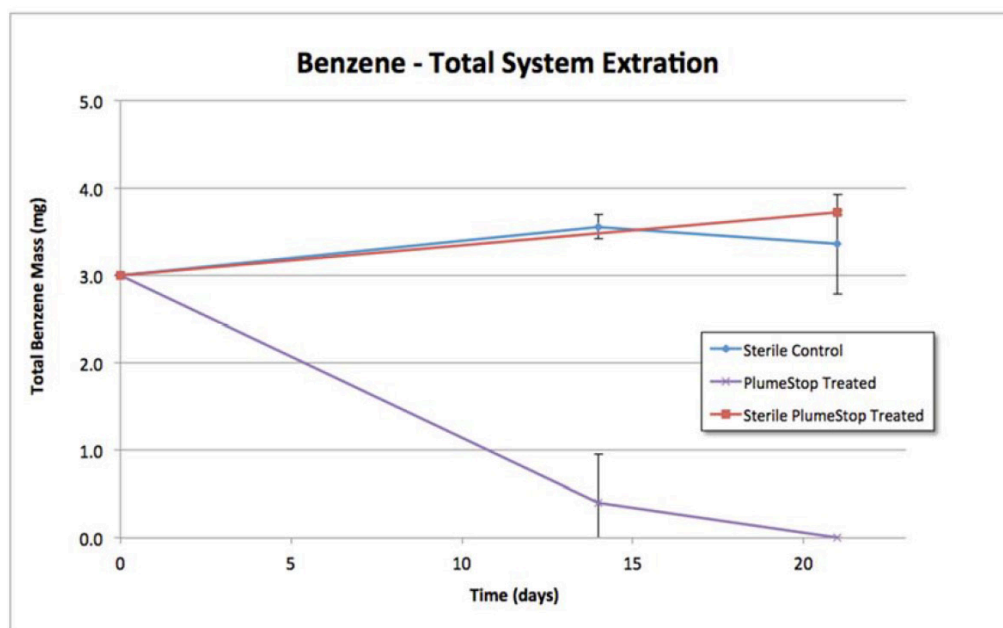


Figure 15. Batch-Equilibrium Study – Total System Extracts

In Figure 15, the total mass of benzene in the system (both aqueous-phase and solid-phase microcosm) are compared over a 21-day period, with the objective of determining whether the on-going reduction in the PlumeStop system could be attributed to a further sorption process, or whether it was indeed a reflection of a separate destructive process. This figure shows that the total mass of benzene in the two sterile treatments remained essentially unchanged throughout the course of the study, while in the biotic PlumeStop-treated sample, the total mass of benzene decreased to non-detect.

4.5.4 Conclusion

The rapid and equal reduction in aqueous-phase concentration over the first sampling period in both the biotic and abiotic PlumeStop systems may reasonably be attributed to abiotic sorption processes. The continued reduction in concentration in the biotic PlumeStop system with a kinetically distinct (Figure 14) and broadly first-order rate approximation is consistent with a biodegradative process. This conclusion also aligns with the biotic nature of this system containing PlumeStop compared to the analogous abiotic system, which showed no further reduction in benzene concentration following the initial change. The destruction of benzene in the biotic PlumeStop system is further confirmed in the total mass extractions shown in Figure 15, in which the full initial mass of benzene was recovered from the abiotic PlumeStop control, confirming non-destructive abiotic sorption (and a method validation of the extractive recovery efficiency). In contrast, the mass-balance of benzene in the biotic PlumeStop system describes a destructive reduction that is consistent with biodegradation. Together, this experiment provides confirmation that sorption of the contaminant by PlumeStop does not inhibit its subsequent biodegradation.

4.6 Test 4. Impact on Biodegradation Efficiency

4.6.1 Introduction

The final question related to proof-of-concept testing of the core PlumeStop technology hypothesis relates to the rate of post-sorption degradation, and whether the concentration of contaminants and microorganisms within the PlumeStop biomatrix increases net biodegradation rate.

Q: Is net contaminant degradation rate enhanced, inhibited, or unaffected by sorption into the biomatrix?

4.6.2 Test Outline

This test broadly follows the protocol of the preceding test, differing principally in that it includes a biotic soil-only control in addition to the biotic PlumeStop system. All systems were again reproduced in triplicate.

4.6.3 Test Results

Test results are presented in Figure 16, which illustrates the total system extracts of benzene (soil + water) over the course of a 28-day study. Abiotic test systems with and without PlumeStop show similar mass recoveries of benzene. In contrast, reductions in the total mass of benzene recovered are evident for the two biotic systems with and without PlumeStop. However, in the case of the PlumeStop system, the mass is reduced to below detection limit within the first sampling period (seven days) whereas the biotic soil-only control took until day 28 to reach non-detect.

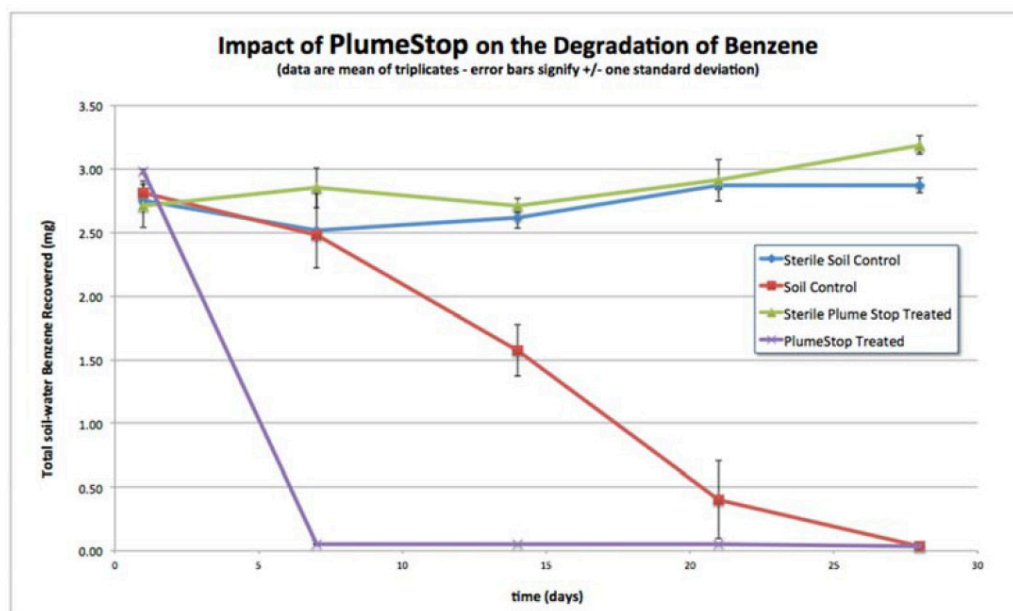


Figure 16. Second Batch-Equilibrium Study – Total System Extracts (all treatments)

4.6.4 Test Conclusions

The total mass of benzene was fully degraded in the biotic PlumeStop system within the first seven days of the test, in contrast with only 12.5% degradation over the same period in the biotic soil-only control. This approximates to a half-life of less than one day in the biotic PlumeStop system as compared to 10 days in the biotic control. Note that the half-life estimated for the biotic soil-only control is consistent with aqueous biotic rates that are published in the literature (11).

Although the absolute rates determined from these laboratory tests cannot be extrapolated to the field, the tests do serve to demonstrate a qualitative difference in the performance between the system containing PlumeStop and the one without. In so doing, they support the hypothesis that the contaminant degradation is enhanced by interaction with the PlumeStop.

4.7 Satisfaction of Laboratory Test Objectives

The preceding sections of this paper described laboratory-scale testing of the principles underpinning the core hypothesis of the PlumeStop technology. The following questions were sequentially addressed:

1. Can the PlumeStop biomatrix be effectively distributed through a saturated soil medium?
2. Does the treatment to enhance distribution negatively affect sorption capacity?
3. Does biodegradation proceed within the biomatrix?
4. Is contaminant degradation enhanced, inhibited, or unaffected by sorption into the biomatrix?

The data presented are consistent with the core hypothesis, confirming that PlumeStop represents a dispersible, sorptive biomatrix that distributes easily through soil to coat the particles without washing out, and is capable of capturing a significant flux of test hydrocarbon (o-xylene). Post-sorption biodegradation is shown to proceed, and is enhanced compared to biotic untreated systems.

5 Performance Testing – Field

5.1 Introduction

Laboratory testing can provide a valuable means of testing specific principles relating to environmental technologies, but cannot be considered a substitute for appropriate field performance testing. Although quantitative data can be obtained in the laboratory to support key principles, extrapolation of the numeric results to the field cannot be technically supported. The following sections of this paper therefore extend the testing program of PlumeStop into field evaluation.

5.2 Field Test Objectives

The specific objectives of the field tests are to answer the following questions:

1. Can the performance shown in the lab be replicated in the field?
2. Can distribution be secured over field-practical distances?
3. Can significant field reductions in groundwater concentration be secured?
4. Can tentative indications of bio-destruction be identified?
5. Can the performance shown with hydrocarbons be replicated with chlorinated solvents?

Data addressing these questions are presented from two sites, one contaminated with hydrocarbons and one with chlorinated solvents. Both studies represent proof-of-concept evaluations rather than formal remediation endeavors.

5.3 Site Test 1 – Hydrocarbons

5.3.1 Introduction

The field impact of PlumeStop on hydrocarbon contamination was evaluated on a historic gasoline plume at a confidential site of a former private high school in the Midwest United States (Figure 17). A leaking gasoline underground storage tank was identified as the source of the dissolved gasoline plume and subsequently removed. The site had a building foundation dewatering/control system that exerted a strong influence on the direction and extent of groundwater flow.

5.3.2 Test Arrangement

The PlumeStop biomatrix was trialed in two areas of the plume: the original source (tank field) area (MW1) and in the plume body (MW2) approximately 14 m (46 feet) down-gradient from the source.

Pre-application groundwater contamination levels were similar in each of the test areas (Table 2). The target application interval in each case was comprised of saturated sandy silt with gravelly interbeds, underlain by a continuous hard silt layer. Depth to groundwater was approximately 2.5 m (7.5–8.0 ft). The building dewatering system imposed an artificial seepage velocity of approximately 200–280 m/yr (650–900 ft/yr) to the southwest (Figure 19).

Table 2. Hydrocarbon Site – Pre-Treatment Contamination Levels

	MW1 – Source Area	MW2 – Plume Area
Gasoline-Range Petroleum Hydrocarbons (TPH-g)	16,000 µg/L	14,000 µg/L
Benzene, Toluene, Ethyl-Benzene and Xylenes (BTEX)	7,000 µg/L	9,000 µg/L

PlumeStop was applied via direct-push injection (Figure 18) in a grid array. Eleven injection points were advanced in the area of MW1, and eight injection points were advanced around MW2, each at an approximate spacing of 1.5 m (5 feet) (Figure 20). The controlled release electron acceptor, ORC-Advanced® (REGENESIS, San Clemente, CA USA), was applied up-gradient and between points to support aerobic conditions appropriate for microbial colonization and activity.

Soil cores were taken before and after the PlumeStop application to provide local detail of the aquifer formation and visual evaluation of the reagent's distribution.



Figure 17. Hydrocarbon Site – Fieldwork



Figure 18. Hydrocarbon Site – Injection

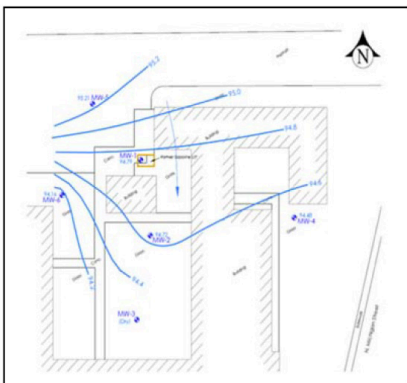


Figure 19. Hydrocarbon Site – Groundwater Contours

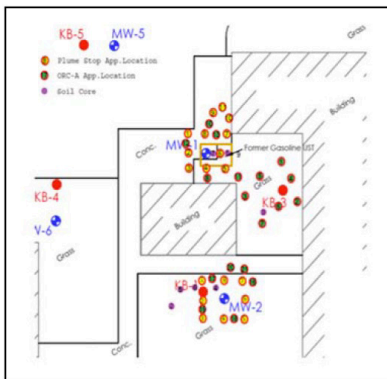


Figure 20. Hydrocarbon Site – Injection Arrangement

5.3.3 Test Results – First Three Months

Pre-application soil core data revealed significant contamination at the vadose/saturated zone interface, centered within a gravelly stratum (Figure 21). PlumeStop distribution extended throughout the entire lateral range that was evaluated by the soil cores (1-2 meters from the closest application point). Close inspection of these soil cores revealed good visual evidence of an even dispersion of the PlumeStop through the permeable strata (Figures 22 and 23).



Figure 21. Pre-Application Soil Core



Figure 22. Post-Application Soil Core



Figure 23. PlumeStop Dispersed Through Permeable Stratum

Hydrocarbon analysis of the groundwater revealed removal of contamination to below detection limits within the first sampling period (16 days). This represented a reduction of over three orders of magnitude (>99.9%) from original concentrations of 14,000–16,000 µg/L to < 100 µg/L. Data are presented in Figure 24. Groundwater concentrations remained below detection limits through the next sampling event, but then at 58 days rebounded to approximately 10% of their pre-treatment levels. Thereafter, the concentration in the plume well (MW2) reduced once more to below detection limits but remained largely unchanged in the source area well (MW1) at 10% of the baseline condition.

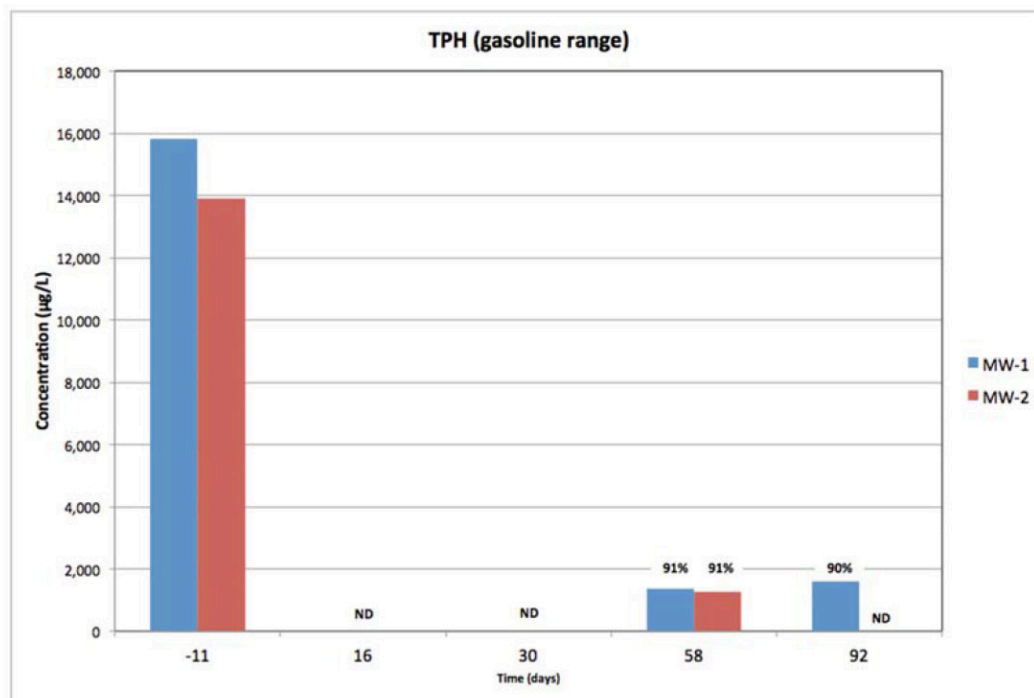


Figure 24. Hydrocarbon Site – Field Results

5.3.4 Test Conclusions

The field study confirms the ability of PlumeStop to be applied and dispersed through an aquifer formation using simple direct-push injection. Distribution through the maximum tested radius of 2.0 m (6.5 feet) was observed, suggesting the actual distribution may have been greater. A relatively even distribution of the reagent was observed within the permeable strata, consistent with the anticipated good dispersion throughout the mobile porosity that was suggested by the preceding laboratory studies. The striking reduction in groundwater hydrocarbon concentrations immediately following application is consistent with the hypothesized sorption of contamination by the PlumeStop. Note that simple displacement of the contaminated groundwater upon injection of PlumeStop could not account for this reduction in concentration, as the total fluid injection was significantly less than one pore volume and would be unlikely to result in an absolute decline. The modest rebound in groundwater concentration at 58 days that was observed at both locations is believed to be due to the saturation ('over-topping') of the sorptive capacity of the PlumeStop owing to the entry of additional contaminant mass into the groundwater. This may either be from soil-sorbed, NAPL, or immobile porosity mass within the test area partitioning or back-diffusing into the groundwater as a result of the initial groundwater concentration reduction. The introduction of such additional mass should be captured directly by the PlumeStop in a manner similar to

the initial sorption of the bulk-porosity contaminants and result in little or no observable impact on groundwater concentration. However, saturation of the PlumeStop would cause groundwater concentrations to rise upon introduction of additional mass. The rate at which concentrations increased would be the balance of the rate of soil-contaminant desorption back-diffusion and the rate of biodegradation within the PlumeStop biomatrix, which would free-up sorption sites in an analogous manner to bio-GAC (28, 30). As a result, any rebound in groundwater concentrations would similarly decline as biodegradation proceeds and the rate of desorption back-diffusion slows with the depletion of the secondary source-mass. This is possibly what occurred at the 92-day point in the plume area well (MW2), where there was presumably less secondary source mass than that in the original source area (MW1).

5.4 Site Test 2 – Chlorinated Solvents

5.4.1 Introduction

The field impact of PlumeStop on chlorinated solvent contamination (chlorinated volatile organic compounds – CVOCs) was evaluated on a mixed trichloroethene (TCE) and trichlorethane (TCA) plume at a former electronics facility in the Midwest United States. These solvents had been used at the site until the late 1980s, and multiple source areas were evident.

5.4.2 Test Arrangement

The PlumeStop was trialed in a single test area located down gradient from the known sources, in an area of the plume believed to comprise dissolved and sorbed-phase contamination only, i.e. without residual non-aqueous phase liquid (NAPL) present (Figure 25). Pre-test concentrations of TCA and TCE were 3,500 µg/L and 1,400 µg/L, respectively. The aquifer soil type was sand to silty-sand, with groundwater located between 3 and 4 m from the surface (10 – 13 feet). Groundwater seepage velocity was approximately 3.7 m/yr (12 ft/yr) to the southwest (Figure 26).



Figure 25. Solvent Site – Test Location

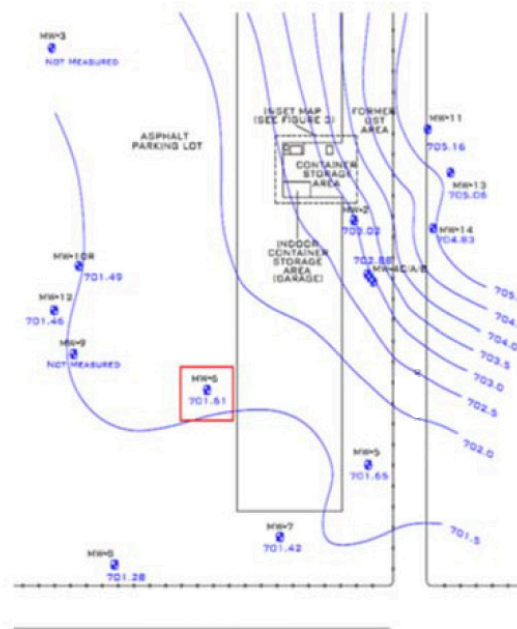


Figure 26. Solvent Site – Groundwater Contours

PlumeStop was applied by direct-push injection in a grid array of 10 injection points around the test well, spaced at a distance of 1.5–2.0 m (5–6.5 feet) (Figure 27 and Figure 28). The target application interval was across a depth of 2.75–6.5 m (9–21 feet) below ground surface.

The controlled release electron donor HRC® (REGENESIS, San Clemente, CA USA) was applied in a linear array of four points immediately up-gradient of the test zone to establish and maintain anaerobic conditions appropriate for microbial colonization and activity (Figure 28).

Soil cores were taken before and after the PlumeStop application to provide local detail of the aquifer formation and visual evaluation of the reagent's distribution.

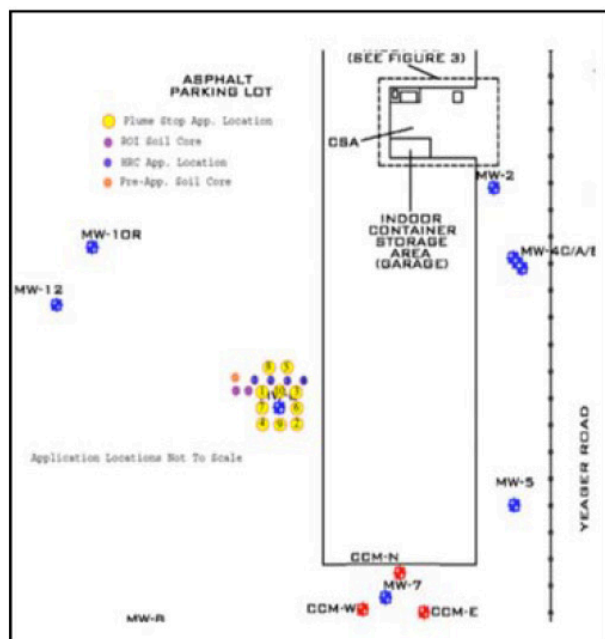


Figure 27. Solvent Site – Injection Arrangement

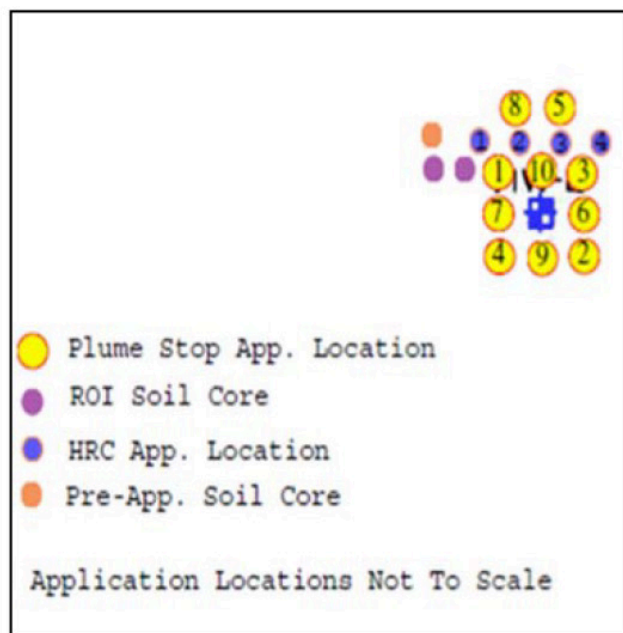


Figure 28. Solvent Site – Injection Arrangement (detail)

5.4.3 Test Results – First Two Months

Post-application soil core data revealed good dispersion of the PlumeStop throughout the radius tested (2 m; 6.5 feet). Groundwater analysis revealed total CVOC concentration had dropped from 5,718 µg/L to 467 µg/L (92% decrease) by the time of the first monitoring event, two weeks after application (Table 3).

Subsequent monitoring rounds showed a consistent decline in concentration to 113 µg/L at one month and 12.9 µg/L at two months, representing concentration reductions from pre-treatment baseline of 98% and >99%, respectively.

The data are presented graphically in Figure 29.

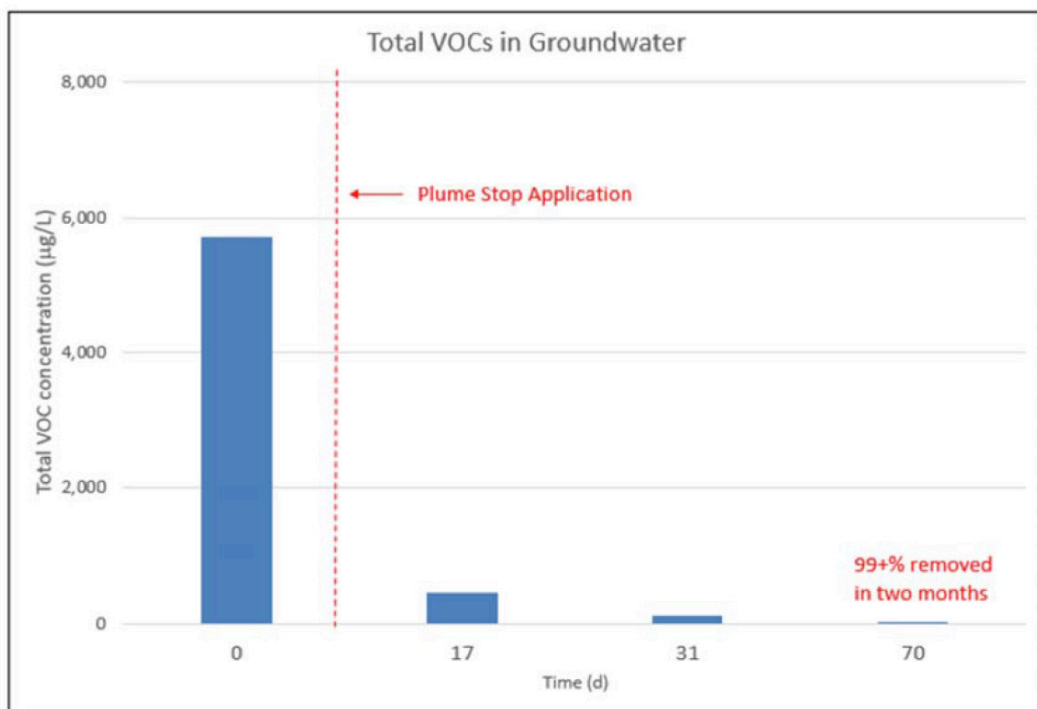


Figure 29. Solvent Site – Field Results

Geochemical changes observed in the groundwater included the establishment of reducing conditions between 17 and 31 days and a rise in dissolved iron from zero to 2,000 µg/L over the first 70 days. pH remained unchanged at 6.6 throughout the test period.

5.4.4 Test Conclusions

Examination of soil cores collected outside of the PlumeStop application area indicated that PlumeStop was transported at least 2 m (6.5 feet) – the maximum interval measured – by the injection process used in this pilot testing program. The actual radius of dispersion was not determined beyond this, but may reasonably be presumed to have been greater.

The sharp reduction in groundwater CVOC concentrations immediately following application is consistent with the hypothesized sorption of contamination by PlumeStop. The on-going reduction following the initial step-change may be due to plume-equilibration and on-going partitioning of contaminant mass into the PlumeStop, biodegradation, or a combination of these processes. The timing, however, would suggest sorption to be the dominant phenomenon in the present case given that conducive conditions for anaerobic biodegradation were only recently becoming established and degradation daughter products were not observed.

5.5 Satisfaction of Field Test Objectives

The preceding sections of this paper describe the testing of PlumeStop performance in the field, for the treatment of hydrocarbons and chlorinated solvents respectively. The following questions were addressed:

1. Can the performance shown in the lab be replicated in the field?
2. Can distribution be secured over field-practical distances?
3. Can significant field reductions in groundwater concentration be secured?

4. Can tentative indications of bio-destruction be identified?
5. Can the performance shown with hydrocarbons be replicated with chlorinated solvents?

The field test data suggest an affirmative answer to each of these questions. Specifically, PlumeStop has been shown to distribute easily through soil over field-practical distances of at least 2.0 m (6.5 ft) (the maximum tested interval) and to rapidly secure reductions of groundwater contaminant concentration of at least one to two orders of magnitude for both hydrocarbon and chlorinated solvent contamination. Field data suggest that biodegradation post-sorption is occurring, and as such, are consistent with the laboratory study data presented in the earlier part of this paper.

6 Discussion

6.1 Technology Implications – Key Features

The development of an injectable, dispersible, sorptive biomatrix has the potential to directly address a number of widespread challenges in the groundwater clean-up sector. Specifically, the principal features of technology are its ability to:

- Widely distribute throughout the subsurface to impact a significant area;
- Adsorb contaminants and rapidly reduce associated groundwater concentrations;
- Inhibit transport of contaminants in the aquifer;
- Provide a “biomatrix” for microorganisms and contaminants;
- Enhance contaminant biodegradation, resulting in remediation of the site; and,
- Address matrix back-diffusion, where applicable.

6.2 Technology Implications – Selected Usage Scenarios

Among the selected usage indicators postulated for PlumeStop are the following:

1. **When time is critical** PlumeStop arguably represents the fastest groundwater risk-reduction/remediation technology presently available³. Immediate risk-reduction is secured through sorption, quickly removing contaminants from groundwater; long-term destruction is then secured through in-matrix biodegradation.
2. **As a long-term control of migrating diffuse pollution** (or migrating pollution per se). PlumeStop can be used in a barrier formation to capture diffuse contaminants, concentrating them within its biomatrix for locally intensive treatment. This would provide a tighter capture-zone than bio-barriers alone, which is valuable where space is limited and/or groundwater is fast-flowing. It would also provide faster enhanced destruction rates and greater timing tolerance between bio-amendment applications.
3. **As a means of treating low-concentration plumes** Bioremediation of low concentrations (e.g. low µg/L range) is often challenging owing to concentrations being insufficient to support microbial activity. PlumeStop overcomes this limitation by accumulating low-level contaminants into the biomatrix until concentrations become sufficient within the matrix to support an active microflora, all while keeping the contaminants out of the groundwater.
4. **To address matrix back-diffusion** Injection of PlumeStop into groundwater results in a rapid drop of contaminant groundwater concentration, typically of one to two orders of magnitude. This drop reverses the concentration gradient between the immobile porosity and the bulk solution (or increases the gradient out of the matrix if the bulk solution concentration has previously been reduced by other means). On entering the bulk solution, back-diffused contaminants are in turn captured by the PlumeStop where they are biodegraded. The reverse gradient is therefore maintained, and diffusion out of the immobile porosity continues until the

³ It is recognized that solid sorptive media may be introduced through other means such as fracture-emplacement, soil-mixing, or tight- application grids. However, beyond the obvious cost and practicality benefits of dispersive liquid activated carbon injection, the application fieldwork itself would be significantly faster.

back-diffusing mass is depleted. PlumeStop is not consumed in this process and will theoretically continue to function in this manner over decades, easily matching the timescales necessary to address back-diffusion and thus providing robust remedy-in-place protection from a one time application.

7 PlumeStop Liquid Activated Carbon – Product Summary

7.1.1 Overview

PlumeStop Liquid Activated Carbon is a new technology for groundwater treatment that allows for wide dispersion of a sorptive medium in the aqueous subsurface. The product has a dual function: it sorbs contaminants, quickly removing them from the mobile phase ('PlumeStop'), and provides a high surface area matrix favorable for microbial colonization and growth ('Biomatrix'). Contaminant availability within a risk pathway is therefore reduced while at the same time contaminant destruction is enhanced. This product offers attributes unlike any reagent on the market today.

7.1.2 Description

PlumeStop is an environmentally compatible, proprietary formulation of liquid activated carbon combined with polymeric and molecular dispersion agents that allow the material to distribute widely throughout soil and groundwater without compromise to sorptive capacity. Once contaminants are embedded within PlumeStop's structure, biodegradation occurs. Intrinsic biodegradation processes can then be further enhanced with the proximal co-application of controlled-release electron acceptors or electron donors if desired.

7.1.3 Applicability

The PlumeStop technology is effective on most organic groundwater contaminants, including hydrocarbons, halogenated compounds, and a wide variety of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). It can be applied to inhibit spreading of contaminant plumes, to protect sensitive receptors, or to prevent contaminant migration across property boundaries. PlumeStop is also a very effective tool for control and treatment of groundwater contamination associated with matrix back-diffusion, and for treating sites with very low contaminant concentrations (oligotrophic bio-limitation).

7.1.4 Performance

Laboratory and field studies with PlumeStop indicate that it has minimal impacts on groundwater quality, oxidation-reduction potential (redox), and geochemistry. Once injected into the subsurface, PlumeStop is expected to last on the order of decades, continually immobilizing and stimulating the biodegradation of contaminants.

Field studies confirm wide-area dispersion, with order of magnitude (>90%) reductions in dissolved-phase concentration at the test sites post-application sampling, which further increased to two orders of magnitude (>99%) within two months for both chlorinated solvent and hydrocarbon species. Laboratory data provided confirmation of post-sorption degradation enhancement, describing a significant difference between contaminant destruction in biotic matrix systems compared to abiotic matrix and biotic non-matrix controls.

8 Further Information

PlumeStop Liquid Activated Carbon has been developed by and is commercially available from REGENESIS, San Clemente, California, USA. U.S. and international patents pending. Further product information and a full listing of technical contact personnel are available at www.REGENESIS.com.

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