FINAL REPORT

Flux-Based Assessment of Post-Remedial Performance

ESTCP Project ER-201583

JULY 2021

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 30-07-2021	**2. REPORT TYPE** ESTCP Final Report	**3. DATES COVERED** *(From - To)* 12/28/2015 - 12/28/2020

4. TITLE AND SUBTITLE
Flux-Based Assessment of Post-Remedial Performance

5a. CONTRACT NUMBER
W912HQ-16-C-0002

5b. GRANT NUMBER
ER201583

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER
ER-201583

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

UNIVERSITY OF FLORIDA
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ALEXANDRIA VA 22350-3600

8. PERFORMING ORGANIZATION REPORT NUMBER
ER-201583

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Environmental Security Technology Certification Program
4800 Mark Center Drive, Suite 16F16
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)
ESTCP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
ER-201583

12. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution A: Approved for public release; distribution is unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

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2. Evaluate overall performance of thermal remediation to date using contaminant discharge history (and inferred reduction of contaminant mass) as the primary metric while accounting for flux and discharge uncertainty.
3. Demonstrate the baffled multi-level sampler (BMLS) as a tool allowing for cost effective long-term flux-based monitoring.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Mark Newman
a. REPORT UNCLASS	**b. ABSTRACT** UNCLASS	**c. THIS PAGE** UNCLASS	UNCLASS	156	**19b. TELEPHONE NUMBER** *(include area code)* 352-392-9537 x1518

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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ACRONYMS AND ABBREVIATIONS

BMLS	baffled multi-level sampler
CV	coefficient of variation
DCE	dichloroethene
DNAPL	dense nonaqueous phase liquid
DoD	Department of Defense
EGDY	East Gate Disposal Yard
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FID	flame-ionization detector
GC	gas chromatography
IDL	instrument detection limit
MDL	minimum detection level
MS	matrix spike
MSD	matrix spike duplicate
MSDS	materials safety data sheets
MTBE	methyl tertiary butyl ether
NBS	national bureau of standards
NITS	National Institute of Standards and Testing
PCE	perchloroethylene
PFM	passive flux meter
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
RPD	relative percent difference
RRF	relative response factors
RRT	relative retention times
SD	standard deviation
SOP	standard operating procedure
SRM	standard reference materials
TCE	trichloroethylene
VC	vinyl chloride
VOA	volatile organic acid

ACKNOWLEDGEMENTS

Mark Newman (University of Florida) was project lead and in charge of fieldwork, data analysis, modeling and Final Report preparation.

Jaehyun Cho (University of Florida) was in charge of laboratory analysis and was a major contributor to field activities and data analysis.

Michael Brooks (United States Environmental Protection Agency) was liaison with JBLM onsite personnel and a major contributor to fieldwork and obtaining all historical site data relevant to this project.

Harald Klammler (University of Florida) was a major contributor to modeling and statistical analysis.

Michael Annable (University of Florida) was co-PI and advised with historical data, site logistics, and assessment of results.

Kirk Hatfield (University of Florida) advised with modeling and assessment of results.

ABSTRACT

INTRODUCTION AND OBJECTIVES

The purpose of this project is to demonstrate the utility of flux-based methods for assessing long-term post-remedial performance. Specific objectives of this project are to:

1. Estimate period of record and post-remedial contaminant mass balance through the use of measured fluxes and calculated contaminant discharges while incorporating estimates of the associated flux and discharge uncertainties (Klammler et al., 2012).
2. Evaluate overall performance of thermal remediation to date using contaminant discharge history (and inferred reduction of contaminant mass) as the primary metric while accounting for flux and discharge uncertainty.
3. Demonstrate the baffled multi-level sampler (BMLS) as a tool allowing for cost effective long-term flux-based monitoring.

TECHNOLOGY DESCRIPTION

For this project local contaminant mass flux and integrated mass discharge were measured using baffled multi-level samplers (BMLS) and passive flux meters (PFM). Both methods collect data to determine the local mass flux [mass per unit area per time] that can be spatially integrated to determine mass discharge [mass per time]. The passive flux meter (PFM) was initially developed at the University of Florida under ESTCP project ER-200114 (US Patent 6401547, Hatfield et al., 2002 and 2004; Campbell et al., 2006). BMLS have been utilized successfully for multiple projects in cooperation with the United States Department of Energy, Lawrence Berkley National Laboratory, and now this project (Newman et al., 2011 and Stucker et al., 2011).

PERFORMANCE AND COST ASSESSMENT

The intent of this project is to provide a more cost-efficient method for long-term flux-based monitoring of contaminated sites. The cost analysis compares the cost of a one-year effort to collect monthly flux data for two scenarios. For the first scenario total cost is based upon all monthly measurements being collected using PFM, while the total cost of the second scenario is based upon one initial PFM and BMLS baseline deployment, with all subsequent monthly measurements being performed with BMLS. The results demonstrate that over a one-year sampling campaign scenario 2 provides a savings of $368,742. For longer sampling campaigns, the savings with scenario 2 would continue to increase. The outcome is a reliable flux-based long-term monitoring strategy using both PFM and BMLS while providing significant savings over a method using just PFM.

IMPLEMENTATION ISSUES

The BMLS and PFM technologies currently function through deployment of custom-built devices designed with specified interrogation zones based upon site conditions. Field implementation is straightforward and staff from the United States Environmental Protection Agency (US EPA), United States Geological Survey (USGS), United States Department of Energy (US DOE) and United States Army Corp of Engineers (USACE) have been successfully trained with minimal issues in methodology transfer.

PUBLICATIONS

Newman, M.A., J. Cho, M.C. Brooks, H. Klammler, M.D. Annable, and K. Hatfield. Demonstration of a new cost-effective method for long-term flux-based monitoring. ES&T. In Preparation.

H. Klammler, M.A. Newman, J. Cho, M.C. Brooks, M.D. Annable, and K. Hatfield. Evaluating contaminant discharge uncertainty of long-term flux-based monitoring. Water Resources Research. In Preparation.

EXECUTIVE SUMMARY

INTRODUCTION

In order to demonstrate the utility of flux-based methods for assessment of long-term post-remedial performance, this project has continued previous work at Joint Base Lewis-McChord (JBLM) (formerly Fort Lewis). JBLM offers a unique opportunity because it is a large DNAPL contaminated site with extensive characterization data and a major source-zone remedial effort that included collection of flux data as a component of the remedial performance assessment. Our research team has published a preliminary assessment of post-remedial performance through 2010 (Annable et al., 2014). This project has built upon previous work conducted at the JBLM East Gate Disposal Yard (EGDY) (Figure 1) using flux-based measurements as a remedial performance metric to evaluate the long-term remedial performance on site using a flux-based mass balance approach that incorporates estimates for flux and mass discharge uncertainties.

This project builds upon previous efforts (Annable et al., 2014; Klammler et al., 2012, and Brooks et al., 2008) to provide a long-term (10-year) assessment of post-remedial performance at the JBLM EGDY site. The resulting analyses and methods provide tools not only for evaluating post-remedial performance at this site, but also for evaluating remedial design, site management, and post-remedial performance at other DoD installations.

OBJECTIVES

The purpose of this project is to demonstrate the utility of flux-based methods for assessing long-term post-remedial performance. Specific objectives of this project are to:

1. Estimate period of record and post-remedial contaminant mass balance through the use of measured fluxes and calculated contaminant discharges while incorporating estimates of the associated flux and discharge uncertainties (Klammler et al., 2012).
2. Evaluate overall performance of thermal remediation to date using contaminant discharge history (and inferred reduction of contaminant mass) as the primary metric while accounting for flux and discharge uncertainty.
3. Demonstrate the baffled multi-level sampler (BMLS) as a tool allowing for cost effective long-term flux-based monitoring.

TECHNOLOGY DESCRIPTION

In order to further develop the mass discharge history for the site from 2010 to the present, follow-up flux and aqueous contaminant measurements were collected using passive flux meters (PFM) and baffled multi-level samplers (BMLS) and the results were implemented with mass discharge models. This additional information provides a long-term post remedial performance assessment (10-year) based on contaminant mass discharge while incorporating methods for estimating flux and discharge uncertainties as presented by Klammler et al., 2012.

The primary advantage of the PFM and BMLS approach is that spatial information on cumulative water and contaminant mass flux are obtained. Methods that exist to estimate uncertainty indicate that the PFM approach produces low errors in integrated mass load (Kubert and Finkel, 2006), while Klammler et al., 2012 have worked to directly evaluate the flux and discharge uncertainties associated with PFM measurements.

PFM provide direct independent measures of water flux (Darcy velocity) and contaminant mass flux. When a PFM and BMLS are constructed to have identical sample zones and deployed within a few days of one another, if the flow conditions are stable between deployments the PFM flux measurements can be used to calibrate BMLS aqueous concentration measurements to PFM fluxes within the sample zones of each device. Once a baseline comparison of PFM-measured fluxes and BMLS-measured aqueous concentrations has been performed all subsequent flux measurements for long term monitoring can be performed using BMLS which can lead to significant cost reductions for long term flux-based monitoring strategies.

The PFM and BMLS data were used to evaluate which source mass models may be most appropriate for characterizing long-term mass discharge for a NAPL site both pre- and post-remediation. Model performance was evaluated through using both historic data and with contemporary (post-2010) data. The methods applied allow for determination of the uncertainty (confidence intervals) associated with model-predicted mass discharge (Klammer et al., 2012).

PERFORMANCE ASSESSMENT

Evaluation of the accuracy of contaminant flux measurements is based upon comparison of contaminant fluxes measured with BMLS and PFM. Comparisons are made for two contaminants: TCE and DCE.

The measured TCE and DCE flux values for both technologies are compared in figures 65 and 67 respectively. Statistical analysis of the results is summarized in figures 66 and 68 which compare the average contaminant flux for each technology to the difference between measured fluxes. The mean difference for TCE flux is 14.94 mg/m^2/day with a standard error of 9.09 mg/m^2/day and limits of agreement between 106.43 to -76.56 mg/m^2/day corresponding to a 95% confidence interval (Bland and Altman, 1986). Results indicate reasonably good agreement between the two technologies with the BMLS estimating TCE fluxes on average 14.94 mg/m^2/day lower than PFM.

The mean difference for DCE flux is 1.77 mg/m^2/day with a standard error of 1.37 mg/m^2/day and limits of agreement between 15.51 to -11.98 mg/m^2/day corresponding to a 95% confidence interval (Bland and Altman, 1986). Results indicate good agreement between the two technologies with the BMLS estimating DCE fluxes on average 1.77 mg/m^2/day lower than PFM.

Evaluation of the accuracy of source model results is based upon comparison of estimated source mass values calculated with an exponential source model and power source model. The estimated source mass for both methods are compared in figure 67 and statistical analysis of the results is summarized in figure 68 which compare the average source mass estimated with each method to the difference between estimates. The mean difference for estimated source mass is 0.16 kg with a standard error of 0.05 kg and limits of agreement between 0.3210 to -0.0059 kg corresponding to a 95% confidence interval (Bland and Altman, 1986). Results indicate good agreement between the two methods with the exponential model estimating source mass values on average 0.16 kg lower than PFM.

Final evaluation of the quantitative performance objectives (Table 9) establishes good agreement between BMLS measures and those provided by PFM. It is important to note that the standard error for TCE mass flux was 9.09 mg/m^2/day which was close to the established performance objective limit. However, this higher standard error was due solely to 4 measurements within well LC208.

As discussed in previously in section 5 of this report there was a significant change in conditions between the BMLS and PFM sampling events in 2018 with a noticeable difference in measured fluxes. If these four measurements from LC208 are removed from the analysis the standard error is reduced to 3.21 mg/m^2/day.

The quantitative performance objective analysis also showed excellent agreement between the exponential source decay model and power model (Table 9) with a standard error of only 0.05 kg.

COST ASSESSMENT

The intent of this project is to provide a more cost-efficient method for long-term flux-based monitoring of contaminated sites. The cost analysis compares the cost of a one-year effort to collect monthly flux data for two scenarios. For the first scenario total cost is based upon all monthly measurements being collected using PFM, while the total cost of the second scenario is based upon one initial PFM and BMLS baseline deployment, with all subsequent monthly measurements being performed with BMLS. The results demonstrate that over a one-year sampling campaign scenario 2 provides a savings of $368,742. For longer sampling campaigns, the savings with scenario 2 would continue to increase. The outcome is a reliable flux-based long-term monitoring strategy using both PFM and BMLS while providing significant savings over a method using just PFM.

IMPLEMENTATION ISSUES

The BMLS and PFM technologies currently function through deployment of custom-built devices designed with specified interrogation zones based upon site conditions. Field implementation is straightforward and staff from the United States Environmental Protection Agency (US EPA), United States Geological Survey (USGS), United States Department of Energy (US DOE) and United States Army Corp of Engineers (USACE) have been successfully trained with minimal issues in methodology transfer.

1.0 INTRODUCTION

1.1 BACKGROUND

In order to demonstrate the utility of flux-based methods for assessment of long-term post-remedial performance, this project has continued previous work at Joint Base Lewis-McChord (JBLM) (formerly Fort Lewis). JBLM offers a unique opportunity because it is a large DNAPL contaminated site with extensive characterization data and a major source-zone remedial effort that included collection of flux data as a component of the remedial performance assessment. Our research team has published a preliminary assessment of post-remedial performance through 2010 (Annable et al., 2014). This project has built upon previous work conducted at the JBLM East Gate Disposal Yard (EGDY) (Figure 1) using flux-based measurements as a remedial performance metric to evaluate the long-term remedial performance on site using a flux-based mass balance approach that incorporates estimates for flux and mass discharge uncertainties.

The previous work was conducted under SERDP project ER-1295 as a collaboration between the University of Florida, Purdue University, the US EPA, the USACE, and JBLM. The focus of the previous work was to measure mass flux and mass discharge across a control plane located immediately down gradient of NAPL Area 1. These measurements were completed both before and after the implementation of thermal heating in DNAPL Area 1, in 2003 and 2006, respectively. These measurements provided some of the first field-based data of its kind demonstrating that source zone remedial treatment can lead to significant decreases in contaminant mass discharge from the source zones (Brooks et al., 2008).

The original JBLM TCE contaminant plume, was approximately 3 km (1.4 miles) long (Figure 2), and the result of a large DNAPL source area at the East Gate Disposal Yard (EGDY) (Figure 1). Extensive source zone characterization was previously undertaken resulting in the delineation of three primary DNAPL contaminated regions identified as NAPL Areas 1, 2 and 3 (Figure 3) . These areas were evaluated for a variety of remedial technologies, and resistive heating was selected as the remedial option. The footprint for each of the three areas was based on site characterization efforts including cores, groundwater samples, historical site activities and drum removal. These treatment areas were sequentially addressed with resistive heating by Thermal Remediation Systems over a period of approximately three years (2005-2007). Details on the remedial performance of the resistive heating of NAPL Area 1 have been reported by Brooks et al., 2008. NAPL Area 1 was treated first and was the most up gradient source and thus was ideal for remedial evaluation. The focus of remedial assessment using flux data was on NAPL Areas 1 and 3. NAPL Area 2 was not evaluated by pre- and post-flux measurements however information from alternative measures can be used to provide mass balance evaluation.

This project builds upon the previous efforts outlined above (Annable et al., 2014; Klammler et al., 2012, and Brooks et al., 2008) to provide a long-term (10-year) assessment of post-remedial performance at the JBLM EGDY site. The resulting analyses and methods provide tools not only for evaluating post-remedial performance at this site, but also for evaluating remedial design, site management, and post-remedial performance at other DoD installations.

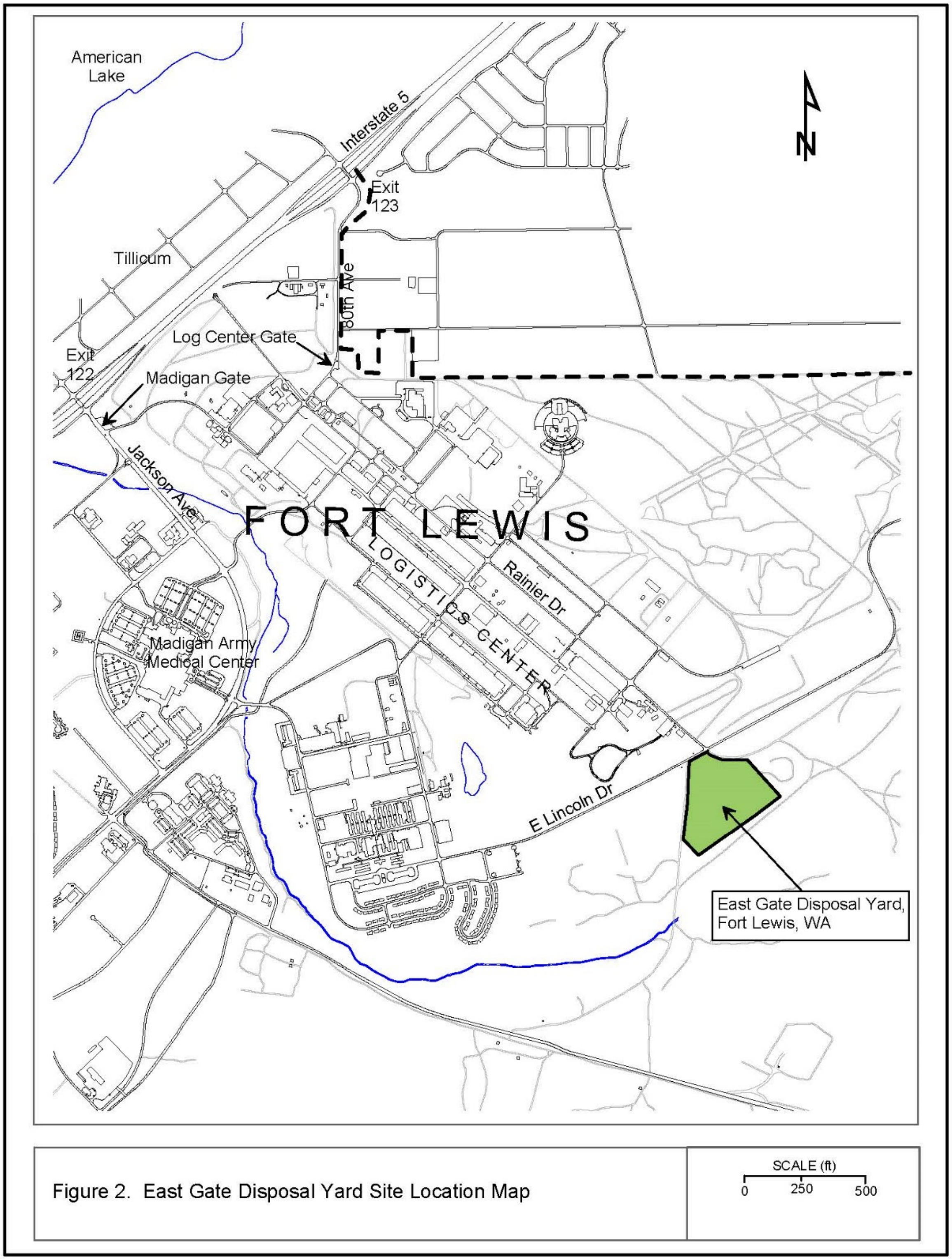


Figure 1. Joint Base Lewis McChord (JBLM) Site Map (formerly Fort Lewis).

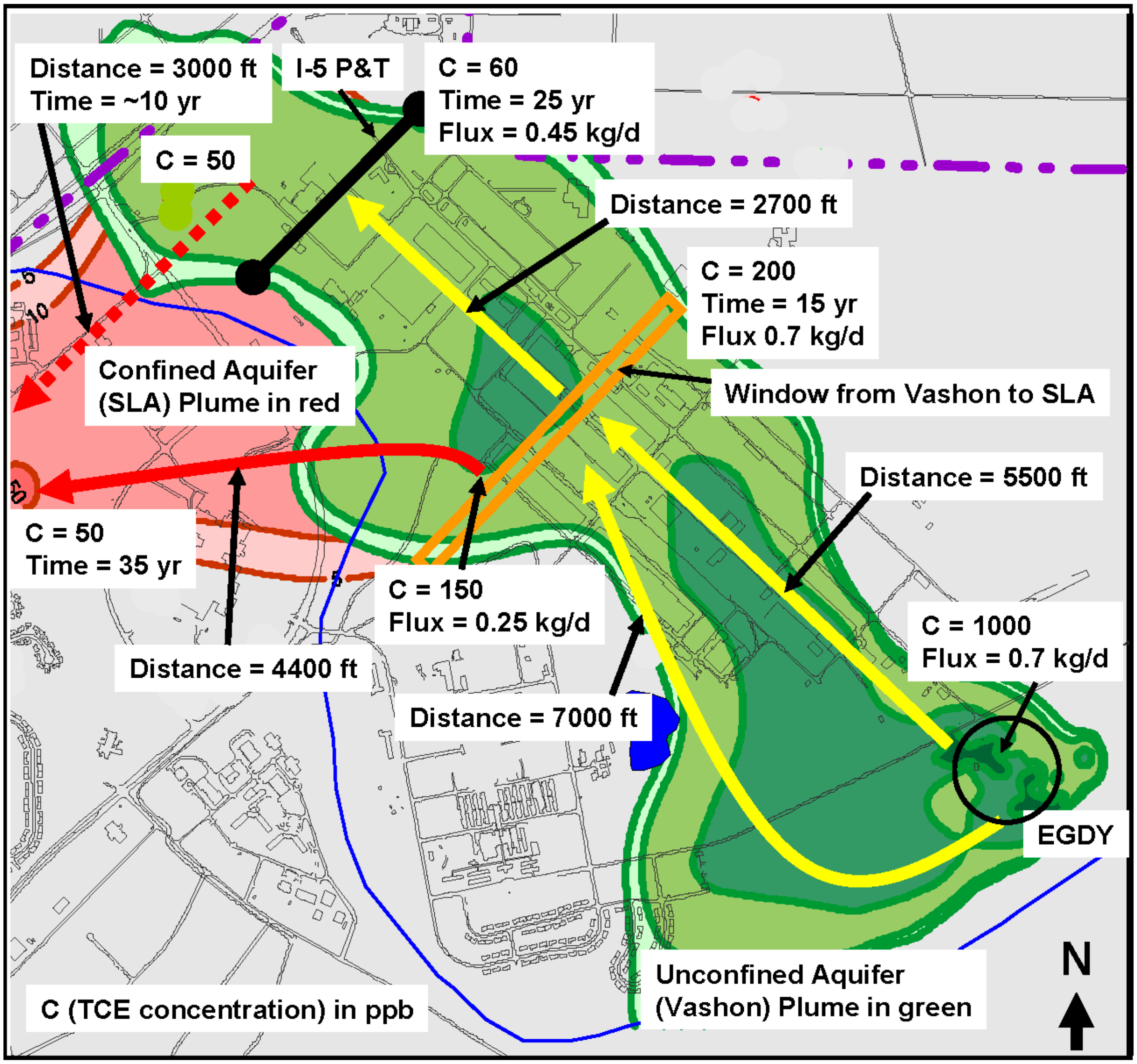


Figure 2. Estimated (TCE) Contaminant Plume Prior to Thermal Remediation (2003).

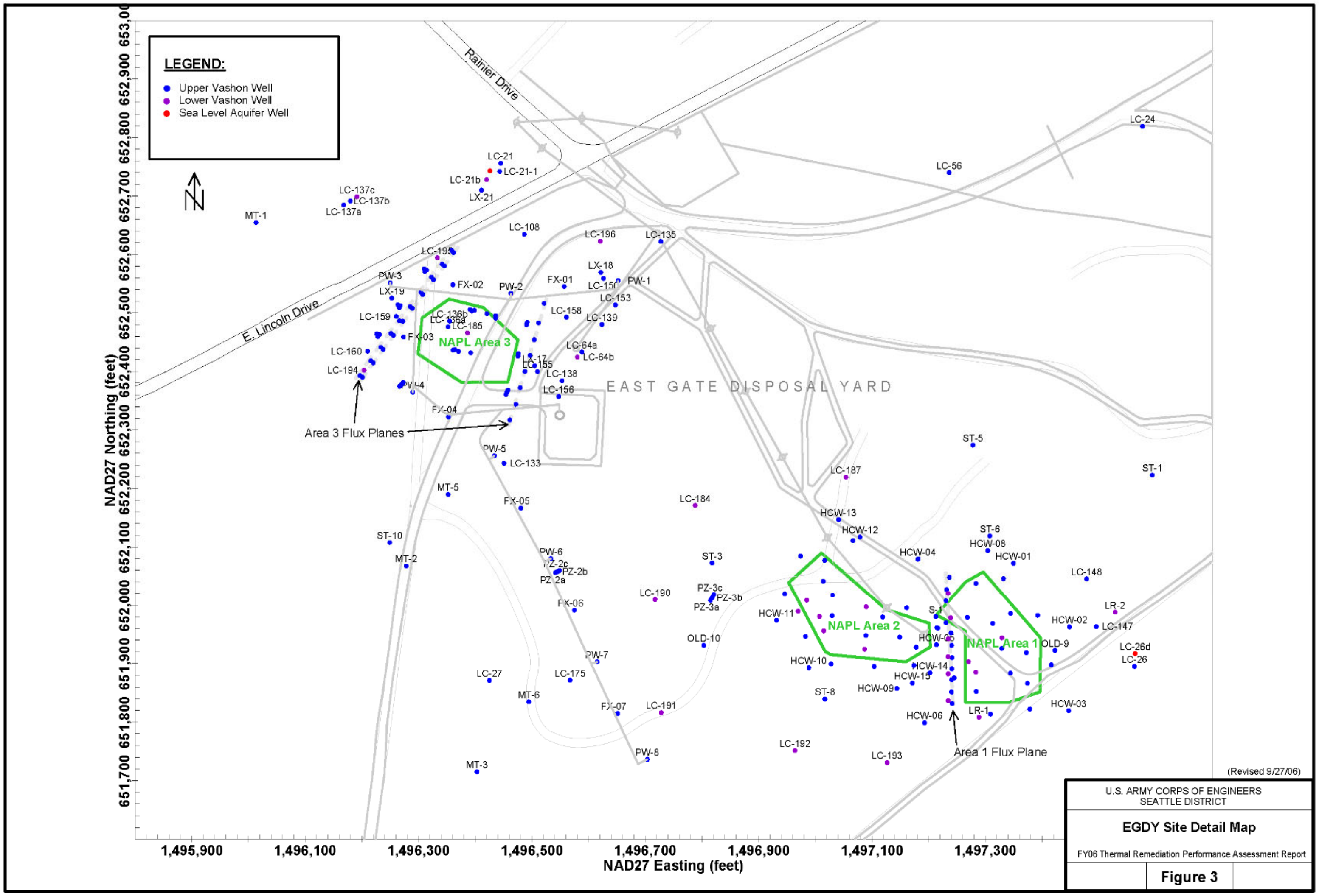


Figure 3. Joint Base Lewis McChord (JBLM) EGDY site NAPL Treatment Areas.

1.2 OBJECTIVE OF THE DEMONSTRATION

The purpose of this project is to demonstrate the utility of flux-based methods for assessing long-term post-remedial performance. Specific objectives of this project are to:

1. Estimate period of record and post-remedial contaminant mass balance through the use of measured fluxes and calculated contaminant discharges while incorporating estimates of the associated flux and discharge uncertainties (Klammler et al., 2012).
2. Evaluate overall performance of thermal remediation to date using contaminant discharge history (and inferred reduction of contaminant mass) as the primary metric while accounting for flux and discharge uncertainty.
3. Demonstrate the baffled multi-level sampler (BMLS) as a tool allowing for cost effective long-term flux-based monitoring.

1.3 REGULATORY DRIVERS

When evaluating post-remedial performance, knowledge of the distribution of contaminant mass within the site and projection of mass discharge history is a critical metric. The collection of mass discharge measurements from the source area to the plume allows for estimates of projections of mass discharge over the life of the NAPL source area. To support these projections some knowledge of current or past mass present in the source area, and/or in the plume is required. Estimates of mass in the source area are inherently difficult to obtain as was demonstrated using historical data collected at the EGDY site. Initial source characterizations conducted resulted in estimates of mass presented in each of the treatment areas. The initial mass estimates were 11,800, 13,400 and 43,100 kg (25,960, 29,480 and 94,820 pounds) of TCE for the three areas, respectively. The resistive heating events removed 2,580, 1,090 and 840 kg (5,676, 2,398 and 1,848 pounds), respectively. (Annable et al., 2014).

From this analysis it was concluded that the initial mass estimates were grossly high for all three treatment areas. This observation was based on the fact that significantly diminishing returns were observed for the mass recovery, suggesting that high fractions of the original mass were removed. Of much more value are the mass removals during resistive heating as they are considered to be much more reliable. From this data one can conclude that NAPL Area 1 was the most significant in terms of mass present and NAPL Areas 2 and 3 were lower (Annable et al., 2014).

As part of this demonstration follow-up flux measurements were performed within the NAPL Area 1 and NAPL Area 3 transects in order to continue the development of mass discharge history for EDGY from 2010 to present. This additional information provides a long-term post remedial performance assessment based upon contaminant mass discharge while incorporating methods for estimating flux and discharge uncertainties by expanding the methods first presented by Klammler et al., 2012.

In addition to passive flux meter deployments, aqueous groundwater samples were collected using baffled multi-level samplers (BMLS) constructed with the same sample intervals as the passive flux meters. The BMLS aqueous concentration data were compared to the PFM flux averaged concentrations to confirm agreement between methods. This allows for subsequent flux and discharge estimates based solely upon BMLS aqueous samples and water level measurements.

The resulting analyses and methods provide a tool not only for evaluating long-term post-remedial performance that accounts for discharge uncertainty at this site, but also for evaluating remedial design, site management, and post-remedial performance at other DoD installations. The introduction of BMLS aqueous concentration data calibrated to the PFM flux averaged concentrations allow for subsequent flux and discharge estimates based solely upon BMLS aqueous samples and water level measurements. Allowing for potential continued tracking of post remedial performance through minimal effort and cost.

2.0 TECHNOLOGY

This demonstration utilized well-established, field tested passive flux meter (PFM) technology (developed by the project team, under ESTCP project ER-0114 (Hatfield et al. 2004; Annable et al., 2005; and Klammler et al. 2007)) to evaluate long-term remedial performance of a NAPL contaminated site. In addition to PFM measurements, aqueous groundwater samples were collected using baffled multi-level samplers (BMLS) allowing for subsequent flux and discharge estimates beyond based solely upon BMLS aqueous samples and water level measurements. PFM and BMLS data were applied with mass discharge models to evaluate the site mass balance over time and estimate the contaminant mass remaining. Multiple mass discharge models were considered as discussed in Annable et al., 2014 and the performance of each was assessed based upon historic and current flux and aqueous concentration data.

2.1 TECHNOLOGY DESCRIPTION

In order to further develop the mass discharge history for the site from 2010 to the present, follow-up flux and aqueous contaminant measurements were collected and applied with mass discharge models. This additional information provides a long-term post remedial performance assessment (10-year) based on contaminant mass discharge while incorporating methods for estimating flux and discharge uncertainties as presented by Klammler et al., 2012.

<u>Theory</u>: When considering flux-based remedial assessments, the terms mass flux and mass discharge are used to describe the rate of contaminant mass transport from the source to the plume and within the plume. The mass flux, J [M/L^2·T] is the product of the Darcy flux, q[L/T], and the local concentration of contaminant, C [M/L^3], in the aqueous phase:

$$J = qC \qquad \text{Eq. 1}$$

The Darcy flux can be calculated applying Darcy's law along the direction of the plume axis at the location of interest:

$$q = -K\frac{dh}{dx} \qquad \text{Eq. 2}$$

where K is the hydraulic conductivity [L/T] and h is the head measurement at the location of interest. For this calculation the x direction is selected as the maximum gradient direction. It should be noted that the groundwater flow direction is dynamic and that the contaminant mass flux changes direction with groundwater flow (e.g., Rein et al., 2009) and for this reason, the predominant groundwater flow direction will be re-evaluated as part of this proposed effort.

The contaminant mass flux is a local quantity that can be measured or calculated across a transect orthogonal to the plume axis. This transect, or control plane, A, then becomes the spatial domain over which the local mass flux values are integrated over the plume extent (width and height within the control plane) to quantify mass discharge, M_D:

$$M_D = \int_A J\,dA \qquad \text{Eq. 3}$$

Mass discharge is likely to change with position along the plume axis, typically the *x* direction and time. Mass discharge measurements quantified near the down gradient edge of the source zone are defined as the source zone mass discharge. How this mass discharge changes with natural dissolution of the source defines the source strength function, $M_D(0,t)$. The link between the source zone and plume can be used to evaluate the source/plume mass balance. While often difficult to quantify accurately, even approximate estimates of mass present in both the source and plume can be used to evaluate site conditions.

One measure of the stage of a site has been referred to as the site *age* (Jawitz et al., 2005). A simple definition of site age is the fraction of the initial source zone mass that has been removed from the source zone through natural processes such as dissolution, volatilization or degradation or through remedial efforts. Given an estimate of the initial mass and the current mass, the age is simply the ratio of the mass lost to the initial mass present. Many factors collectively determine how fast a site ages such as: the solubility limit of the contaminant, the groundwater flow velocity, the size of the source zone in the flow direction and average NAPL saturation along the flow path.

The mass flux at a specified location within a plume can be averaged over different fractions of the cross-section. This may be useful for measurements taken over larger scales such as an integral pump test with multiple wells that form a transect or traditional sampling from the wells. Average mass flux over portions of the transect represented by area *B*, may also be useful for calculating the flux averaged concentration perhaps representing what would be expected at an impacted pumping well that has a capture zone of the same area. Thus, the average mass flux can be calculated as follows:

$$\overline{J} = \frac{\int_B J\,dB}{B} \qquad \text{Eq. 4}$$

A flux averaged concentration can be calculated for a well having a capture area *B* simply using $C=J/q$. This approach allows one to relate flux values to target concentration on a flux average basis. Through these basic relationships targets based on concentration and flux can be linked.

The collection of measurements of mass discharge from the source zone to the plume can allow for estimated projections of mass discharge over the life of the DNAPL source area as demonstrated by Annable et al., 2014. For this project local contaminant mass flux, $J(x,y,z)$ and integrated mass discharge (M_D) will be measured using baffled multi-level samplers (BMLS) and passive flux meters (PFM). Both methods collect data to determine the local mass flux [mass per unit area per time] that can be spatially integrated to determine mass discharge [mass per time]. The passive flux meter (PFM) was initially developed at the University of Florida under ESTCP project ER-200114 (US Patent 6401547, Hatfield et al., 2002 and 2004; Campbell et al., 2006). The PFM contains an internal permeable sorbent which is impregnated with tracers and exposed to flowing groundwater. During deployment, the tracers preloaded on the sorbent are gradually eluted at rates proportional to the average specific discharge, q (volume of water per unit cross-sectional area per unit time). Thus, by measuring tracer mass loss during deployment, pore water specific discharge can be computed. Similarly, the cumulative mass of contaminants sorbed during deployment provide a direct measure of the contaminant mass flux, J (mass of contaminant per unit cross-sectional area per unit time). From q and J the flux-averaged contaminant concentration (C = J/q) can be directly calculated. PFM applications before and after remediation provide a robust evaluation of flux and mass discharge reduction that take into consideration both changes in concentration and groundwater flow (Brooks et al., 2008; Annable et al., 2014).

The primary advantage of the PFM approach is that spatial information on cumulative water and contaminant mass flux are obtained. Methods that exist to estimate uncertainty indicate that the PFM approach produces low errors in integrated mass load (Kubert and Finkel, 2006), while Klammler et al., 2012 have worked to directly evaluate the flux and discharge uncertainties associated with PFM measurements.

2.2 TECHNOLOGY DEVELOPMENT

Technology Maturity. The passive flux meter (PFM) was initially developed at the University of Florida under ESTCP project ER-200114 and received the 2006 ESTCP Project of the Year Award (US Patent 7,284,448, Hatfield et al., 2002 and 2004; Campbell et al., 2006) and was independently identified as the only device that provides direct in-situ measurements of groundwater and contaminant fluxes (Verreydt et al., 2010). The PFM technology has been applied widely at over 60 sites (Annable et al., 2005, Basu et al., 2006, 2007, 2009; Lee et al., 2007; Klammler et al., 2007a, 2007b, 2012; Brooks et al., 2008; Stucker et al., 2011; Johnston et al., 2014; Wang et al., 2014) to measure groundwater fluxes of many hydrophobic organic contaminants (MTBE, PCE, TCE, DCE, VC, BTEX), inorganic compounds (Sulfate, Nitrate, and Phosphate), and heavy metals (Uranium, Vanadium, Arsenic).

Baffled multi-level samplers (BMLS) are devices used to obtain vertically isolated aqueous water samples that once calibrated to PFM measures can be used to provide estimates for contaminant mass flux. PFM provide direct independent measures of water flux (Darcy velocity) and contaminant mass flux. When a PFM and BMLS are constructed to have identical sample zones and deployed within a few days of one another, if the flow conditions are stable between deployments the PFM flux measurements can be used to calibrate BMLS aqueous concentration measurements to PFM fluxes within the sample zones of each device. Once a baseline comparison of PFM-measured fluxes and BMLS-measured aqueous concentrations has been performed all subsequent flux measurements for long term monitoring can be performed using BMLS which can lead to significant cost reductions for long term flux-based monitoring strategies. BMLS have been utilized successfully for multiple projects in cooperation with the United States Department of Energy, Lawrence Berkley National Laboratory, and now this project (Newman et al., 2011 and Stucker et al., 2011).

Each of the mass discharge models evaluated have been considered previously (Sale and McWhorter, 2001; Rao et al., 2002; Rao and Jawitz, 2003; Lemke et al., 2004; Parker and Park, 2004; Enfield et al., 2005; Jawitz et al., 2005; Wood et al., 2005). One of the objectives of this study was to evaluate which method is most appropriate for characterizing long-term mass discharge for a NAPL site both pre- and post-remediation. Model performance was evaluated through using both historic data and with contemporary (post-2010) data. The methods applied allow for determination of the uncertainty (confidence intervals) associated with model-predicted mass discharge (Klammer et al., 2012).

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Application of PFM technology can be limited by the availability of onsite water quality monitoring infrastructure (existing wells and monitoring schedules). One risk for this project was that infrastructure changes on site since the last flux-based efforts were performed in 2010.

There were issues with the integrity of the well screen for three monitoring wells which impacted the ability to deploy and retrieve PFM and BMLS, but all devices were retrieved and usable data was obtained. The current pump and treat system was not operational during previous flux measurements on site. As such, the current hydraulic gradients and groundwater flow conditions were considerably different than previously observed. This is specifically important to note when working with flux transects, which ideally should be perpendicular to the direction of flow. It was observed that with the current pump and treat system, the local flow directions were altered significantly which has a direct effect on the measured fluxes and estimated mass discharge. Instances where this was observed are clearly discussed in the results and conclusions.

3.0 PERFORMANCE OBJECTIVES

Performance objectives are a critical component of any demonstration plan, as they provide the basis for evaluating the performance and costs of an innovative technology.

Table 1 lists the Performance Objectives evaluated during this demonstration. With regards to the quantitative performance objectives, it is understood that future field application of the technology is contingent upon rigorous comparison of BMLS and PFM measures (e.g., solute and groundwater fluxes) in order to demonstrate that BMLS-measured aqueous concentrations that have been calibrated to PFM-measured fluxes are capable of providing subsequent flux estimates. Thus, as part of this demonstration, statistics are presented and comparisons made between BMLS and PFM measures for each qualitative performance objective.

Table 1. Performance Objectives.

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives		
Accuracy of contaminant flux measurements	Measurements from PFM and BMLS.	Standard error less than 10 mg/m^2/day within 95% confidence interval
Accuracy of mass discharge models	Source mass estimates from power model and exponential model.	Standard error less than 10 kg within 95% confidence interval
Qualitative Performance Objectives (to be evaluated during Field Demonstration)		
Ease of use	Operator acceptance	Field technicians able to effectively take measurements
Acceptability of sample analysis	Sample analysis evaluated by external lab	Environmental laboratory acceptance

3.1 PERFORMANCE OBJECTIVE: ACCURACY OF CONTAMINANT FLUX MEASUREMENTS

Evaluation of flux measurement accuracy is based upon comparison of contaminant flux values estimated from BMLS to those determined with PFM.

3.1.1 Data Requirements

PFM measures of TCE and DCE contaminant fluxes were compared to fluxes from BMLS.

3.1.2 Success Criteria

Comparative analyses were performed to determine if BMLS measurements were statistically different from field measurements produced by PFM (Bland and Altman, 1986). The performance objective was considered met if the standard error between BMLS and PFM measurements was less than 10 mg/m^2/day within the 95% confidence interval.

3.2 PERFORMANCE OBJECTIVE: ACCURACY OF MASS DISCHARGE MODELS

In order to evaluate long term remedial performance a mass discharge model must be utilized to assess the contaminant mass balance. Two different source decay models: exponential and power were used to estimate the apparent source mass based upon measured contaminant mass flux and calculated mass discharge values.

3.2.1 Data Requirements

The mass discharge models relied upon water and contaminant flux data obtained from PFM, BMLS, and standard aqueous samples.

3.2.2 Success Criteria

Comparative analyses were performed to determine if source mass estimates using exponential and power models were statistically different (Bland and Altman, 1986). The performance objective was considered met if the standard error between exponential and power estimates was less than 10 kg within the 95% confidence interval.

3.3 PERFORMANCE OBJECTIVE: EASE OF USE

Qualitative approaches were used to characterize the BMLS technology in term of ‘ease of use’.

3.3.1 Data Requirements

Data evaluated measured operator’s acceptance of the technology. Data requirements include comments on the ‘ease of use’ and ‘required level of training’ in the context of competing technologies. General assessments were made concerning the quality and resolution of data generated. System reliability were evaluated (e.g., number of deployments that fail). Advantages and disadvantages of the BMLS were reported for consideration by the potential users of the technology.

3.3.2 Success Criteria

The objectives were considered met if field technicians were able to effectively take measurements given a reasonable level of training.

3.4 PERFORMANCE OBJECTIVE: ACCEPTABILITY OF SAMPLE ANALYSIS

Qualitative approaches were used to characterize the BMLS technology in terms of ‘acceptability of sample analysis’.

3.4.1 Data Requirements

Data requirements included sample analysis evaluated by an external lab

3.4.2 Success Criteria

The objectives were considered met if samples received environmental laboratory acceptance.

4.0 SITE DESCRIPTION

JBLM offers a unique opportunity because it is a large DNAPL contaminated site with extensive characterization data and a major source-zone remedial effort that included collection of flux data as a component of the remedial performance assessment. Our research team published a preliminary assessment of post-remedial performance through 2010 (Annable et al., 2014). The previous work was conducted under SERDP project ER-1295 as a collaboration between the University of Florida, Purdue University, the US EPA, the USACE, and JBLM. The focus of the previous work was to measure mass flux and mass discharge across a control plane located immediately down gradient of NAPL Area 1. These measurements were completed both before and after the implementation of thermal heating in DNAPL Area 1, in 2003 and 2006, respectively. These measurements provided some of the first field-based data of its kind demonstrating that source zone remedial treatment can lead to significant decreases in contaminant mass discharge from the source zones (Brooks et al., 2008).

This project builds upon the previous efforts outlined above (Annable et al., 2014; Klammler et al., 2012, and Brooks et al., 2008) to provide a long-term (10-year) assessment of post-remedial performance at the JBLM EGDY site. The resulting analyses and methods provide tools not only for evaluating post-remedial performance at this site, but also for evaluating remedial design, site management, and post-remedial performance at other DoD installations.

4.1 SITE LOCATION AND HISTORY

The East Gate Disposal Yard (EGDY) site is located on the Ft. Lewis Military Reservation near Tacoma, Washington, and is part of the Ft. Lewis Logistics Center Superfund site. The EGDY was used from 1946 to 1960 as a disposal area for drums of used solvents and oils that were placed in excavated trenches, and is the source for a large chlorinated solvent plume (predominantly TCE) which extends to the northwest for ~4 km (~2.5 miles) towards the American Lake (USACE, 2002). The operation of a pump-and-treat system was started in 1995 for hydraulic control purposes, and drum excavation activities at the EGDY site were conducted between late 2000 and mid-2001. Site characterization work conducted in 2001 and 2002 identified three main areas of DNAPL contamination within the EGDY site, which are referred to as NAPL Areas 1, 2, and 3.

4.2 SITE GEOLOGY/HYDROGEOLOGY

At the EGDY site, the surficial, unconfined aquifer is composed of the Vashon Recessional Outwash/Steilacoom gravel unit (consisting of loose, well-graded sandy, cobbly gravel or gravelly sand). In the immediate vicinity of NA1, this unit is underlain by Vashon Till (consisting of loose to dense silty, sandy gravel with some clay), which is considered to be a generally continuous intermediate aquitard. This layer, in turn, is underlain by more Vashon Recessional Outwash/Steilacoom gravel or Vashon Advance Outwash (loose sandy gravel to gravelly sand with cobbles) (USACE, 2002).

4.3 CONTAMINANT DISTRIBUTION

The JBLM TCE contaminant plume, which is approximately 3 km (1.4 miles) long (Figure 2), is the result of a large DNAPL source area at the East Gate Disposal Yard (EGDY) (Figure 1).

Extensive source zone characterization was previously undertaken resulting in the delineation of three primary DNAPL contaminated regions identified as NAPL Areas 1, 2 and 3 (Figure 3) . These areas were evaluated for a variety of remedial technologies, and resistive heating was selected as the remedial option. The footprint for each of the three areas was based on site characterization efforts including cores, groundwater samples, historical site activities and drum removal. These treatment areas were sequentially addressed with resistive heating by Thermal Remediation Systems over a period of approximately three years (2005-2007). Details on the remedial performance of the resistive heating of NAPL Area 1 have been reported by Brooks et al., 2008. NAPL Area 1 was treated first and was the most up gradient source and thus was ideal for remedial evaluation. The focus of remedial assessment using flux data was on NAPL Areas 1 and 3. NAPL Area 2 was not evaluated by pre- and post-flux measurements however information from alternative measures can be used to provide mass balance evaluation.

The EGDY source areas NAPL Area 1 and NAPL Area 3 were evaluated by constructing transects of wells screened across the contaminated surficial aquifer to quantify mass flux distributions and integral mass discharge. For NAPL Area 1 a single transect of 10 wells was located immediately down gradient of the treatment zone (Figure 3). For NAPL Area 3 two transects were installed, one up gradient of the treatment area and one down gradient.

In NAPL Area 1 both pre-remediation (2003) and post-remediation (2006) flux distributions were measured with PFM as shown in Figure 4. It can be seen that the pre-remediation flux was localized with approximately 90% of the mass flux contained within 33% of the control plane cross section. This mass was likely originating from DNAPL source zones located up gradient of the control plane. The post-remediation flux distribution shows a significant decrease in flux magnitude with a noticeable shift in the flux distribution.

Post-remediation (2006) flux distributions were measured at NAPL Area 3 in both the up gradient and down gradient well transects. The up gradient flux distribution was less localized than that observed at NAPL Area 1. This was considered likely due to the much larger travel distance between the source of the mass flux and the control plane. This allows more time and travel distance for mixing and dispersive processes to be realized. This demonstrates that for design purposes the control plane should be as close to the source area as possible.

The down gradient control plane at NAPL Area 3 is about 50 ft in saturated thickness and much thicker than the control plane at NAPL Area 1. This is the result of the till unit at the base of the surficial aquifer declining rapidly in the treatment zone. The flux distribution along this control plane was again more localized providing evidence of DNAPL source zones present in NAPL Area 3.

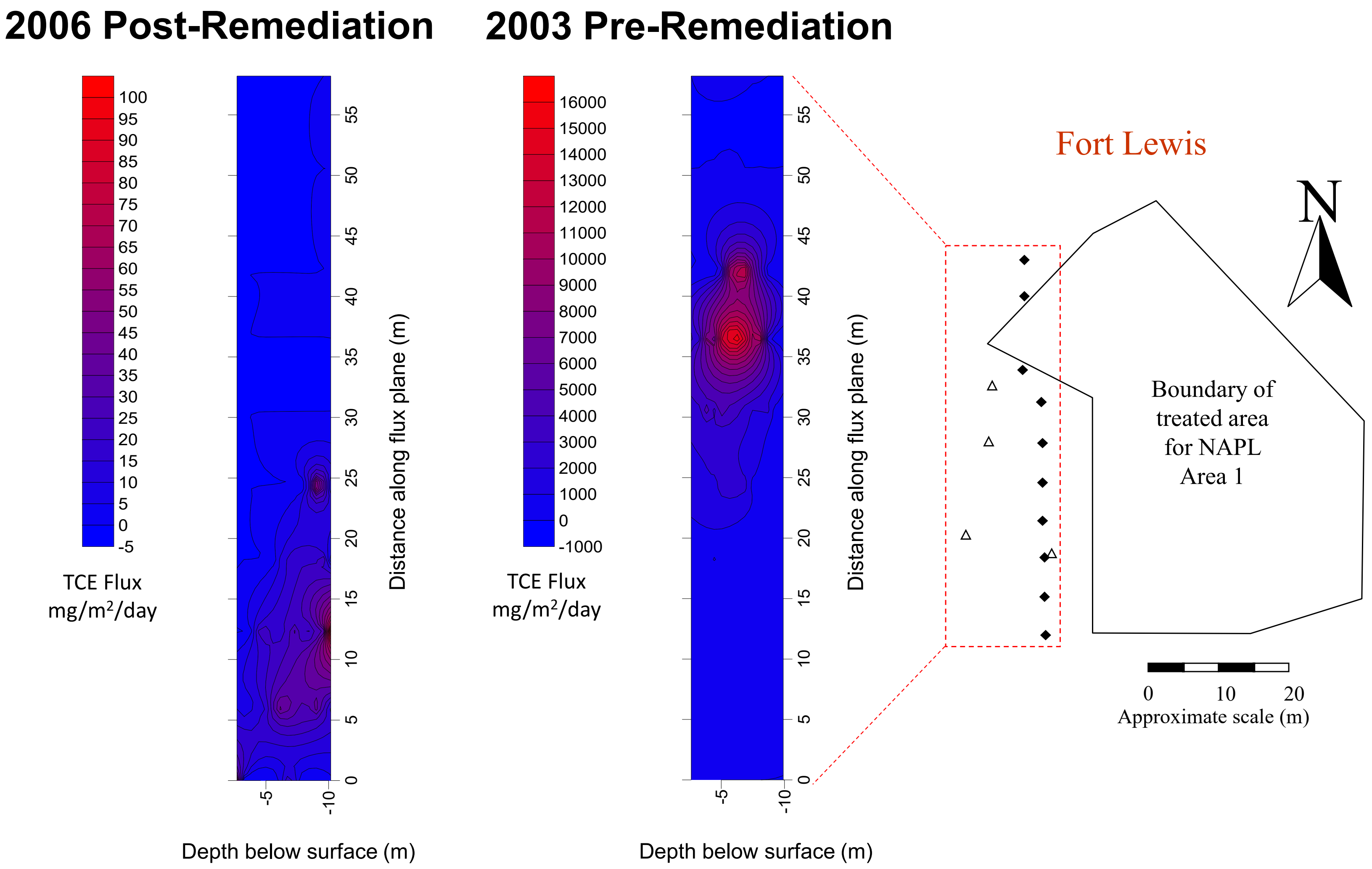


Figure 4. **APL Area 1 Comparison of Historical Pre-remediation (2003) and Post Remediation (2006) TCE Mass Flux Distribution.**

Note the significant decrease in flux magnitude and shift in spatial distribution.

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

As part of the previous research effort (SERDP project ER-1295), mass discharges were measured on site using both integral pump tests (IPT) and passive flux meters (PFM). The measured mass discharges at NAPL Areas 1 and 3 were 6,700/7,300 mmoles/day (IPT/PFM) and 2,300/8,800 mmoles/day (Annable et al., 2014). This information was used to estimate mass discharge histories for both treatment areas. In order to perform the calculations, some assumptions were required. A model must be applied to evaluate the mass discharge vs. mass remaining relationship (Falta et al., 2005a; Jawtiz et al., 2005). The simplest model to assume is exponential decay. Using pre- and post-mass discharge measurements, the mass at the beginning of the treatment was 2,600 kg (5,720 lb) and the mass after treatment was 19 kg (42 lb). Based upon this, a mass removal of 99.3% was estimated. In addition, if a date is assumed for the initial spill of DNAPL (for this analysis 1950 was assumed), an initial mass in NAPL Area 1 of 5,200 kg (11,400 lb) can be estimated. Applying the same analysis to NAPL Area 3 provides an initial mass estimate of 2,800 kg (6,200 lb). While NAPL Area 2 did not have local pre- and post-treatment mass flux measurements, based on the mass removed, we can estimate an additional source area mass of 3,100 kg (6,800 lb). Using all of the estimates, the total initial TCE mass estimate for the EGDY was approximately 10,000 kg (22,000 lb) (Annable et al., 2014). This estimate was compared to mass estimates for the TCE present in the dissolved plume generated by the source mass at EGDY of approximately 5,000 kg (11,000 lb). These values were considered as a basis of comparison for all subsequent TCE measurements (as proposed here) in order to evaluate changes in mass and mass discharge looking for trends over the long term monitoring period following thermal remediation.

The previous site-wide IPT conducted at EGDY also provides insight into the site-wide mass balance (Annable et al., 2014). While the measurement was impacted by treatment of NAPL Areas 1 and 2, since it was conducted six months after heating was terminated in Area 1, it still provided valuable data for comparison. In the northern and central sections the results can be compared with the mass discharge from NAPL Area 3. The site-wide based IPT mass discharge of 3,450 mmoles/day compares favorably with the IPT measurement of 3,200 mmoles/day, while the PFM was higher at 8,800 mmoles/day (Annable et al., 2014).

In order to estimate the site-wide mass discharge prior to treatment the mass discharge from NAPL Area 1 was summed with an unknown contribution from NAPL Area 2. The complication arises because NAPL Area 2 is down gradient of NAPL Area 1 and thus mass discharge from this zone may be reduced due to the presence of TCE in solution from NAPL Area 1. Total estimates of mass discharge from EGDY were conducted under two extreme cases, NAPL Area 2 contributes no additional mass, and NAPL Area 2 contributes a mass discharge scaled to the mass removed during remediation based on results from other treatment zones. This analysis resulted in an estimated mass discharge of 11,000 to 14,000 mmoles/day.

As part of the current effort follow-up flux measurements were performed within the NAPL Area 1 and NAPL Area 3 transects in order to continue the development of mass discharge history for EDGY from 2010 to present. This additional information provides a long-term post remedial performance assessment (10-year) based on contaminant mass discharge while incorporating methods for estimating flux and discharge uncertainties as presented by Klammler et al., 2012.

In order to continue the development of the site mass discharge history beyond 2010, a review of all existing site data (2010-present) was performed. Of particular interest was existing pump and treat data which was used for two purposes: to assess the total contaminant mass removed to date, and to assess the mass discharge from the landfill as a function of time since the pump and treat system began.

In addition to review of existing data, new field measurements were performed in order to assess the current conditions on site. Field efforts consisted of estimating the predominant groundwater flow direction, collecting aqueous water samples, and flux measurements in the NAPL Area 1 and NAPL Area 3 transects.

To confirm that current discharge conditions are comparable to previous flux measurements on site, the predominant groundwater flow direction must be determined. This is because the control plane discharge estimates can be considered an instantaneous measurement that is the result of groundwater flow imposed on the DNAPL source area for the travel time required between source and control plane. Previously, for NAPL Area 1 this travel time was approximated as the travel time through the treatment area given that groundwater sampling had established that contaminant concentrations were very low up gradient of the resistive heating treatment area. The travel distance was approximated as 50 m, or roughly 160 ft. Given an average Darcy velocity based on the PFMs of 0.25 m/day (0.82 ft/day) and assuming a porosity of 0.33 the travel time is approximately 70 days. Thus, the predominant gradient over the previous 70 days should be considered to locate up gradient source areas. Recognizing that gradient shifts in direction and magnitude are evident at this and many other sites, the mean gradient magnitude weighted direction should be calculated. For many sites the gradient direction and magnitude shift between wet and dry seasons. To account for this, 23 pressure transducers were deployed in select wells throughout the site which continuously collected water level data throughout the entire duration of field investigations.

Prior to flux meter deployment low-flow groundwater samples were collected from the screened interval of both NAPL Area 1 and 3 wells to evaluate the distribution of aqueous contaminant concentrations throughout the site. The aqueous concentrations along with predominant groundwater direction were used to design a targeted passive flux meter deployments in the NAPL Area 1 and NAPL Area 3. In addition to passive flux meter deployment, aqueous groundwater samples were collected using baffled multi-level samplers (BMLS) constructed with the same sample intervals as the PFM. The BMLS aqueous concentration data were then compared to the PFM flux averaged concentrations providing a baseline which allows for subsequent flux and discharge estimates beyond 2016 based solely upon BMLS aqueous samples and water level measurements.

In order to further evaluate the onsite mass balance and mass discharge history at the JBLM site appropriate source mass models had to be considered. Several modeling approaches have been used to evaluate how mass discharge or flux changes as a result of mass removal from DNAPL source zones (Sale and McWhorter, 2001; Rao et al., 2002; Rao and Jawitz, 2003; Lemke et al., 2004; Parker and Park, 2004; Enfield et al., 2005; Jawitz et al., 2005; Wood et al., 2005). The impacts of reductions in mass discharge resulting from source treatment on the dissolved plume have also been examined through development of models such as REMCHLOR (Falta et al., 2005a, b; Basu et al., 2008; Falta, 2008). Results from these models suggest that a wide range of flux behavior may occur as a function of hydrogeological conditions and DNAPL distributions.

The combination of data collected as part of this project (pump and treat data along with field measurements of flux and mass discharge using BMLS and PFM) when implemented with the appropriate models allow for a long-term detailed estimate of the site mass balance and discharge history including.

It is known that the mass flux within a given site can vary widely over time and space. For example, a study using multilevel samplers at four sites (Guilbeault et al., 2005) found a range of integrated mass load estimates ranging from 41 to 85 g/day for TCE, but the individual mass flux values varied enormously over short distances. For this reason, it is critical to quantify the uncertainty associated with mass flux and discharge estimates.

Klammler et al., (2012) developed a geostatistical approach for estimating contaminant plume discharges and uncertainties from local PFM mass flux measurements across a transect. The method accounts for spatial heterogeneity, data skewness (non-normality) and possibly uneven sampling patterns by implementing a conditional simulation approach. Two simplified methods based on ordinary kriging weights in combination with classical bootstrap and a transformation of the Student t-statistics are also presented. In principle, these methods can be applied to the pre and post-remediation data independently, for subsequent comparison using confidence intervals based on uncertainty estimates. However, given that sampling campaigns are likely to be performed at the same transect (or even in the same wells), some degree of positive correlation between pre and post-remediation data at equal locations may be expected. In other words, besides the spatial correlation of local fluxes for a single sampling event over a transect, there may also exist correlation in time between co-located pre and post-remediation fluxes. Intuitively speaking, this may be a reflection of the fact that a plume may become weaker due to source degradation, while maintaining its internal structure of heterogeneity (i.e., high and low flux zones remain stationary).

Such a between-sampling-event-correlation may be highly beneficial for quantifying changes in mass discharge, because it implies a positive correlation between estimation errors of pre and post-remediation discharges. Thus, when taking the difference or ratio of pre and post-remediation discharges as a measure of remediation success, the individual discharge estimation errors tend to cancel out to some degree, resulting in a reduced uncertainty in the remediation performance measure. For example, in the extreme and hypothetical scenario of perfect correlation (i.e., when plume discharge reduction occurred by a uniform down-scaling of all local fluxes) there is still uncertainty about pre and post-remediation discharges, but since local data indicate that all fluxes were reduced by the same factor, the uncertainty in remediation performance would vanish.

As a direct extension of Klammler et al., (2012), the geostatistical tools for considering this spatio-temporal correlation are provided by the methods of ordinary co-kriging and conditional co (joint)-simulation of multiple auto and cross-correlated variables (Goovaerts, 1997). For example, pre-remediation flux data may be treated as the primary variable, while post-remediation data represents the secondary variable in a co-kriging / simulation system. Such a system can be used to *directly* estimate a difference or ratio of pre and post-remediation mass discharges with an associated uncertainty in terms of a variance or cumulative distribution function (confidence intervals). Moreover, once auto and cross-correlation properties are characterized for a site or plume, the co-kriging / simulation approach holds potential for future sampling design optimization given a target uncertainty in discharge reduction estimates. Intuitively speaking, this means that future post-remediation sampling can be significantly sparser, if cross-correlation in time is known to be significant (showing that internal plume structure does not significantly change), without inflating remediation performance uncertainty. Application of this approach to other spatially discrete sampling techniques (e.g., multi-level sampling) is straight-forward and extensions to consider different pre and post-remediation sampling techniques can be investigated.

This project expands the methods of Klammler et al., 2012 to assess the overall performance of thermal remediation to date using contaminant discharge history and inferred reduction of contaminant mass as the primary metrics while accounting for flux and discharge uncertainty. This in turn allows for evaluation of the uncertainty associated with the overall long-term remedial assessment.

5.2 BASELINE CHARACTERIZATION

Baseline characterization activities included the following:

1) Measured instantaneous groundwater levels using water level tape;
2) Recorded groundwater level time series over the entire duration of fieldwork using 23 water level loggers (pressure transducers) in order to evaluate groundwater gradient;
3) Measured contaminant concentrations using standard low-flow aqueous groundwater samples (volumetric average sample over entire screened depth);
4) Measured vertically distributed aqueous contaminant concentrations using BMLS;
5) Measured groundwater and contaminant fluxes using PFM.

5.2.1 Instantaneous Groundwater Level Measurements

During this demonstration tests were performed under natural gradient and pumping conditions in numerous well-characterized monitoring wells. Groundwater levels were measured in all wells before and after PFM deployments. The intent was to monitor for potential changes in gradient produced by transient hydrologic conditions (e.g., rainfall events and pumping).

5.2.2 Groundwater Level Time Series

Water level transducers were used to record groundwater level time series data over the entire duration of field activities (one year) in order to evaluate the groundwater gradient.

5.2.3 CONTAMINANT CONCENTRATION MEASUREMENTS USING STANDARD AQUEOUS GROUNDWATER SAMPLES

Low-flow groundwater samples were collected from each test well for analysis of aqueous contaminant concentrations. These samples were collected during Trip 1 as outlined in Section 5.5 Field Testing. The intent was to assess ambient aqueous contaminant concentrations within the wells to inform where best to sample during future activities.

5.2.4 Contaminant Concentration Measurements Using BMLS

BMLS were deployed to measure the vertical distribution of aqueous contaminant concentrations within selected monitoring wells during Trips 2 and 3 (as outlined in Section 5.5 Field Testing). The wells sampled were determined based upon the results of the low-flow sampling performed during Trip 1. The intent was to strategically target wells with quantifiable contaminant concentrations while avoiding wells with little to no contaminant present.

5.2.5 Measure Groundwater and Contaminant Flux Using PFM

PFM were deployed to quantify groundwater and contaminant flux. The PFM deployment strategy was informed by previous aqueous contaminant concentrations measured with low-flow sampling and BMLS during Trips 1 and 2 respectively (as outlined in Section 5.5 Field Testing). The intent was to strategically target wells with higher contaminant flux while avoiding wells with little to no contaminant flux.

5.2.6 Disposal of Investigation-Derived Waste (IDW)

It is estimated that the demonstration produced 5 kg of spent activated carbon waste, 1 kg of nylon socks, and 1 kg of plastic mesh. The University of Florida disposed of this waste.

5.3 TREATABILITY OR LABORATORY STUDY RESULTS

No laboratory studies were implemented for this project as all procedures have been tested and documented in previous work (Hatfield et al., 2002 and 2004; Campbell et al,. 2006; Annable et al., 2005; Basu et al., 2006, 2007, 2009; Lee et al., 2007; Klammler et al., 2007a, 2007b, 2012; Brooks et al., 2008; and Stucker et al., 2011).

5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

Passive flux meters (PFMs) and baffled multi-level samplers (BMLS) were utilized to quantify groundwater and contaminant flux.

5.4.1 PASSIVE FLUX METER (PFM)

The Passive Flux Meter (PFM) is a device developed at the University of Florida (Hatfield et al, 2002 and 2004; Campbell et al., 2006) under ESTCP project ER-200114 (receiving the 2006 Project of the Year Award) and is the only device that provides direct measurements of contaminant and geochemical fluxes (Verreydt et al., 2010). The PFM is a self-contained permeable unit (Figure 5) that is inserted into a well where it captures target contaminants from the groundwater flowing through it. The sorbent matrix is also impregnated with known amounts of one or more fluid soluble resident tracers. These tracers are leached from the sorbent at rates proportional to the fluid flux. After a specified period of exposure to groundwater flow, the PFM is removed from the well or boring and the sorbent carefully extracted to quantify the mass of all contaminants intercepted by the meter and the residual masses of all resident tracers. An important feature of the PFM technology is that sorption of semi-volatile, hydrophobic contaminants to the solid sorbent within the passive flux meter pre-concentrates compounds prior to laboratory analysis.

This substantially lowers detection limits of the device and improves the accuracy of flux calculations for trace contaminants. The contaminant and geochemical masses are used to calculate time-averaged contaminant and geochemical mass fluxes, while residual resident tracer masses are used to calculate cumulative fluid flux. Depth variations of both water and contaminant fluxes can be measured in an aquifer from a single flux meter by vertically segmenting the exposed sorbent packing and analyzing for resident tracers and contaminants. The PFM has been applied widely at over 60 sites (Annable et al., 2005, Basu et al., 2006) to measure fluxes of MTBE, PCE, TCE, DCE, VC, Uranium, Vanadium, Arsenic, Sulfate, Nitrate, and Phosphate. The PFMs are now being combined with simple passive aqueous sampling devices that capture anions and other aqueous constituents needed for MNA evaluation. The co-deployment of the samplers allows for more streamlined field work and results in less cost while providing needed parameters.

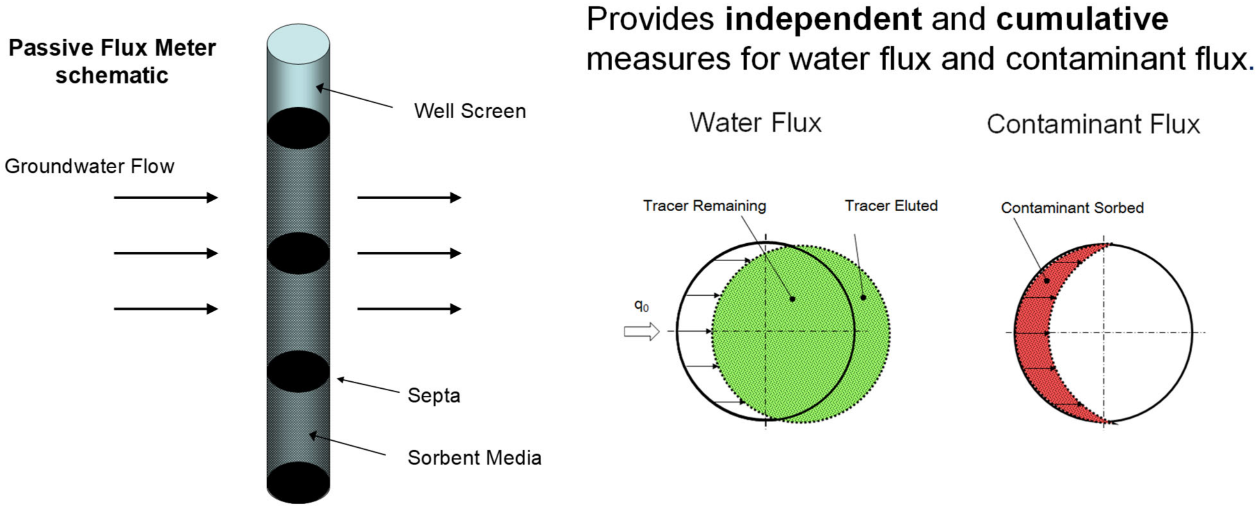


Figure 5. Passive Flux Meter (PFM) Schematic.

5.4.2 BAFFLED MULTI-LEVEL SAMPLER (BMLS)

Baffled multi-level samplers (BMLS) are devices used to obtain vertically isolated aqueous water samples that once calibrated to PFM measures can be used to provide estimates for contaminant mass flux. A schematic of a typical BMLS is provided in Figure 6. BMLS are typically sampled by pulling three purge volumes each equivalent to the volume of the sampling tube (from submerged port to top of casing), and then a subsequent 40 ml sample is drawn for analysis. This is not true low-flow sampling, but the intent is to minimize the volume and rate of extraction in order to ensure that the sample volume withdrawn does not exceed the aqueous volume isolated vertically between the baffles for each sample zone.

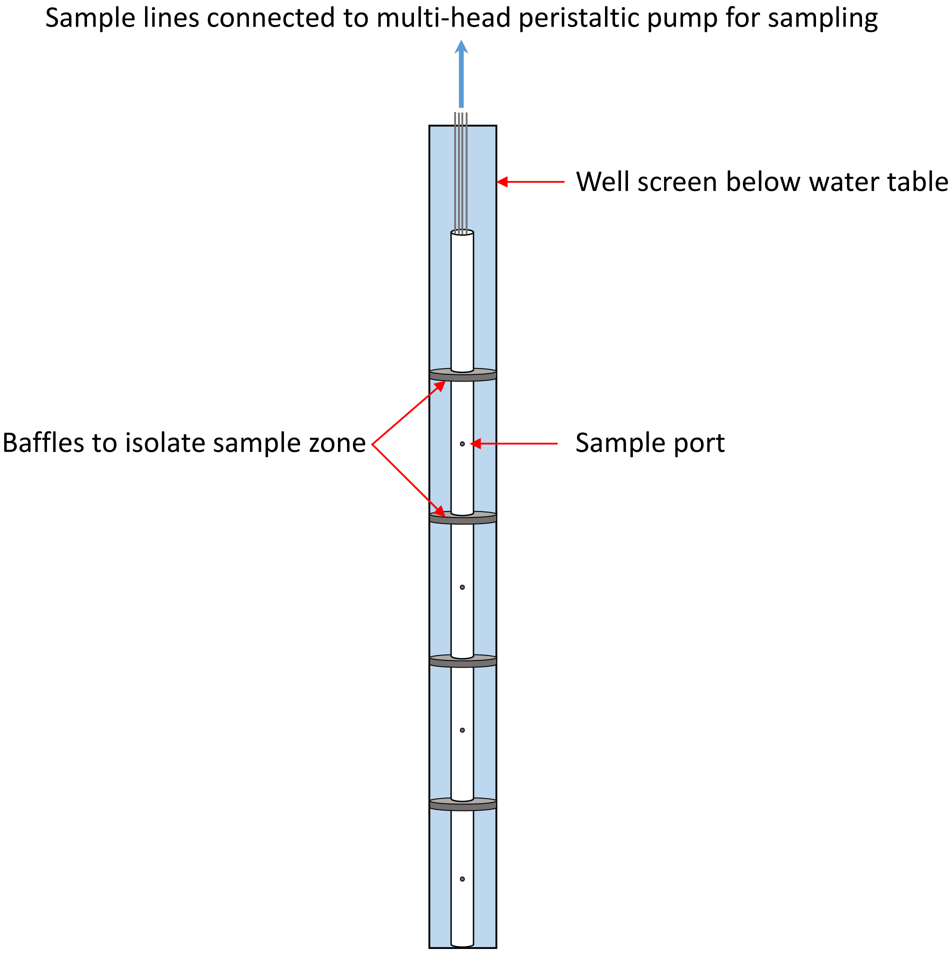


Figure 6. Baffled Multi-level Sampler (BMLS).

PFM provide direct independent measures of water flux (Darcy velocity) and contaminant mass flux. When a PFM and BMLS are constructed to have identical sample zones and deployed within a few days of one another, if the flow conditions are stable between deployments the PFM flux measurements can be used to calibrate BMLS aqueous concentration measurements to PFM fluxes within the sample zones of each device. Where the BMLS contaminant mass flux is calculated as:

$$J_C = q_w C$$

Where J_C is the contaminant mass flux, q_w is the Darcy velocity (specific discharge) and C is the contaminant aqueous concentration measured with the BMLS. The Darcy velocity (q_w) can be determined directly from PFM measurements or calculated based upon observed hydraulic gradient and aquifer hydraulic conductivity data. For sites with stable flow conditions, the baseline Darcy velocity measured with PFM can be used with subsequent future BMLS measurements to estimate contaminant flux values. While for sites with variable hydraulic gradients the PFM-measured Darcy velocity can be used as a baseline to estimate adjusted Darcy velocities using observed water levels during the BMLS deployment along with aquifer hydraulic conductivity data. The water levels can be recorded using water level loggers (pressure transducers) and the hydraulic conductivities can be estimated from slug tests within the monitoring well.

Once a baseline comparison of PFM-measured fluxes and BMLS-measured aqueous concentrations has been performed all subsequent flux measurements for long term monitoring can be performed using BMLS which can lead to significant cost reductions for long term flux-based monitoring strategies.

5.5 FIELD TESTING

In order to expand upon previous flux assessments on site with the intent of providing a long-term post-remedial assessment of the JBLM EGDY site, the following five stages of work were performed. Some of the tasks outlined below were performed in parallel. Table 2 provides a detailed schedule of all project activities.

Stage 1: Evaluate existing site data to establish baseline (mass balance). Building upon previous work by our team to estimate a site mass balance and discharge history for EGDY (Annable et al., 2014) we reviewed all relevant site data from 2010-present. Review of existing pump and treat data was of primary interest for two purposes: to assess the total contaminant mass removed to date (establishing a baseline for future comparison), and to assess mass discharge from the landfill as a function of time since the pump and treat system began. Previous research efforts focused on using mass flux and mass discharge measurements for site management purposes. In particular, we have evaluating predictive models of how mass discharge changes with time through application of source strength functions and incorporation of flux and mass discharge uncertainty from field based data (SERDP ER-1613; Annable et al., 2014; Klammler et al., 2012; and Jawitz et al., 2005). Mass discharge estimates based on existing pump and treat data were used to provide an assessment of the post-remedial performance.

Stage 2: Field measurements to supplement existing data and evaluate present conditions on site. Field measurements consisted of four types: hydraulic head measurements, low-flow groundwater sampling, BMLS, and PFM deployments. The field efforts were divided into three trips as outlined below.

Trip 1: Collect low-flow water samples, deploy pressure transducers, and re-survey top of well casings. When measuring mass flux and discharge it is important to understand the magnitude and direction of groundwater flow as well as how it may change over time. During the first trip 23 pressure transducers were deployed in wells around NAPL Area 1 and 3 (Figure 7). These transducers were left in place and recording over the entire duration of the field activities (one year) to observe the predominant groundwater gradients throughout the site. As an initial contaminant mass screening process, low-flow groundwater samples were collected over the screened interval of all wells within NAPL Area 1 down-gradient transect and targeted wells within NAPL Area 3. The initial water samples were used to provide an overview of the contaminant mass distribution within the site, and provide critical information for planning of subsequent flux measurements.

Trip 2: Download pressure transducers and leave deployed, collect BMLS water samples based upon Trip 1 low-flow aqueous concentrations. During the second trip, groundwater samples were collected using baffled multi-level samplers (BMLS) from the NAPL Area 1 down-gradient transect and select NAPL Area 3 down-gradient transect wells. The sampled wells were selected based upon results of low-flow water sampling during Trip 1.

These measurements were used for two purposes: as a basis of comparison to previous PFM flux average concentrations obtained on site (pre-remediation 2003 and post-remediation 2006), and to guide the strategy of subsequent targeted PFM deployments to quantify mass flux and discharge.

Trip 3: Retrieve pressure transducers, collect BMLS water samples, and perform PFM deployments. This final trip was divided into two parts (Trip 3-1 and 3-1) in order to accommodate the difference in groundwater velocities between the shallow and deep wells.

Trip 3-1: Water samples were collected using BMLS in the NAPL Area 1 down-gradient transect and select NAPL Area 3 down-gradient transect wells. The sampled wells were selected based upon results of initial BMLS water sampling during Trip 2. Once BMLS sampling was complete, PFM were deployed in the NAPL Area 1 down-gradient transect and select NAPL Area 3 down-gradient transect wells to measure both groundwater and contaminant flux. The PFM deployed in shallow wells were retrieved and sampled following a 5-day deployment.

Trip 3-2: Retrieved and sampled deep well PFM after 14-day deployment. Pressure transducers were retrieved having provided a project-duration (one year) record of predominant groundwater gradients. Equipment was demobilized, waste was disposed of, and site was vacated.

5.5.1 STARTUP

Because much of the desired baseline characterization data existed for all of the test wells; the primary start up activity, included a thorough review of existing data and the measurement of water levels and contaminant concentrations prior to field testing. Groundwater levels were measured in each monitoring well and in nearby wells before and after testing.

5.5.2 LOW-FLOW SAMPLING

Prior to sampling, water level measurements were taken in each well to determine the current depth of the water column within the well screen and calculate the water volume within the well. Low-flow sampling was performed using peristaltic pumps to first remove three purge volumes (each purge volume being equal to the current water column volume) from each well prior to collecting a 40 ml aqueous sample. All spent water from the wells was disposed of through the onsite pump and treat system.

5.5.3 BMLS

Prior to sampling, water level measurements were taken in each well to establish the depth of the water table below top of casing. BMLS were sampled using multi-head peristaltic pumps so that all ports could be sampled at the same time in order to minimize inducing local vertical gradients within the well during sampling. Each BMLS port was sampled by first drawing three purge volumes (calculated based upon the tubing cross-sectional area and the depth of the sample port below the water table) in order to purge any pre-existing water from the sample tube, and then collecting 40 ml aqueous sample. The intent was to ensure that the total removed volume from each port was less than the interrogated volume within the well screen enclosed within the baffles. All spent water from the wells was disposed of through the onsite pump and treat system.

5.5.4 PFM AND BMLS

BMLS were sampled using the same procedure outlined in above section 5.5.3. PFM were sampled by homogenizing the granular activated carbon sorbent within each PFM segment by manually mixing prior to taking a sample in a 40 ml VOA vial. The depth to the center of each segment was recorded in the field to confirm the depth of flux measurements. All waste materials were disposed of by the University of Florida.

5.5.5 DEMOBILIZATION

It is estimated that the demonstration produced 5 kg of spent activated carbon waste, 1 kg of nylon socks, and 1 kg of plastic mesh. The University of Florida disposed of this waste. No equipment was left on site and no wells were decommissioned.

Table 2. Field Activity Gantt Chart

Task	2017												2018							
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug
Trip 1. Low-flow Sampling and depploy pressure transducers							XX													
Pressure transducers in place for water level measurements							--	--	--	--	--	--	--	--	--	--	--	--		
Trip 2. Field measurements to supplement existing data											XX	XX								
Trip 3-1. BMLS samples, Deploy shallow and deep well PFM, Retrieve shallow well PFM																		XX		
Trip 3-2. Retrieve deep well PFM, retrieve transducers, demobolize and leave site																		XX		

5.6 SAMPLING METHODS

The objective of the sampling plan is to acquire sufficient data to validate the technology performance in the field and allow regulatory agencies and managers to evaluate the innovative technology. Because the PFM provides time integrated measures of both water and contaminant fluxes temporal variations in flux are not a concern. However, spatial variations in flux can be significant. It is for this reason that PFM and BMLS are both designed to take samples at multiple depths in order to assess the vertical flux distribution. Subsequently, when the PFM and BMLS are deployed in well transects, the data can be used to assess the spatial distribution of flux through a planar boundary.

Sample Collection. Two types of samples will be collected during this study, ground water samples and sorbent samples from PFM. Tables 2 and 3 respectively provide details on the number and type of samples collected and methods of analysis. Sampling methods and sample handling procedures are briefly described here and discussed in more detail in Appendices B-D.

Water samples will be collected in 40-ml EPA VOA vials with zero headspace. Samples will be analyzed for target contaminants (TCE, DCE, and VC).

Sorbent samples will be collected from PFM following retrieval. Regular intervals of the PFM sorbent will be segmented and transferred to 40-ml VOA vials containing an extraction fluid such as isobutanol. Approximately 20 grams of sorbent will be extracted with 20 ml of solvent.

Sample Analysis. All samples will be analyzed at laboratories at the University of Florida. Volatile organics, including alcohol tracers, will be analyzed by direct liquid injection on Gas Chromatographs. Details of analytical methods are provided in Appendix B-D.

Detection limits are approximately 1 mg/L. Headspace analysis (HS) will be used in the event that low concentrations are encountered. Detection limits for HS is approximately 50 ug/L

Data Quality Parameters. Data quality will be maintained and checked throughout the project. Details on approaches for maintaining data quality are provided in the QA/QC plan in Appendix E.

Quality Assurance Sampling. A description of the quality assurance (QA) samples that will be collected, such as field duplicates, equipment blanks, trip blanks, and field blanks are provided in the QA/QC plan in Appendix E.

Calibration Procedures, Quality Control Checks, and Corrective Action. Initial and continuing calibration procedures for analytical instrumentation, quality control checks, and corrective actions are required to maintain reproducible experiments. These procedures are fully described in the QA/QC plan in Appendix E.

Data Quality Indicators. Simple regression analysis will be used to assess the quality of data collected at any single well. However, more sophisticated techniques of spatial analysis will be performed with data collected to assess the spatial mean and variance of contaminant and water fluxes evaluated over transects or within a plume.

Table 3. Total Number and Types of Samples Collected

Component	Matrix	Number of Samples	Analyte	Location
Lo-flow sampling	Groundwater	70	TCE, DCE	One from each well plus QA/QC.
PFM sampling	GAC Sorbent	5 per PFM	Contaminants: TCE, DCE Alcohol tracers: Methanol Ethanol Isoproponal Tert-butyl alcohol 2,4 dimethyl - pentanol	One PFM per each well.
BMLS sampling	Groundwater	200 or 10 per BMLS	TCE, DCE	One BMLS per each well.

Table 4. Analytical Methods for Sample Analysis

Matrix	Analyte	Method	Container	Preservative[1]	Holding Time
Groundwater	TCE, DCE	Appendices B-D	EPA VOA Vials	None	14 days
GAC sorbent	Alcohol tracers: Methanol Ethanol Isopropanol Tert-butyl alcohol 2,4 dimethyl - pentanol	Appendices B-D	EPA VOA Vials	Isobutyl Alcohol	14 days
GAC sorbent	TCE, DCE	Appendices B-D A	EPA VOA Vials	Isobutyl Alcohol	14 days

5.7 SAMPLING RESULTS

As outlined in section 5.5 the fieldwork was organized into a series of three trips:

Trip 1: Low-flow water sampling

Trip 2: BMLS sampling

Trip 3-1 and 3-2: BMLS and PFM sampling

A site map showing the distribution of wells used for recording water levels along with BMLS and PFM sampling is provided in Figure 7. The sampling results for each trip are summarized in the following sections.

5.7.1 TRIP 1: LOW-FLOW WATER SAMPLING.

The research team completed the first phase of fieldwork at JBLM during the period July 18 – July 25, 2017. A team of six researchers (two from the University of Florida and 4 from the U.S. EPA) spent 8 days on site and completed the following tasks:

1. Performed low flow sampling of 57 wells in order to evaluate the current spatial distribution of aqueous contaminants on site. Sample results are summarized below.
2. Deployed 23 pressure transducers to evaluate the groundwater gradient on site. Pressure transducers continuously record water levels for the entire duration of fieldwork on site (one year).

Summary of low-flow sampling results:

Number of wells sample 57 (with additional QA/QC samples)

Average DCE concentration: 10 ppb
Minimum DCE concentration: 1 ppb (with 26 Non-Detects and 7 Below Detection Limit (1 ppb)
Maximum DCE concentration: 72 ppb (mg/L)

Average TCE concentration: 43 ppb
Minimum TCE concentration: 1 ppb (with 1 Non-Detect and 3 Below Detection Limit (1 ppb)
Maximum TCE concentration: 837 ppb (mg/L)

It was observed that TCE concentrations were highest in NAPL Area 1 (Figure 8) with a maximum value of 837 mg/L, while DCE concentrations were highest in NAPL Area 3 (Figure 9) with a maximum value of 72 mg/L. The results from Trip 1 were used to inform the deployment strategy of baffled multilevel samplers (BMLS) during Trip 2 with the objective being to deploy in wells with significant contaminant concentrations and avoid sampling wells with no aqueous contaminants present.

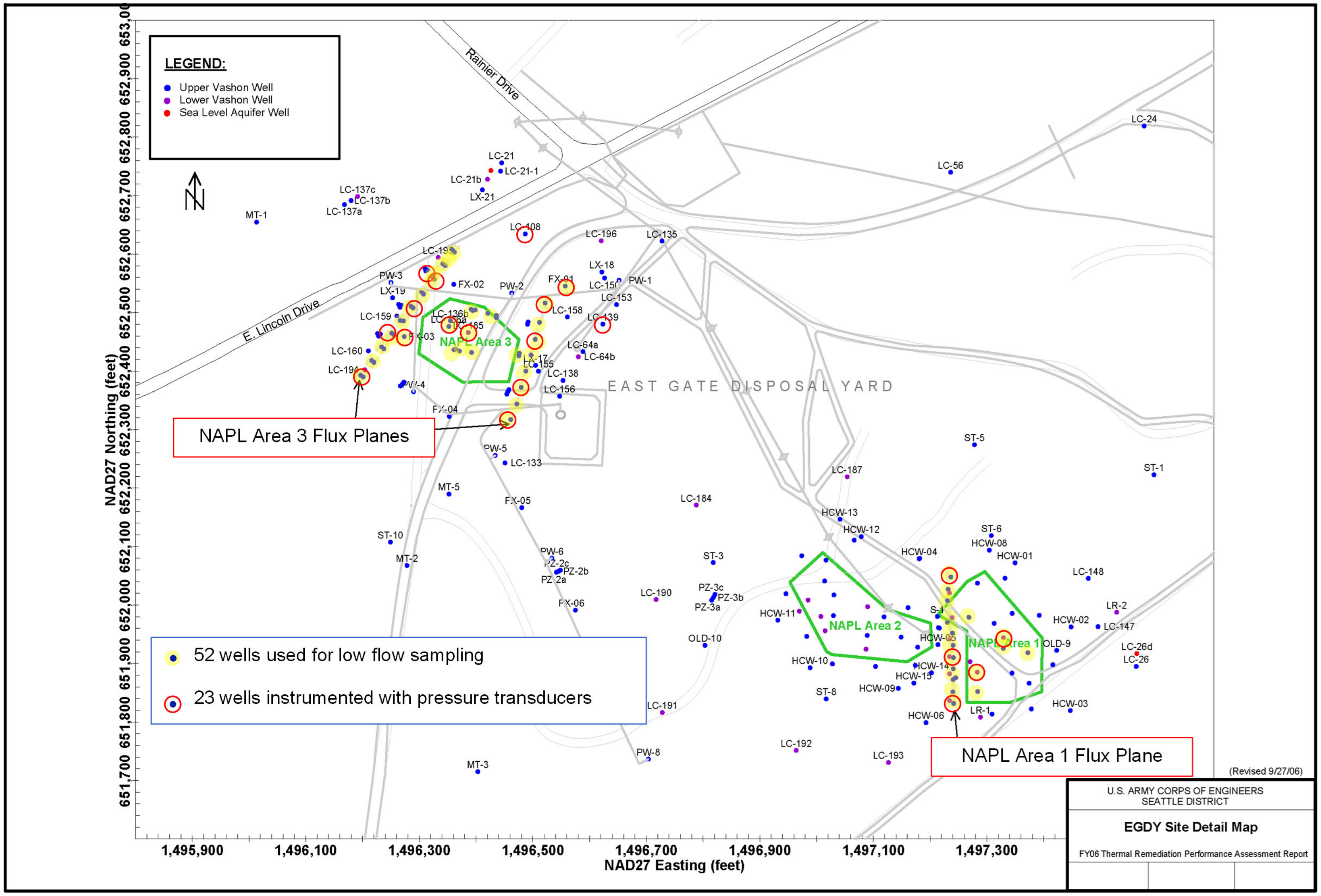


Figure 7. Monitoring Well Distribution Used for Low-Flow Sampling, BMLS and PFM Deployments.

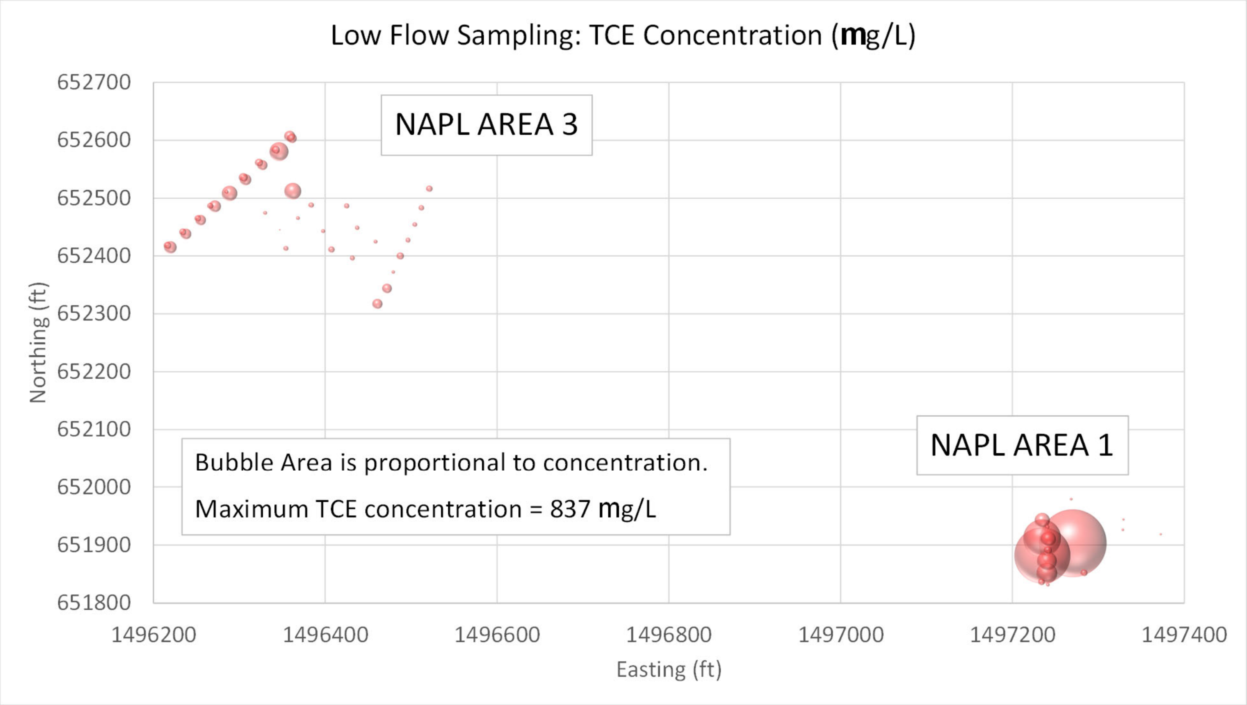


Figure 8. **Low-flow Sampling TCE Aqueous Concentrations.**

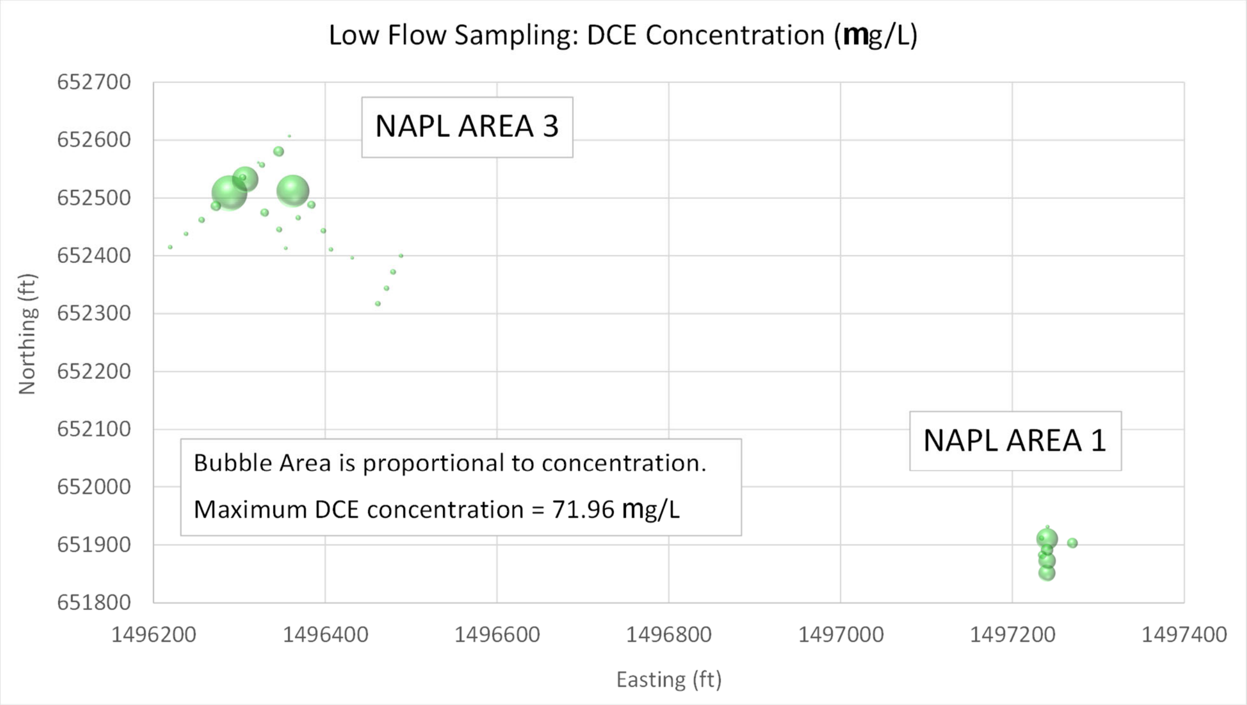


Figure 9. **Low-flow Sampling DCE Aqueous Concentrations.**

5.7.2 TRIP 2: BMLS SAMPLING.

The research team completed the second phase of fieldwork at Joint Base Lewis-McChord during the period (November 29 – December 10, 2017). A team of researchers (two from the University of Florida and 2 from the U.S. EPA) spent 8 days on site performing the following tasks:

1. Assembled and deployed baffled multi-level samplers (BMLS) in 14 wells composing two flux transects, one down-gradient of NAPL Area 1 (Figure 10) and one down-gradient of NAPL Area 3 (Figure 12). The BMLS were constructed with a 2.5 ft (0.76 m) vertical separation between ports allowing for measurement of the vertical distribution of aqueous contaminant concentrations within the wells.
2. The BMLS were allowed to equilibrate for a 24-hour period and then aqueous samples were collected from multiple ports over the screened interval of each well. In total 108 ports were sampled (108 aqueous samples collected).
3. BMLS were retrieved and stored on site for use during the final stage of fieldwork (Trip 3).
4. Downloaded data from 23 pressure transducers to evaluate the groundwater gradient on site. Pressure transducers were left in place for continued measurement of the onsite hydraulic gradient.

The results are summarized below:

Number of water samples: 108 (with additional QA/QC samples)

Average DCE concentration:	61.55 ppb (mg/L)
Minimum DCE concentration:	0 ppb (mg/L)
Maximum DCE concentration:	1446 ppb (mg/L)
Average TCE concentration:	151.5 ppb (mg/L)
Minimum TCE concentration:	8.2 ppb (mg/L)
Maximum TCE concentration:	1848 ppb (mg/L)

The BMLS aqueous contaminant concentrations from Trip 2 are shown in Figures 11 and 13. It can be seen that aqueous TCE concentrations vary by an order of magnitude between Area 1 and Area 3, with the highest concentrations observed in wells LC205 and LC208 in NAPL Area 1 (Figure 11). The BMLS samples indicate that wells with higher concentrations show considerable vertical variation in aqueous contaminant concentrations.

In NAPL Area 3 the highest TCE concentrations were observed in well FX3-05 and footprint well NW EW-1a (Figure 13). It should be noted that DCE concentrations were also elevated in both of these wells.

Within both Area 1 and Area 3 a footprint well was included along with the flux transect wells. These wells are within the footprint of the original remediation zone for each area and were identified during low-flow sampling because they have high contaminant concentrations. The highest aqueous TCE concentration observed during low-flow sampling (837 mg/L) was measured in the NAPL Area 1 footprint well (NAPL1-F11). Historic flux data does not exist for the footprint wells, but they were included due to their high contaminant concentrations and for contemporary comparison to flux values within each transect.

The BMLS results from Trip 2 were used to inform the deployment strategy of BMLS and PFM during the final phase of the fieldwork (Trip 3) in order to evaluate the spatial distribution of contaminant flux through the NAPL Area 1 and NAPL Area 3 transects.

The pressure transducer data were used to evaluate the hydraulic gradient on site, and results suggest that the gradient may have decreased significantly in some parts of the site (by an order of magnitude) when compared to historical data from previous PFM deployments on site. This is likely due to the presence of the pump and treat system.

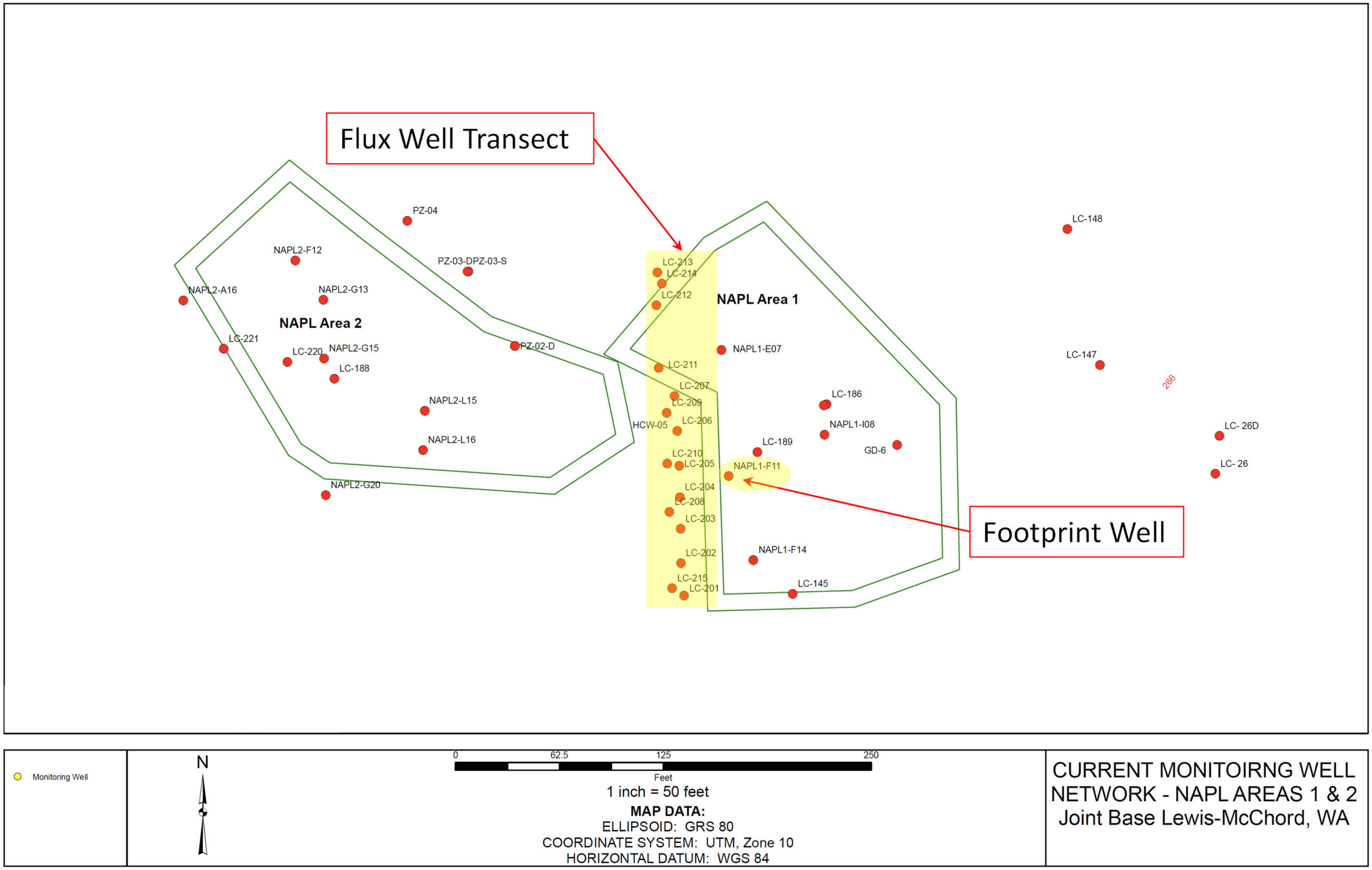
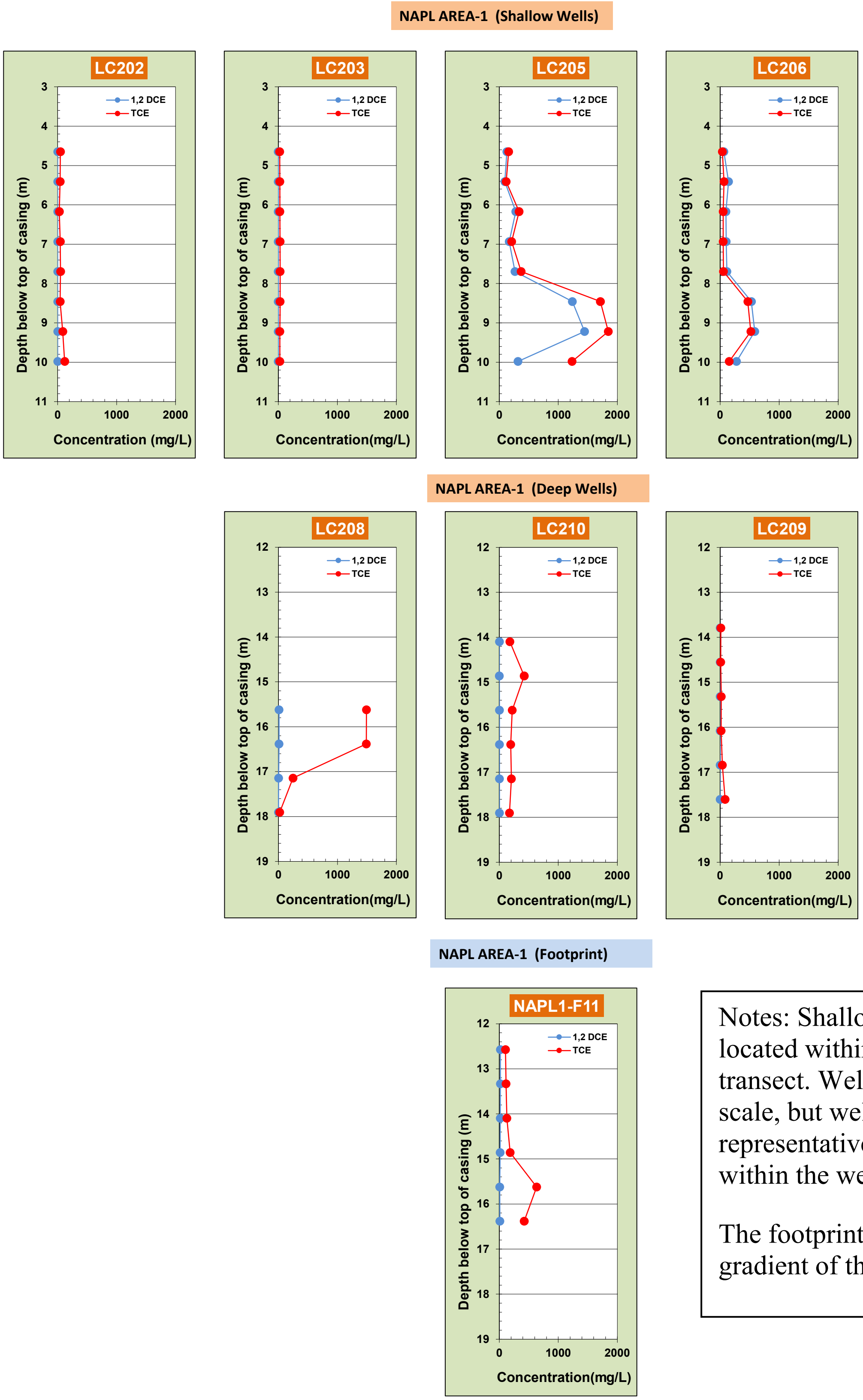


Figure 10. NAPL Area 1 Monitoring Wells.



Notes: Shallow and deep wells are located within the same flux transect. Well spacing is not to scale, but well order is representative of the spatial order within the well transect.

The footprint well is located up-gradient of the flux transect.

Figure 11. NAPL Area 1 BMLS (2017) Aqueous Contaminant Concentrations.

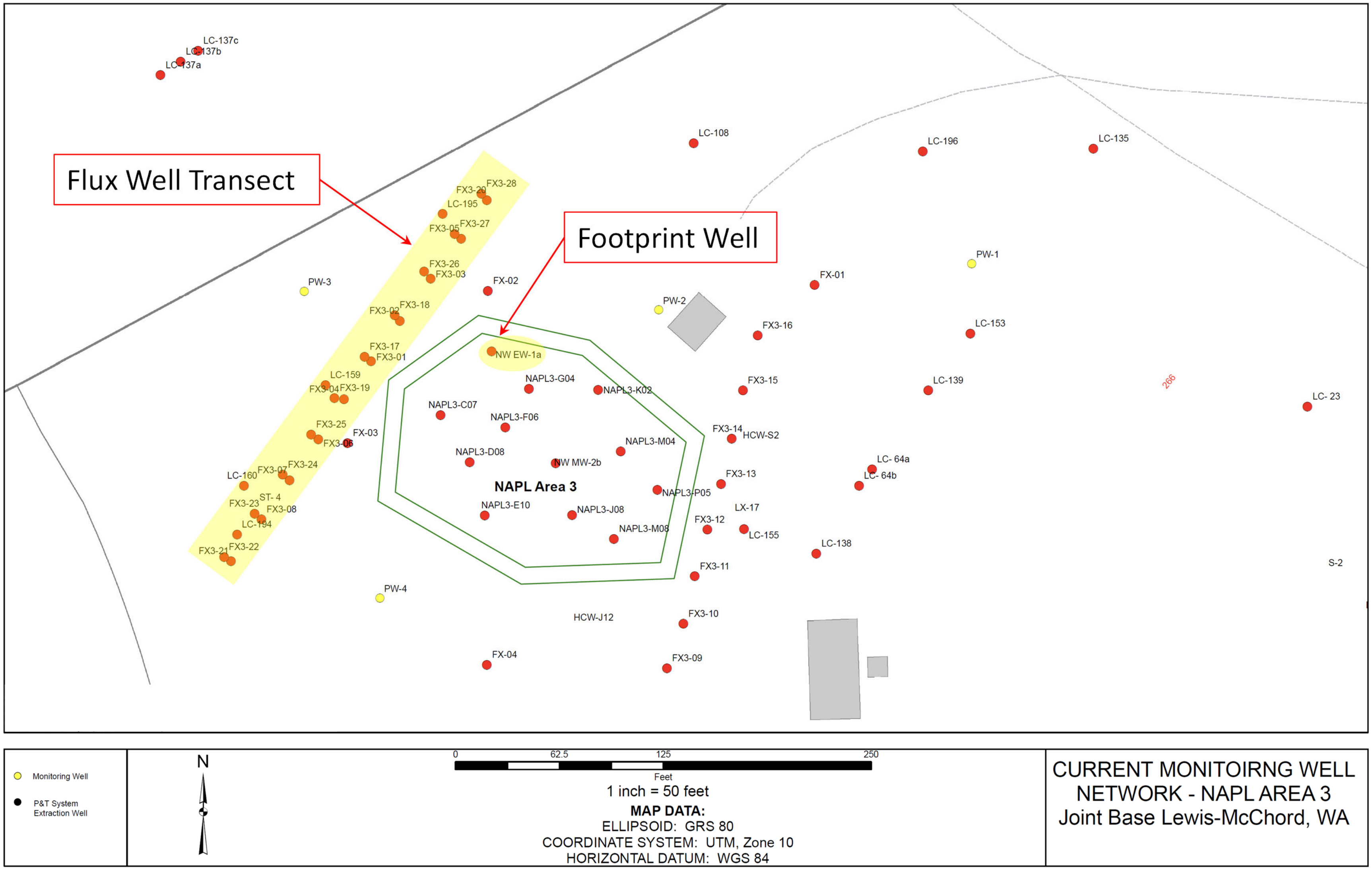
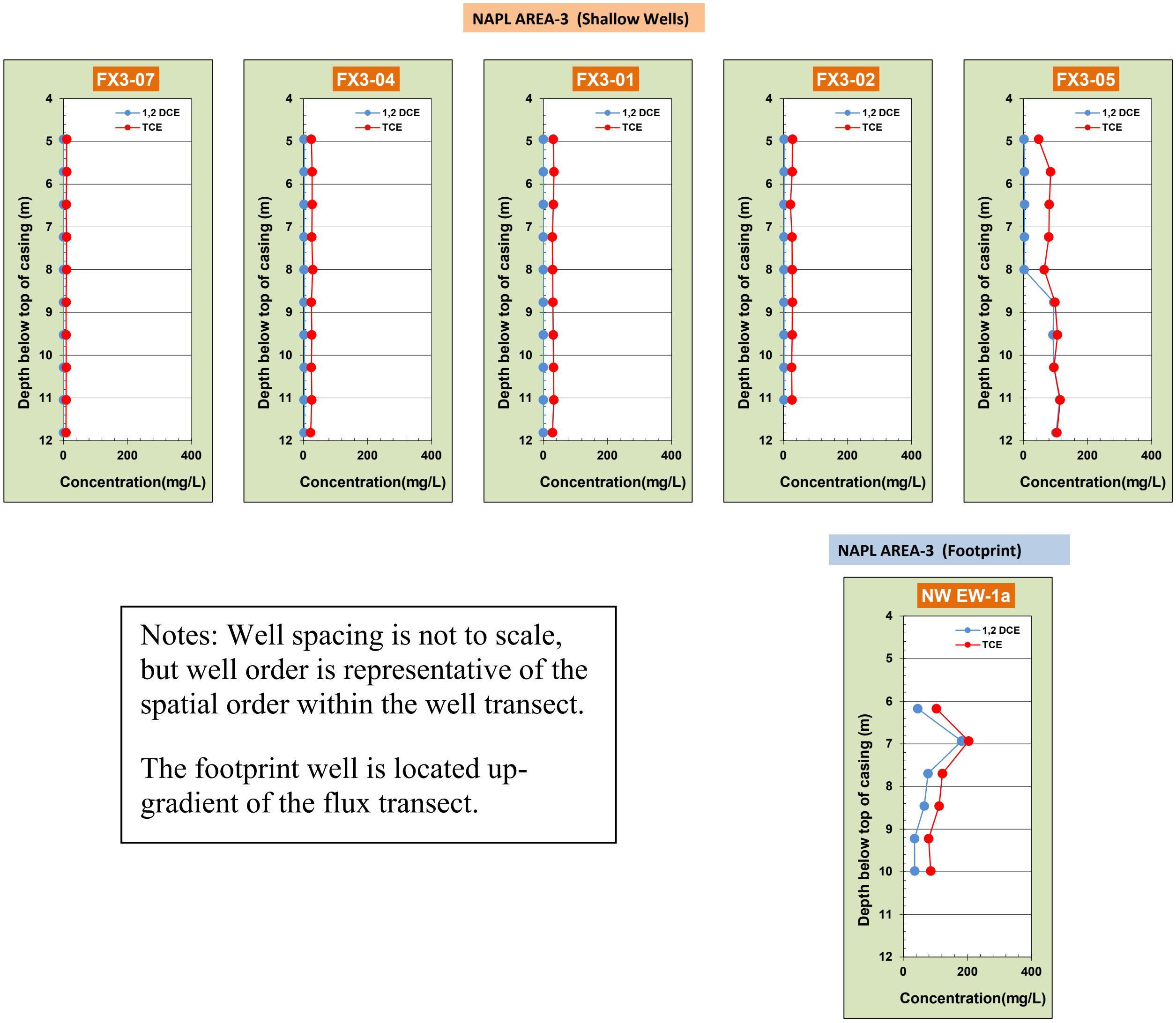


Figure 12. NAPL Area 3 Monitoring Wells.



Notes: Well spacing is not to scale, but well order is representative of the spatial order within the well transect.

The footprint well is located up-gradient of the flux transect.

Figure 13. NAPL Area 3 BMLS (2017) Aqueous Contaminant Concentrations.

5.7.3 TRIP 3: BMLS AND PFM SAMPLING

The research team completed the final phase of fieldwork during June 2018.

During Trip 3-1 (June 4-14, 2018) the following tasks were performed:

1. Deployed baffled multi-level samplers (BMLS) in 10 wells comprising two flux transects, one in NAPL Area 1 and one in NAPL Area 3. The BMLS were constructed with a 2.5-ft (0.76 m) vertical separation between ports allowing for measurement of the vertical distribution of aqueous contaminant concentrations within the wells.

2. The BMLS were allowed to equilibrate for a 24-hour period and then aqueous samples were collected from multiple ports over the screened interval of each well. In total 100 ports were sampled (100 aqueous samples were collected along with additional QA/QC samples).

3. BMLS were then retrieved and PFM were deployed in the same 10 wells to quantify both water and contaminant mass flux.

4. Based upon historical data and estimated gradients from water level data obtained during this study, the groundwater velocity in the shallow wells is considerably higher than that in the deep wells. In order to avoid complete elution of resident tracers (by leaving the devices in too long) or contaminant mass fluxes below device detection limit (by not leaving the devices in long enough), the PFM had to be deployed for different durations. The shallow well PFM were deployed for 5 days, while the deep well PFM were deployed for 14 days. Due to the shorter duration deployment, the shallow wells were retrieved and sampled during Trip 3-1. While the longer duration deep wells were retrieved and sampled during the final Trip 3-2.

During the final Trip 3-2 (June 22-26, 2018) the following tasks were performed:

1. Retrieved and sampled 28 PFM from deep wells.

2. Downloaded data from 23 pressure transducers to evaluate the groundwater gradient on site during the entire duration of this study.

3. Surveyed top of casing for subset of wells to assure all data was accurate and consistent.

4. All equipment and materials were retrieved and the site was cleared.

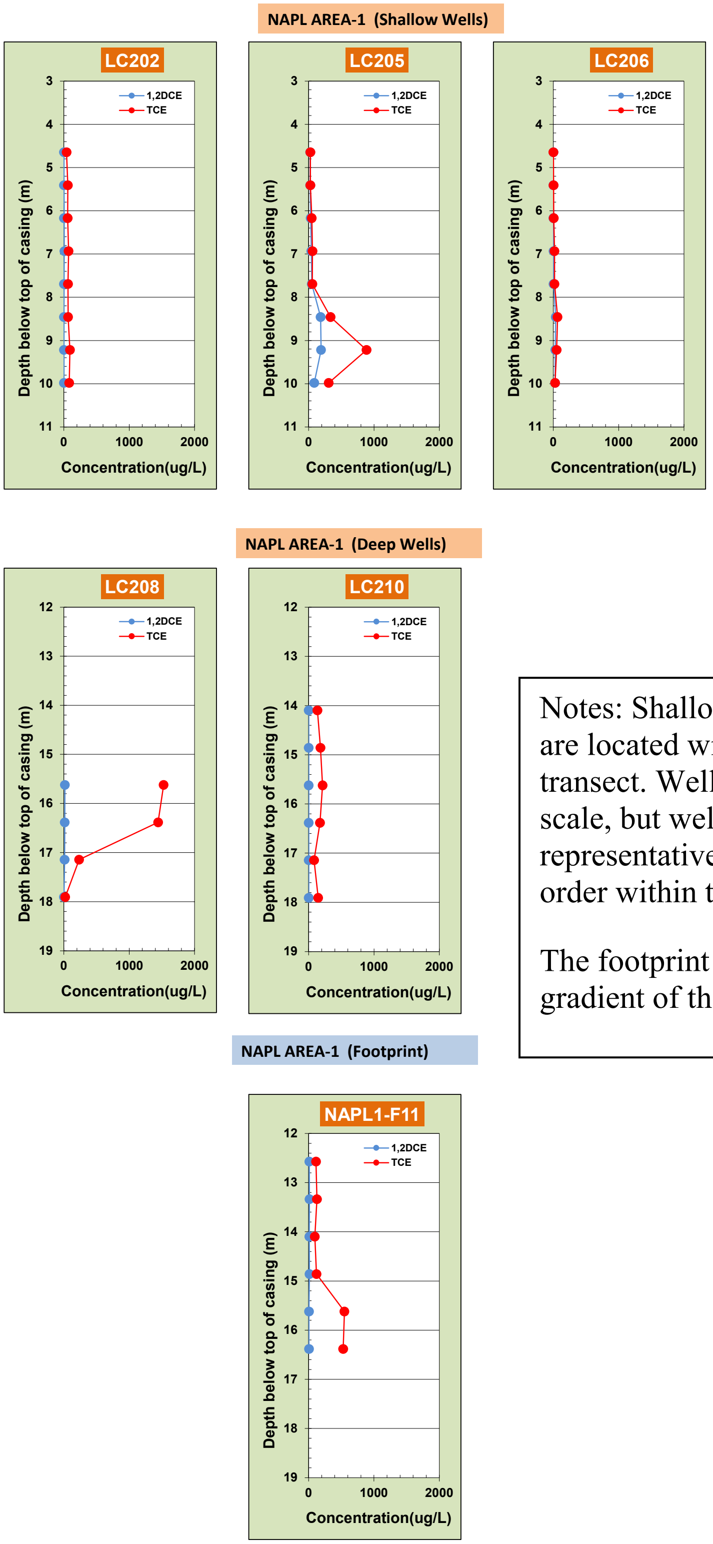
The BMLS aqueous contaminant concentrations from Trip 3-1 are summarized in Figures 14 and 15. As with the 2017 BMLS data, it can be seen that aqueous TCE concentrations vary by an order of magnitude between Areas 1 and Area 3, with the highest concentrations observed in wells LC205 and LC208 in NAPL Area 1. The 2018 concentrations in LC208 were similar to those observed in 2017, but wells LC205 and LC206 exhibited significant decreases in concentrations from 2017 to 2018. The footprint well NAPL1-F11 had consistent concentrations between 2017 and 2018.

In NAPL Area 1, the BMLS measured concentrations decreased slightly in FX3-05 and remained consistent in footprint well NW EW-1a when compared to 2017 values.

When compared to the BMLS aqueous concentrations, the 2018 PFM measured fluxes show a slightly different depiction of the conditions in NAPL Areas 1 and 3 (Figures 16 and 17 respectively). In NAPL Area 1, the highest TCE fluxes were observed in wells LC208, LC210 and the footprint well NAPL1-F11, while well LC205 had much lower TCE fluxes.

In NAPL Area 3 the highest TCE fluxes were observed in well FX3-04 and footprint well NW EW-1a (it should be noted that DCE fluxes were also elevated in NW EW-1a).

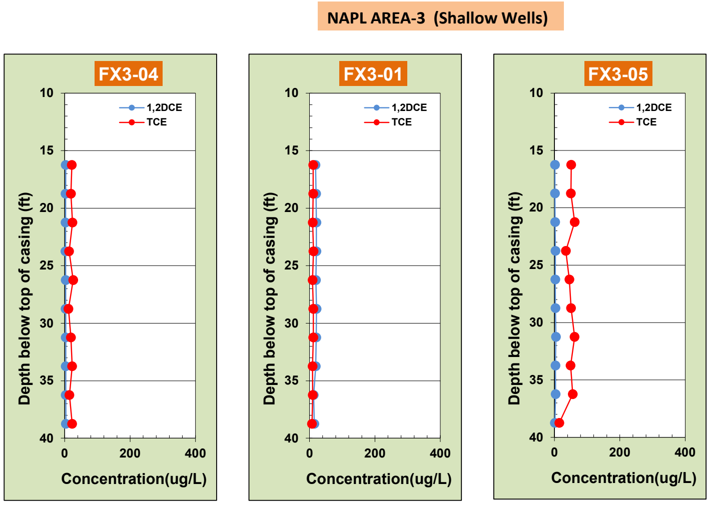
It can be seen that comparison of aqueous concentrations and contaminant mass flux may not provide similar details, so it is better to compare results using a consistent measure. By using the PFM measured Darcy Velocities, the BMLS aqueous concentrations can be used to calculate TCE and DCE fluxes for direct comparison. These comparisons and subsequent analysis are discussed in the next section.

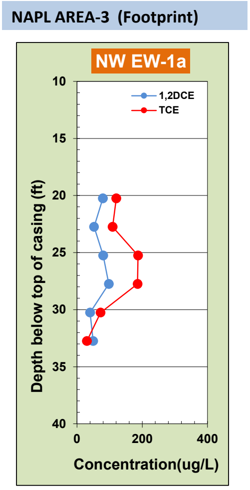


Notes: Shallow and deep wells are located within the same flux transect. Well spacing is not to scale, but well order is representative of the spatial order within the well transect.

The footprint well is located up-gradient of the flux transect.

Figure 14. NAPL Area 1 BMLS (2018) Aqueous Contaminant Concentrations.

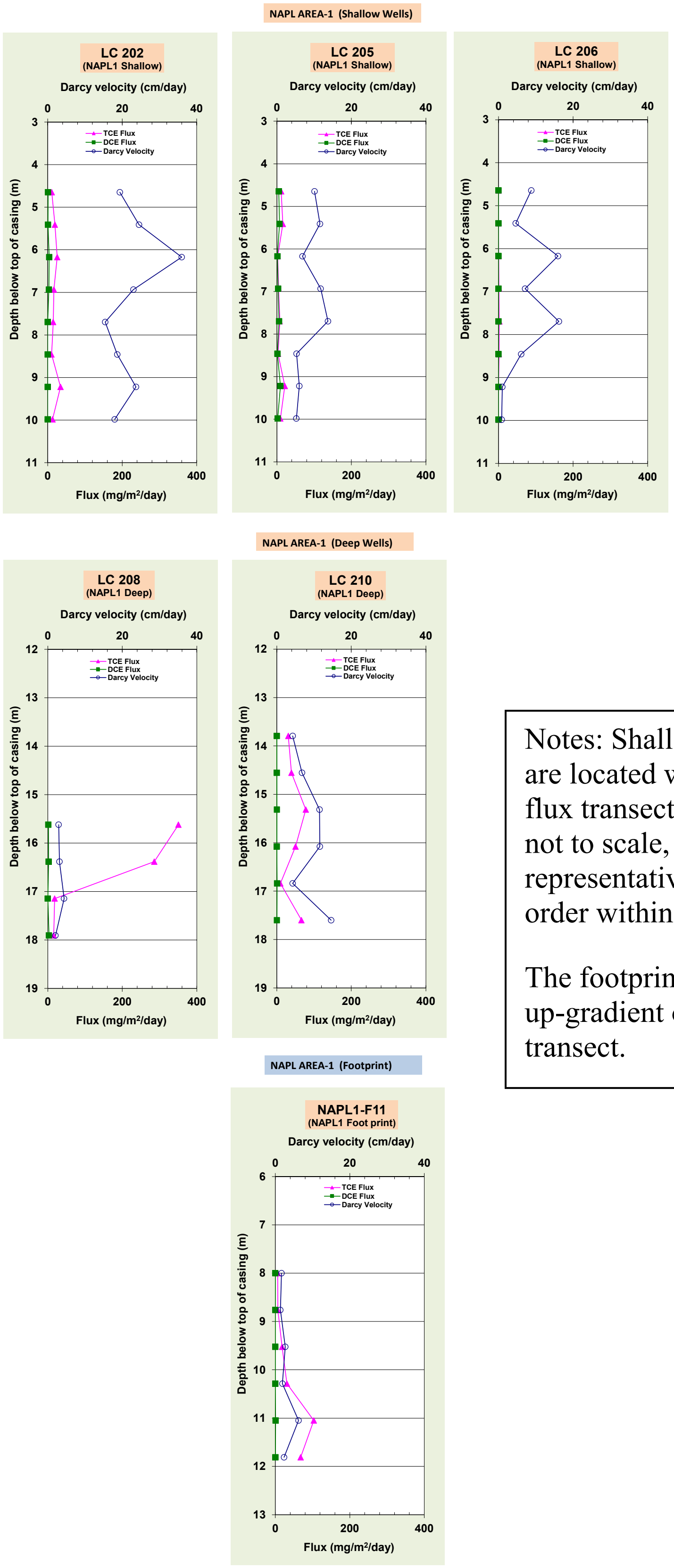




Notes: Well spacing is not to scale, but well order is representative of the spatial order within the well transect.

The footprint well is located up-gradient of the flux transect.

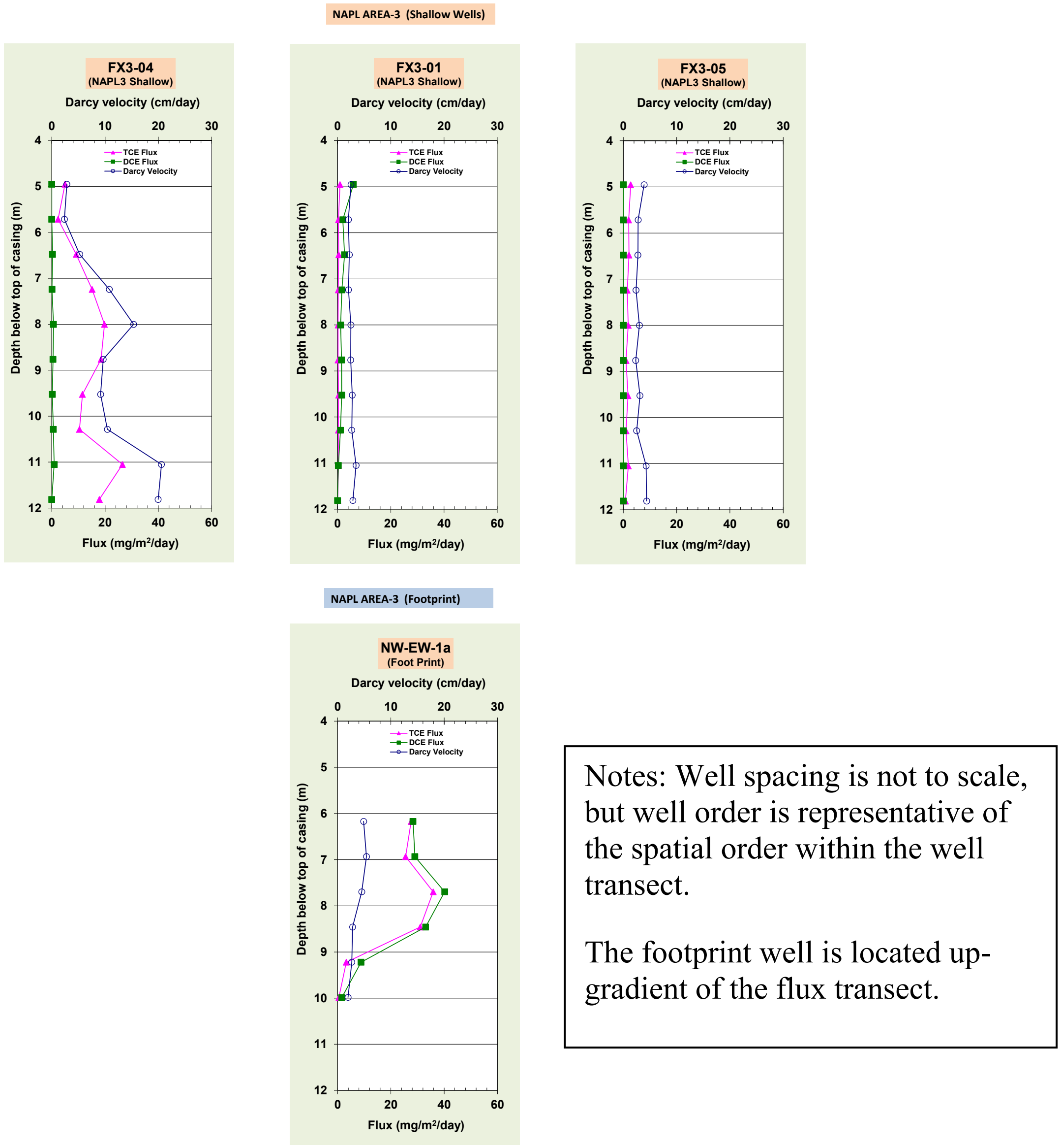
Figure 15. NAPL Area 3 BMLS (2018) Aqueous Contaminant Concentrations.



Notes: Shallow and deep wells are located within the same flux transect. Well spacing is not to scale, but well order is representative of the spatial order within the well transect.

The footprint well is located up-gradient of the flux transect.

Figure 16. NAPL Area 1 PFM (2018) Fluxes.



Notes: Well spacing is not to scale, but well order is representative of the spatial order within the well transect.

The footprint well is located up-gradient of the flux transect.

Figure 17. NAPL Area 3 PFM (2018) Fluxes.

5.8 MODELING AND ANALYSIS

5.8.1 TIME SERIES DATA: NAPL AREA 1 SHALLOW WELLS

Since pre-remediation, the NAPL Area 1 shallow well transect has been the basis of multiple studies by our team (Brooks et al., 2008; Klammler et al., 2012; and Annable et al., 2014). As such, this transect has the most complete record of flux data on site and will be the primary focus of the following discussion. The record of TCE and DCE fluxes for the NAPL Area 1 shallow well transect is summarized in Figures 18 and 19. Figure 18 encompasses the right portion of the transect when looking down-gradient through the transect, while Figure 19 encompasses the left portion. Not all wells from the shallow well transect shown in Figure 10 are represented in these figures. Wells that had minimal TCE and DCE concentrations during the 2017 low-flow sampling event were not included in subsequent sampling, such as the wells at either end of the transect (LC-213 and LC-201).

It is important to note the change in scale for the measured fluxes when comparing the pre-remediation and post-remediation flux values. In the right portion of the transect (Figure 18) the pre-remediation fluxes were four orders of magnitude greater than post-remediation, while in the left portion of the transect (Figure 19) the pre-remediation fluxes were an order of magnitude higher than the post-remediation fluxes. It can be seen that pre-remediation the highest TCE and DCE fluxes were observed in right side of the transect with well LC207 having the highest TCE fluxes and well LC212 having the highest DCE fluxes.

A comparison of PFM-measured flux distributions from pre-remediation to 2018 post-remediation is provided in Figure 20. Post-remediation there was a significant decrease in contaminant mass flux throughout the entire transect, and the spatial distribution of flux was shifted to the left side of the transect with little to no measurable flux in the right side. These results are more clearly evident when looking at the estimated TCE and DCE mass discharge in Figures 21 and 22 respectively. It can be seen that pre-remediation both the TCE and DCE mass discharge was predominantly in the right side of the transect with wells LC205, LC206, LC207 and LC211 having the highest TCE discharges (Figure 21) and the center of mass appearing to be located in the proximity of LC206, LC207 and LC211. Then, post-remediation, there is a significant decrease in the overall discharge magnitude and a significant shift spatially as mass discharge is predominantly in the left side of the transect with wells LC202, LC203 and LC205 having the highest TCE discharges (Figure 21).

Throughout the post-remediation sampling events measured mass discharges can be seen to fluctuate, with the earliest 2006 values (recorded soon after remediation) typically having the highest values in most wells. However, during the 2017 BMLS sampling event, the discharges were elevated throughout the site and wells LC205 and LC206 were observed to have TCE discharges greater than the initial 2006 post-remediation values. The exact reason for this increase is not certain, but the pump and treat system had been shut down for maintenance prior to this sampling event which could likely lead to an apparent contaminant rebound and an increase in aqueous contaminant concentrations. All subsequent sampling events showed significantly lower contaminant discharges. However, it is important to note that other than during the initial low flow sampling event, wells LC205 and LC206 consistently had similar or higher TCE discharges in the more recent sampling events (2017-2018) when compared to the initial 2006 post-remediation measurements (Figure 21).

Figure 18. Comparison of Pre- and Post-remedial Fluxes Within the NAPL Area 1 Shallow Well Flux Transect (Right Portion of the Transect When Looking Down-gradient Through the Transect).

There is a Significant Change in Flux Magnitude from Pre-remediation to Post-remediation.

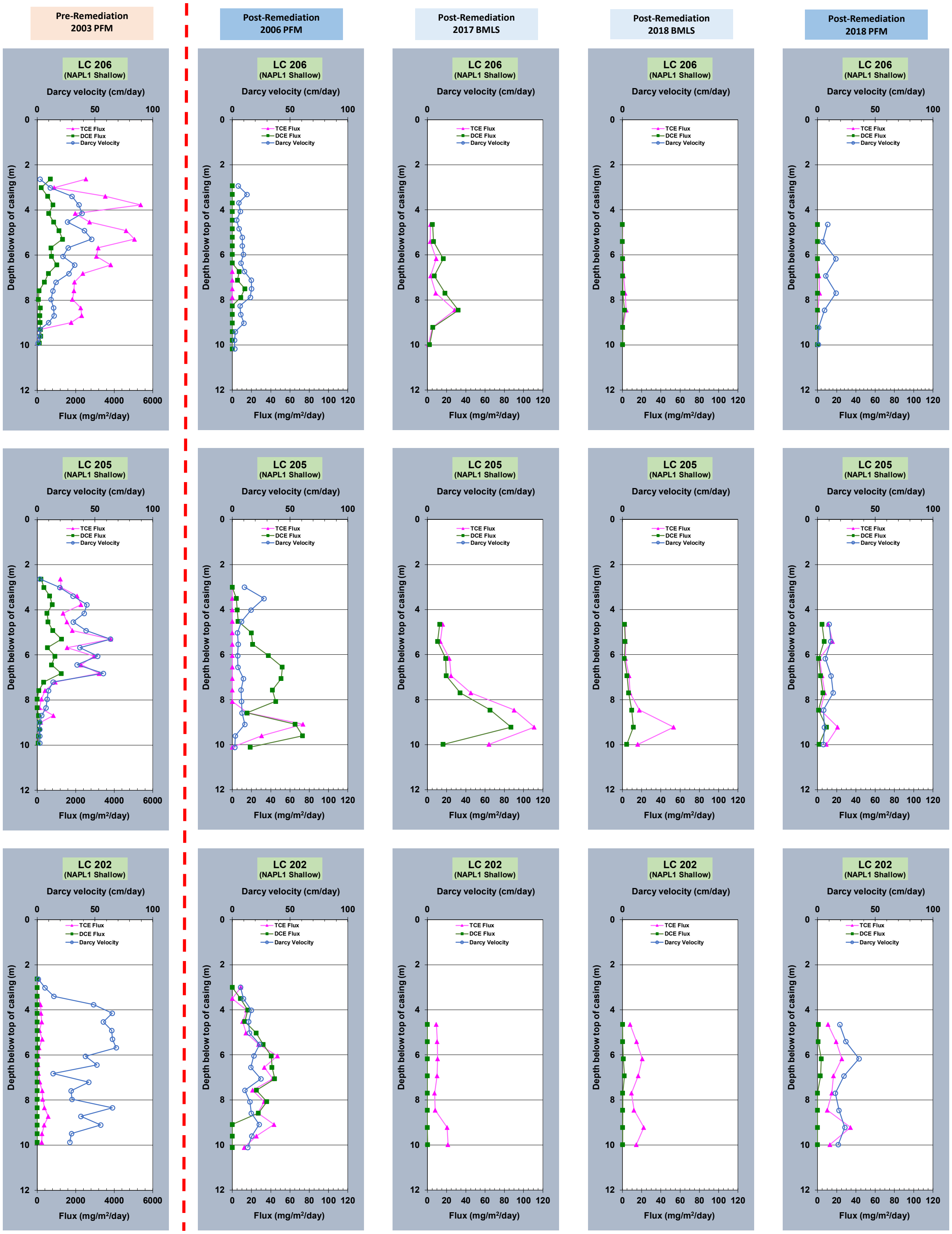


Figure 19. Comparison of Pre- and Post-remedial Fluxes Within the NAPL Area 1 Shallow Well Flux Transect (Left Portion of the Transect When Looking Down-gradient Through the Transect).

There Is a Significant Change in Flux Magnitude from Pre-remediation to Post-remediation.

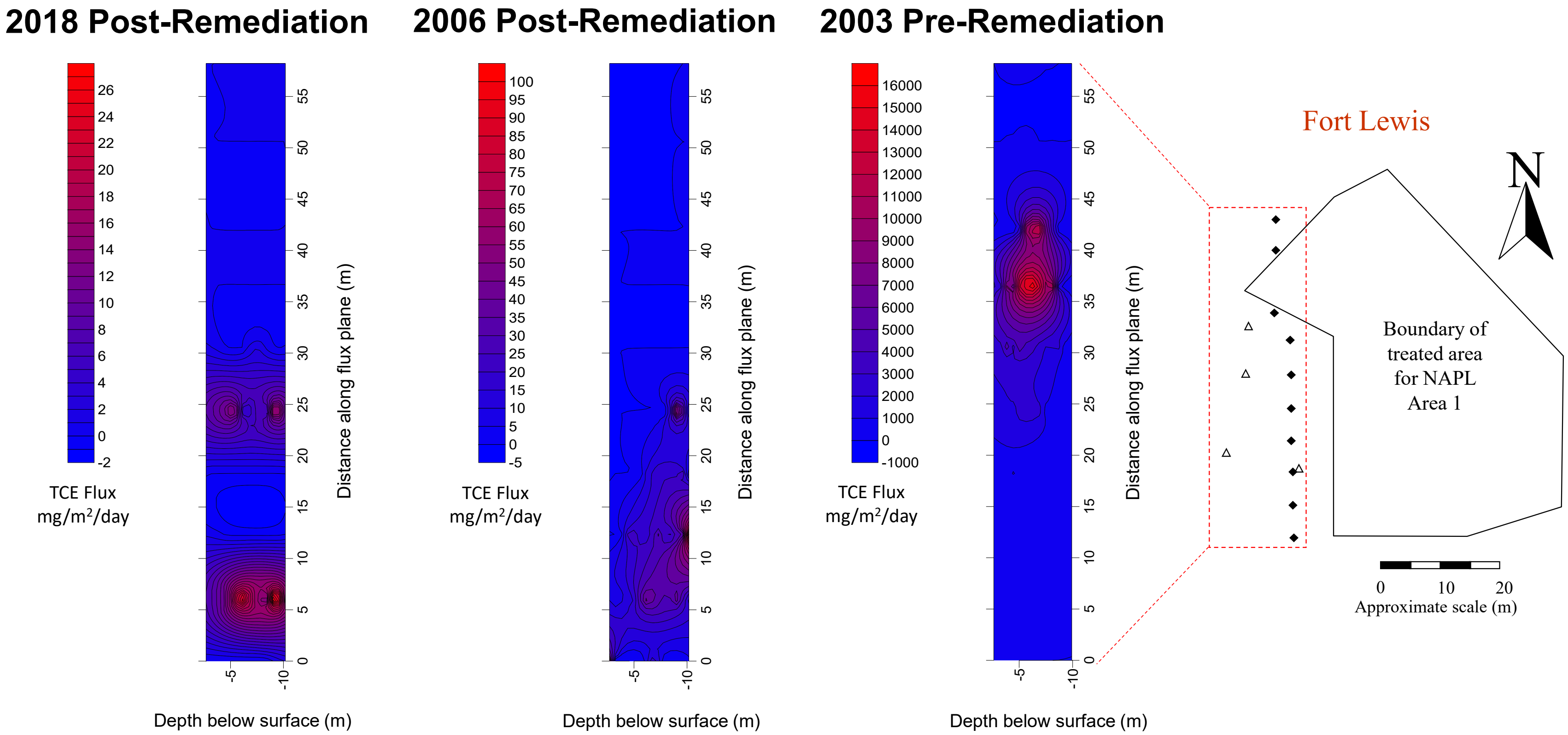
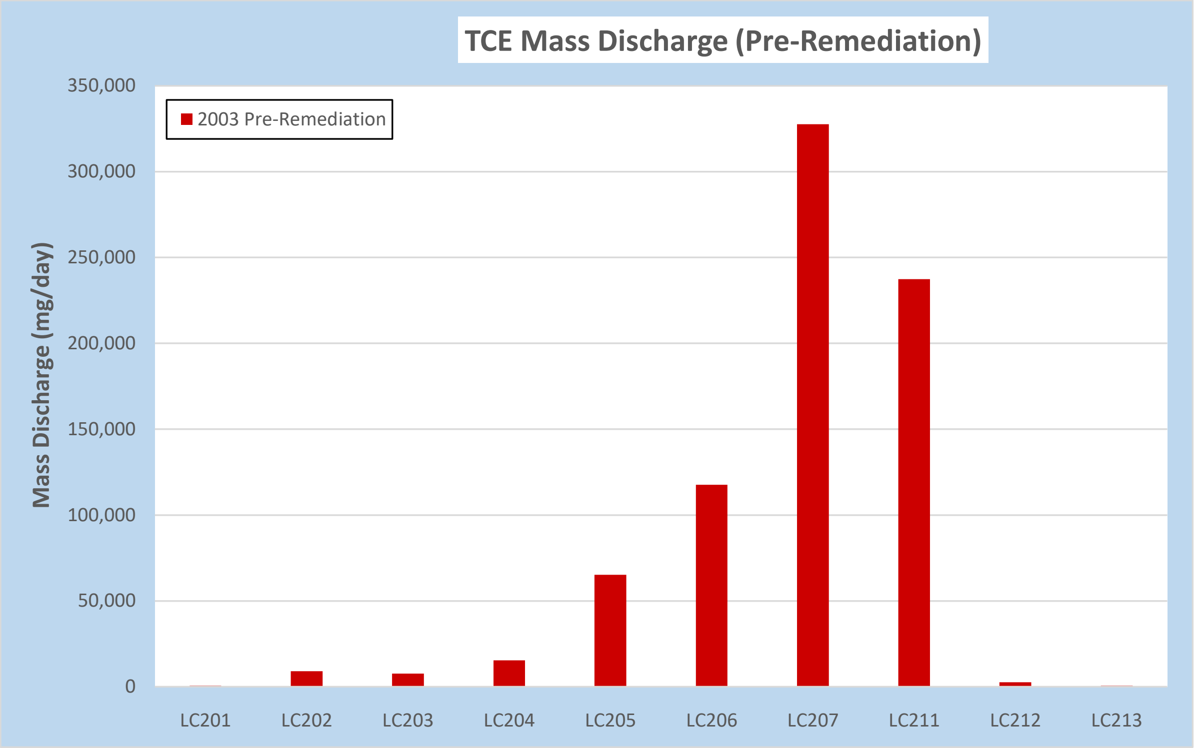


Figure 20. NAPL Area 1 Comparison of Pre-remediation (2003) and Post remediation (2006 and 2018) TCE Mass Flux Distributions.

Note the significant decrease in flux magnitude and shift in spatial distribution from pre-remediation to post-remediation.



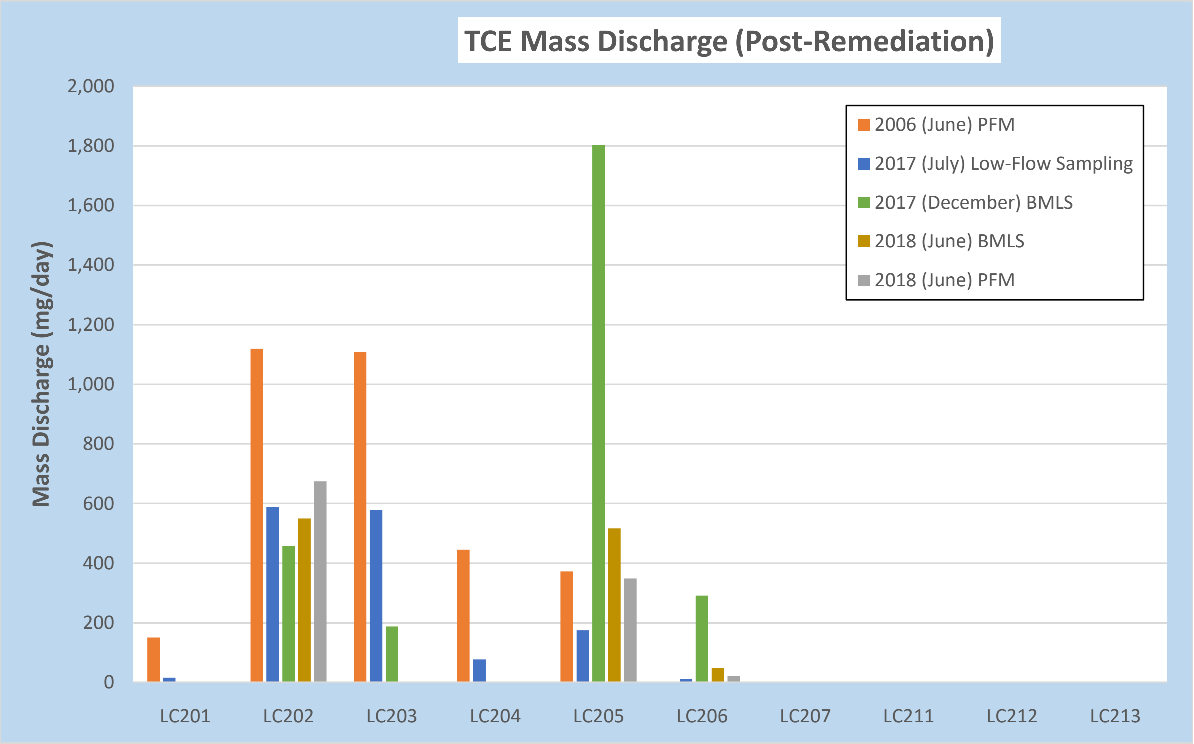


Figure 21. Record of Estimated TCE Mass Discharges through NAPL Area 1 Shallow Well Transect.

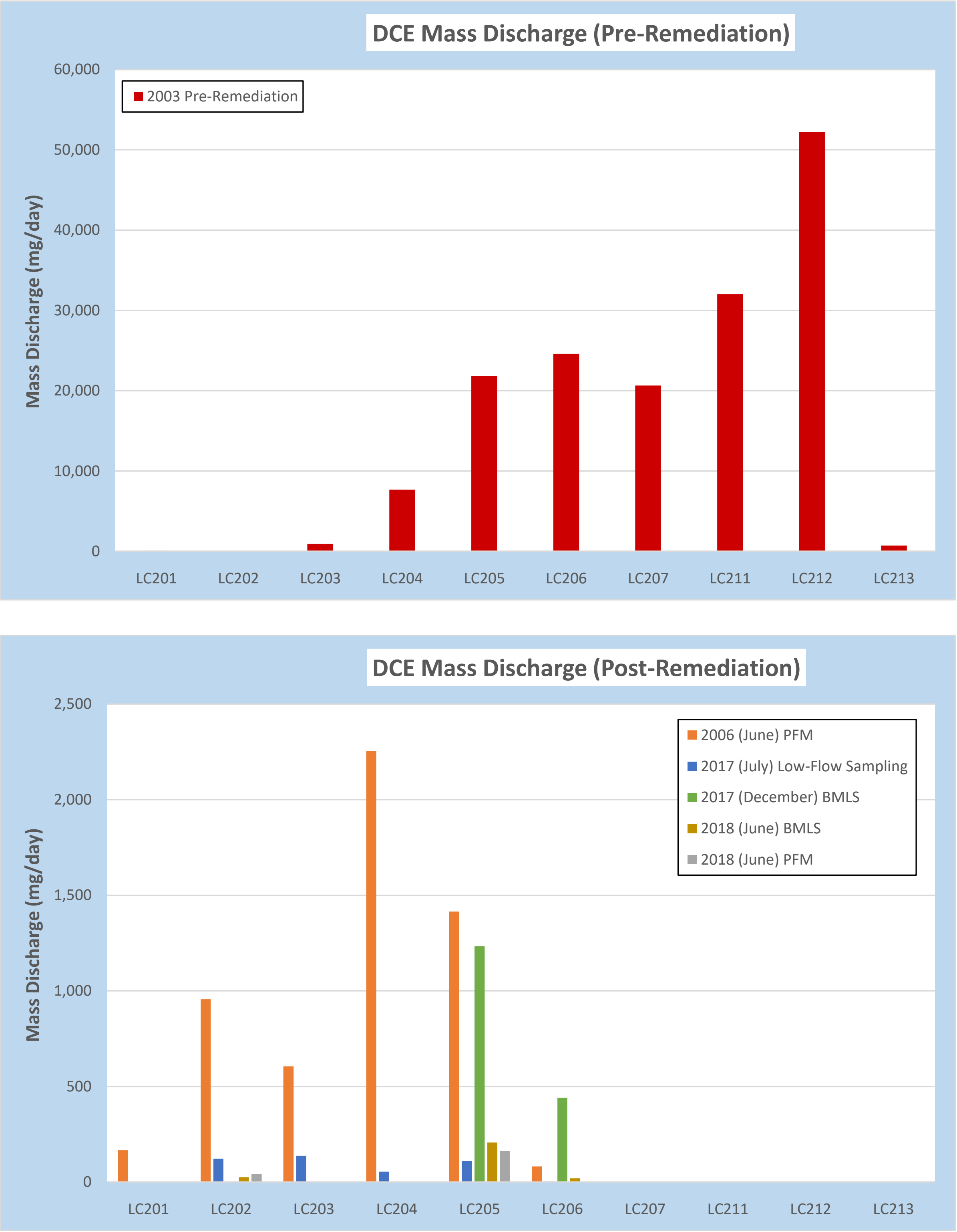


Figure 22. Record of Estimated DCE Mass Discharges through NAPL Area 1 Shallow Well Transect.

5.8.2 TIME SERIES ANALYSIS: NAPL AREA 1 SHALLOW WELLS

Based upon the general observations from the flux and discharge time series data, the overall goal of this analysis is to probabilistically quantify the differences in contaminant discharges (TCE and DCE) across the well transect for different sampling events starting with pre-remediation and continuing through a period of 15 years. We achieve this through an extension of the approach presented by Klammler et al., 2012, which provides cumulative distribution functions (cdfs) of individual discharge estimates, as well as of the pairwise discharge differences. We infer the geostatistical characteristics of the fluxes from the available measurements and stochastically simulate fluxes at unmonitored locations. Hereby, we explore the possible cross-correlation between flux measurements in different years, while allowing for a spatial shifting of the plume within the transect to maximize the cross-correlation.

A large cross-correlation between sampling events is beneficial for the estimation of discharge differences, because estimation errors of individual transect discharges tend to cancel each other out to some degree, when taking the difference of discharges. Theoretically, for perfect correlation between fluxes of different sampling events, there would still be uncertainty about individual discharge estimates due to the spatial interpolation of fluxes at unmonitored locations; however, the uncertainty about the estimate of the discharge difference would vanish.

In principle, the measured fluxes across the transect at different moments in time could be regarded as a realization of a three-dimensional stochastic process, with the third dimension being time. However, the computational effort for considering all (five) sampling events simultaneously would be very large and require the inference of space-time cross-correlations from quite limited data. Hence, we proceed by taking a simplified hierarchical approach (Goovaerts, 1997, p. 391) between pairs of sampling events and use collocated co-simulation to avoid numerical instabilities due to large amounts of highly redundant conditioning data (Goovaerts, 1997, p. 239).

As an example, consider the sampling events of 2003 (pre-remediation) and 2006 (post-remediation). We simulate contaminant fluxes for 2003 as in Klammler et al., 2012 for TCE using the (Gaussian) LU-decomposition method with normal score transformation and conditioning on the data obtained in 2003. Next, we simulate contaminant fluxes for 2006 using sequential (Gaussian) simulation with conditioning onto the data obtained in 2006, plus the collocated flux value simulated for 2003, if available. Since this “collocated location” is different for each grid point in 2006, the sequential approach was necessary here. As “collocated” we define the nearest grid point with a simulated flux value for 2003 (that is within 30 cm of the grid location) for which a flux is to be simulated in the 2006 transect. Since the plume may have shifted across the well transect between sampling events, but the wells remained the same, some portions of the 2006 simulation grid may not have a collocated 2003 flux value nearby for conditioning.

The conditioning to the collocated fluxes considers the correlation between fluxes measured in 2003 (pre-remediation) and 2006 (post-remediation). For this purpose, we compute a cross-correlation surface, which represents the values of flux cross-correlation obtained for different spatial shifting of the 2006 data with respect to 2003. The maximum magnitude of cross-correlation indicates the likely distance of plume shifting and provides the value of collocated cross-correlation for use in the co-simulation.

The procedure is first applied to evaluate changes in contaminant discharges between 2003 (pre-remediation) and 2006 (post-remediation). Sampling events after 2006 occurred in 2017 (BMLS) and 2018 (BMLS and PFM) at a reduced number of monitoring wells and are compared to 2006 as a post-remediation baseline with the most comprehensive sampling grid.

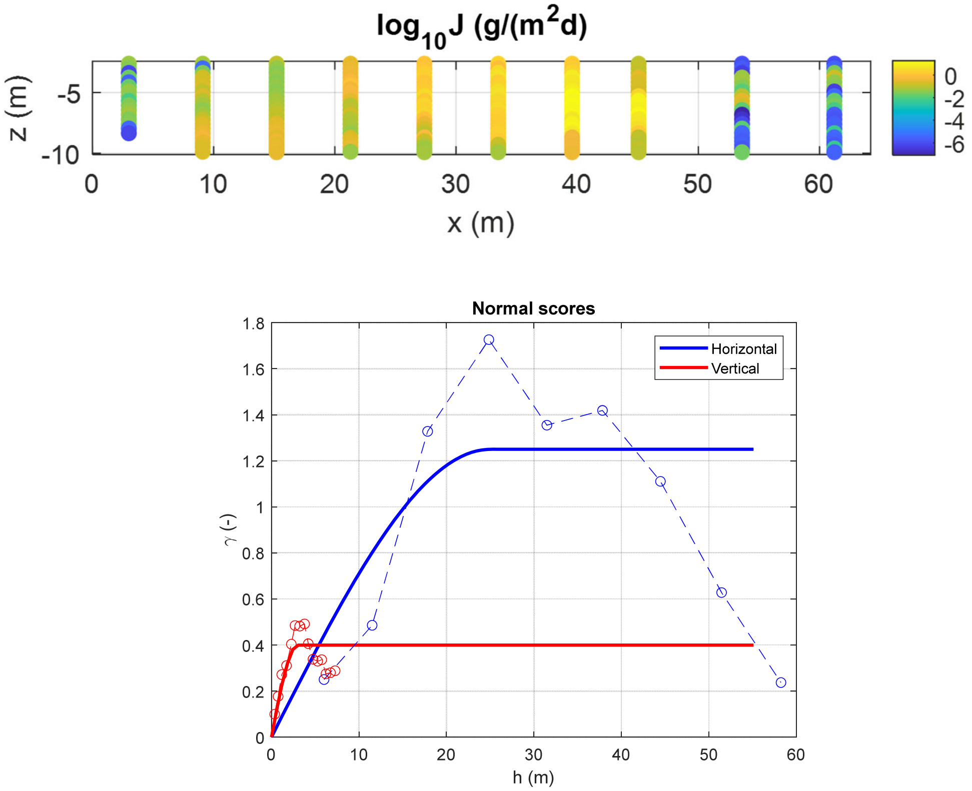


Figure 23. 2003 TCE Log-flux Measurements and Normal Score Variograms (circles).

The variogram in Figure 23 was generated using the methods of Klammler et al., 2012 and shows the presence of zonal anisotropy as the flux variability in the horizontal direction is larger than that in the vertical direction as expressed by the different sill values. There is also a stronger spatial continuity of fluxes in the horizontal direction, which is reflected by the larger range of the horizontal variogram. The spherical variogram fits (continuous lines) are used for the stochastic simulation of local contaminant flux values over a regular grid spanning the transect for subsequent computation of discharge estimates. The ensemble of discharge estimates for all realizations generated allows constructing the cumulative distribution function (cdf) of discharges for each sampling event, or of pairwise differences in discharges between sampling events.

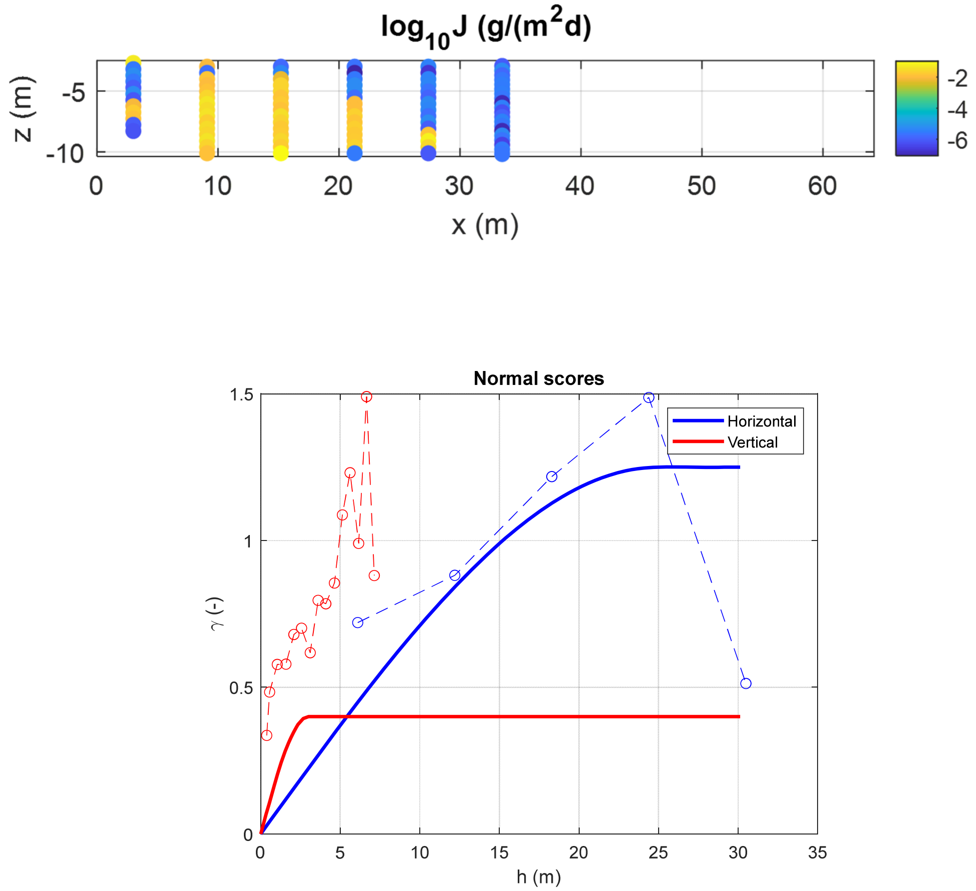


Figure 24. 2006 TCE Log-flux Measurements and Normal Score Variograms.

As observed previously in Figures 21 and 22, the four wells in the right side of the transect (LC207, LC211, LC212, and LC213) all had flux measurements of zero and were removed so not to distort the normal score transformation. The overall aspect of the empirical variograms (circles) is less well behaved and the number of data points (wells) is also significantly reduced with respect to 2003. We assume that the plume preserves its internal spatial structure (although it can be shifted as a whole across the transect), such that the variogram fits (continuous lines) of 2003 remain applicable, which appears reasonable here and in subsequent years shown below (Figures 25-27).

Similar DCE flux measurements and variograms are shown for all sampling events in Figures 28-32. Based on the empirical variograms (circles) shown in each figure, we maintain the variogram fits (continuous lines) are consistent with that shown in Figure 23 for the pre-remediation (2003) TCE plume 2003.

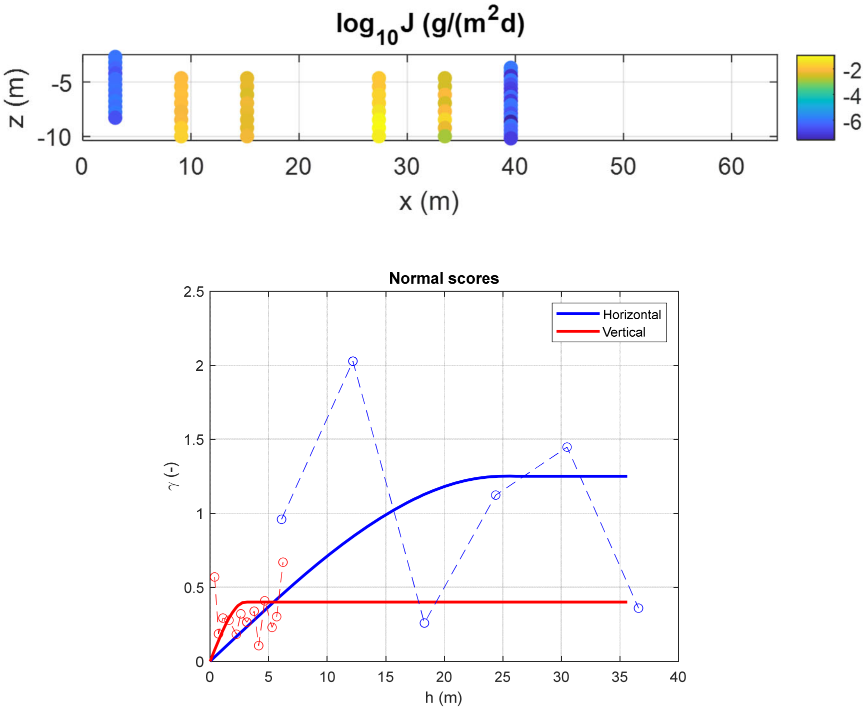


Figure 25. 2017 TCE log-flux measurements and normal score variograms.

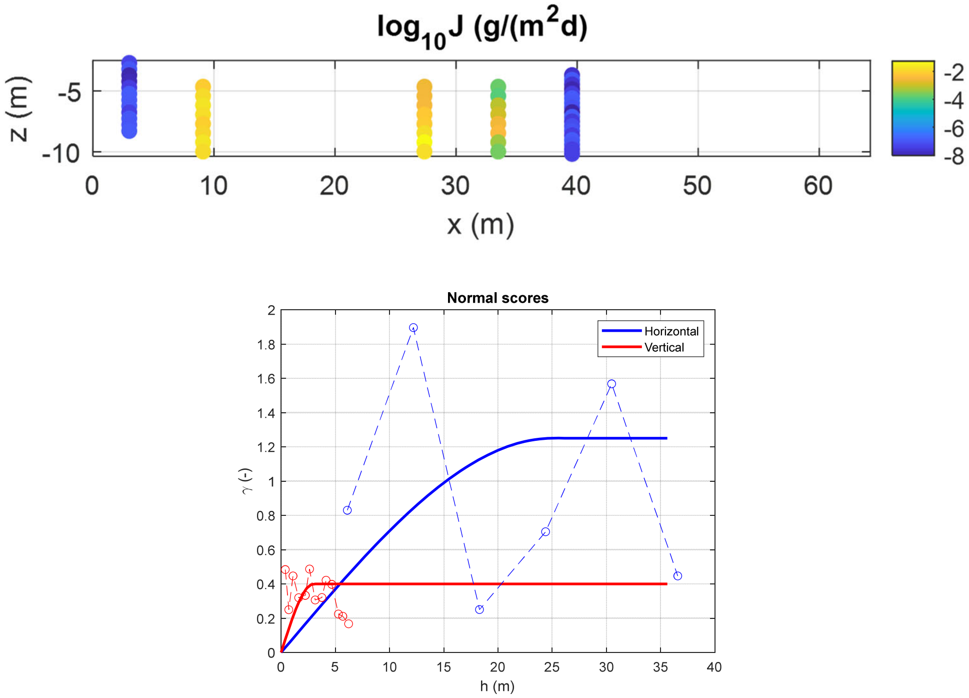


Figure 26. 2018 BMLS TCE Log-flux Measurements and Normal Score Variograms.

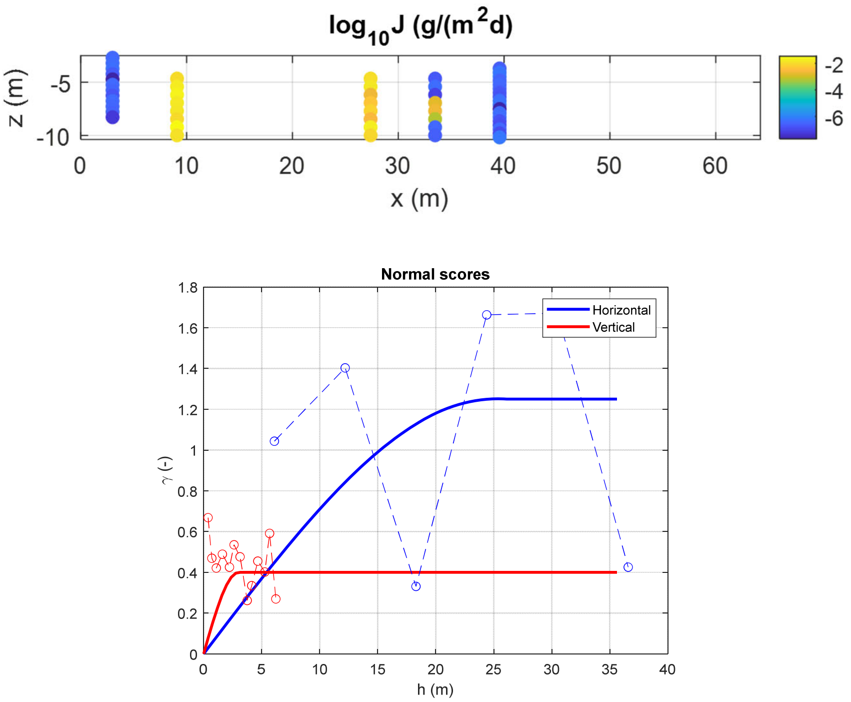


Figure 27. 2018 PFM TCE Log-flux Measurements and Normal Score Variograms.

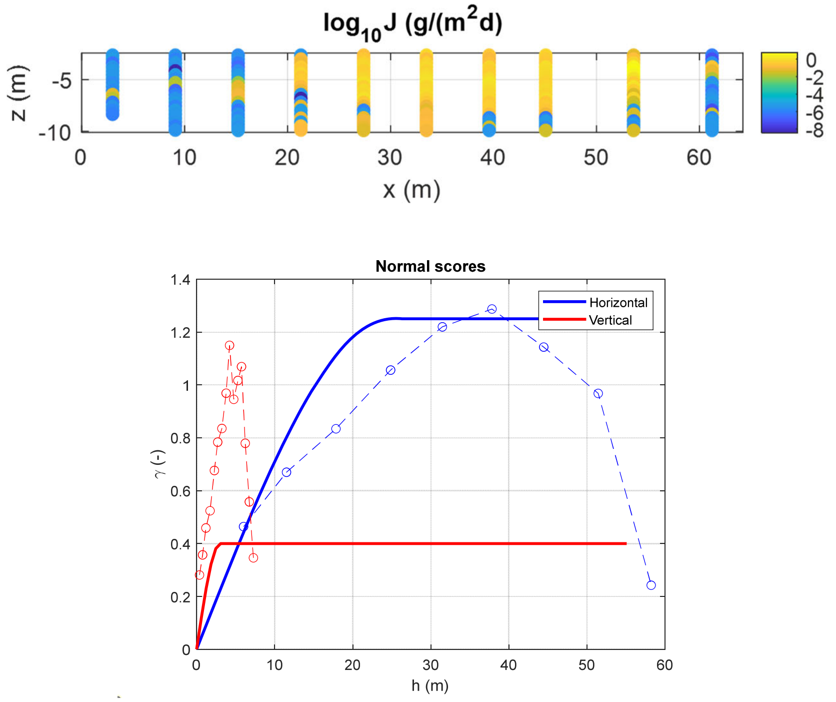


Figure 28. 2003 DCE Log-flux Measurements and Normal Score Variograms.

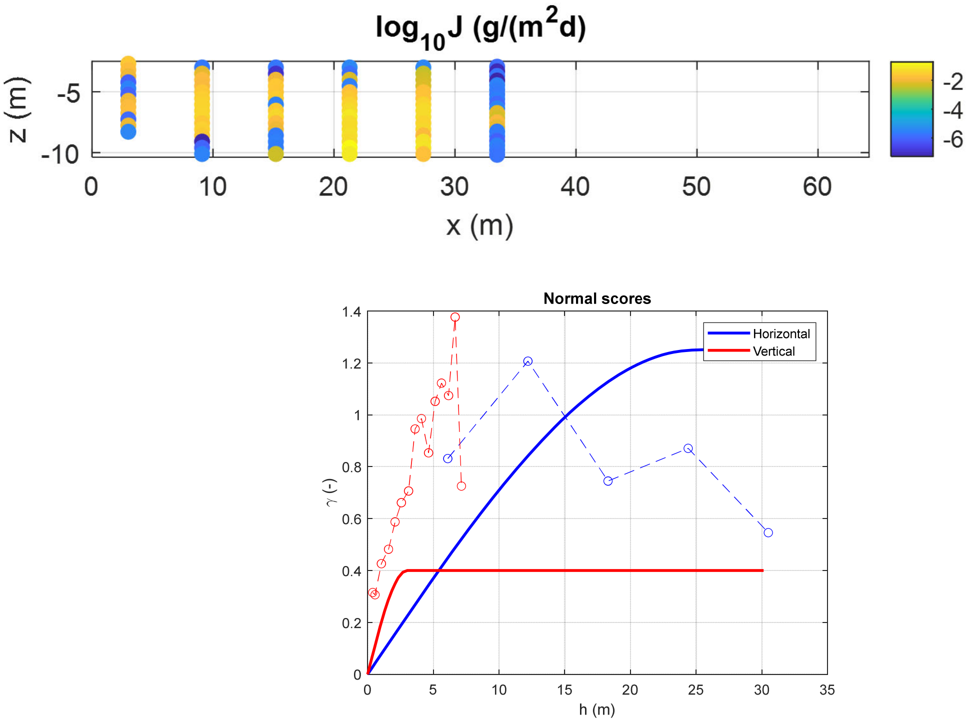


Figure 29. 2006 DCE Log-flux Measurements and Normal Score Variograms.

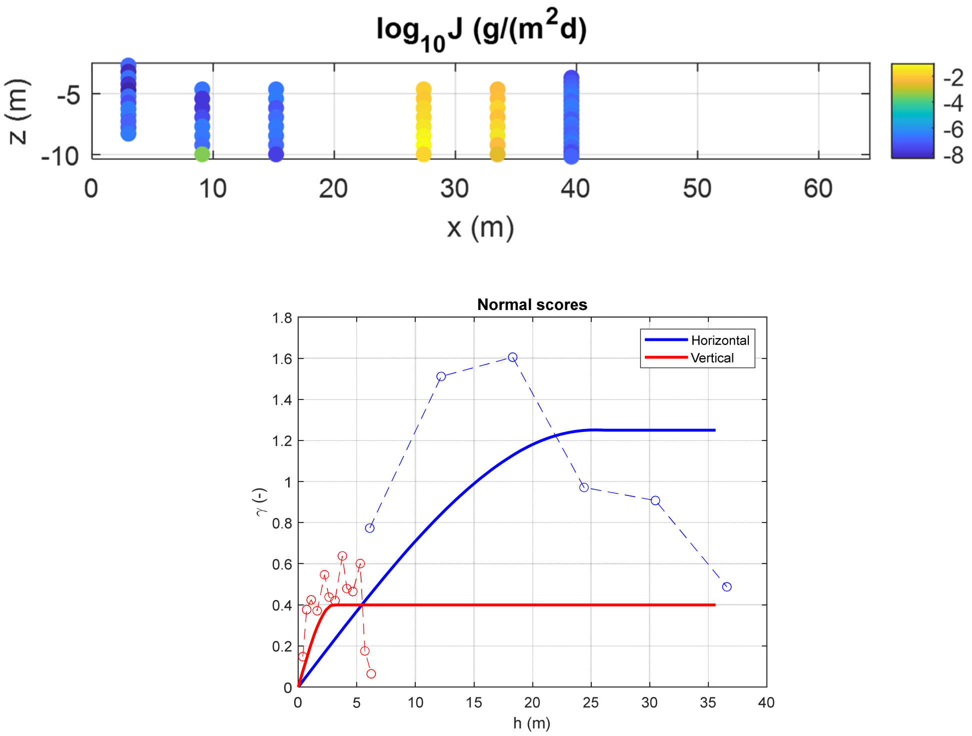


Figure 30. 2017 DCE Log-flux Measurements and Normal Score Variograms.

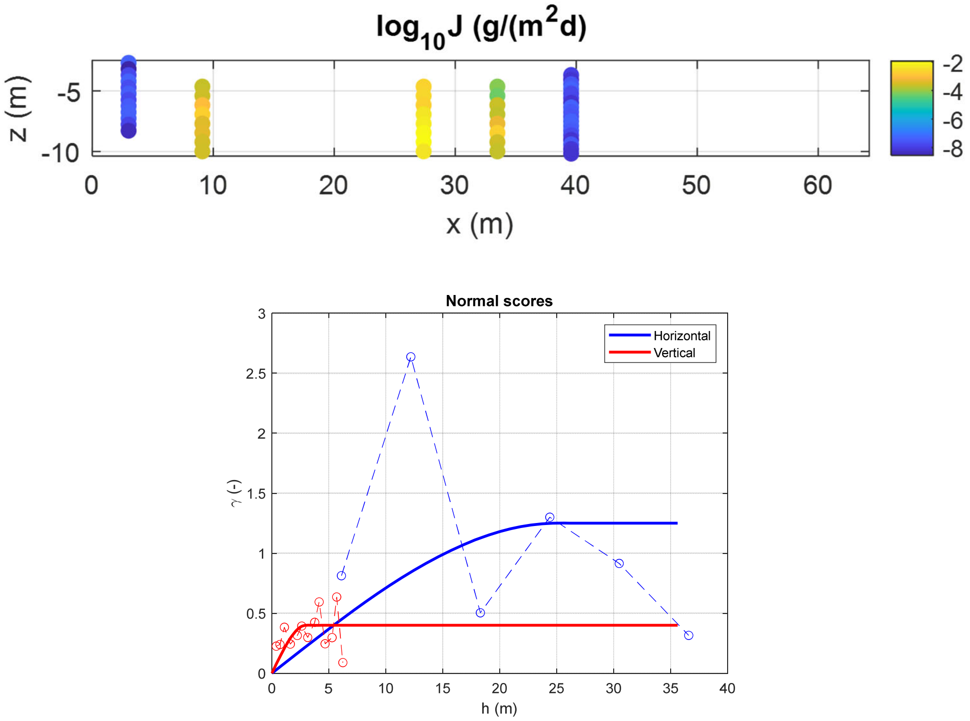


Figure 31. 2018 BMLS DCE Log-flux Measurements and Normal Score Variograms.

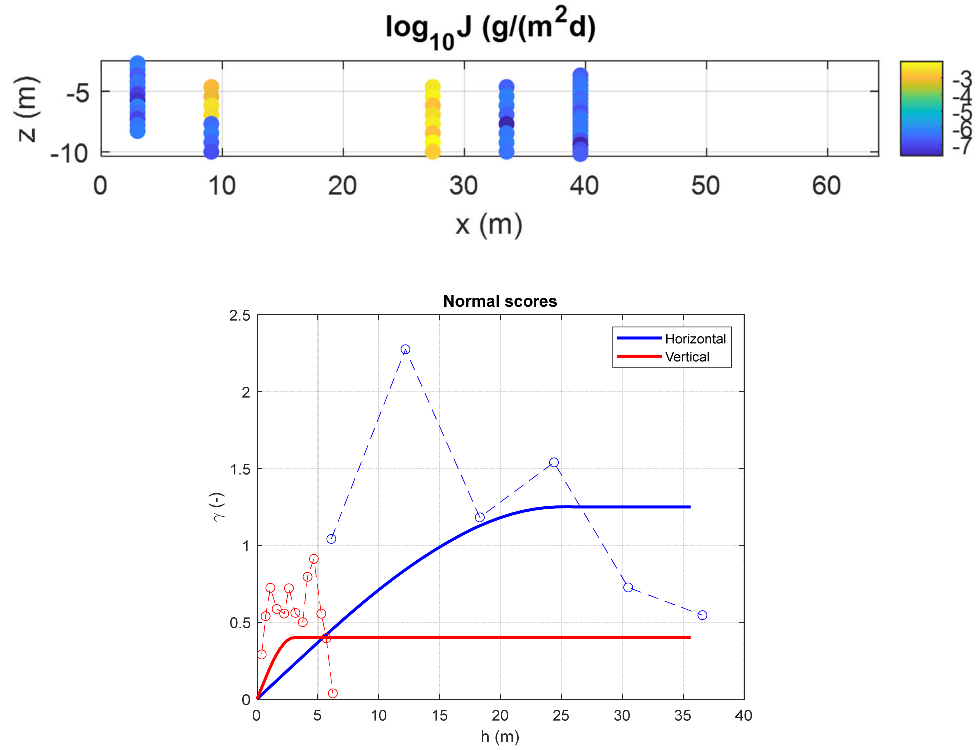


Figure 32. 2018 PFM DCE Log-flux Measurements and Normal Score Variograms.

Figures 33-36 are cross-correlation surfaces between different sampling events that provide a temporal comparison of spatial flux distributions. The cross-correlation surfaces indicate the required spatial shifts Δx and Δz to maximize correlation between sampling events (removing plume migration within transect). Locations with maximum correlation are indicated in yellow and the scale of the required spatial shifts to maximize this correlation are shown on the horizontal and vertical axes.

Figure 33A shows the TCE spatial correlation between the 2003 pre-remediation PFM flux measurements and the 2006 post-remediation PFM flux measurements. Due to the significant reduction in TCE contaminant mass between these sampling events (from remedial efforts) and the previously observed shift in mass discharge from 2003 to 2006 (Figure 21) it can be seen that there is significant spatial shifting required to obtain spatial correlation between sampling events. Figure 33A indicates that for maximum correlation the 2006 plume has to be shifted between 20 to 35 meters in the horizontal direction and just under 5 meters in the vertical direction to maximize correlation between sampling events. What this indicates is that the center of mass of the TCE plume in 2003 (pre-remediation) was located 20 to 35 meters to the right and 5 meters above the center of mass of the TCE plume in 2006 (post-remediation).

Figure 33B shows the DCE spatial correlation between the 2003 pre-remediation PFM flux measurements and the 2006 post-remediation PFM flux measurements. As with the TCE plume, there was a significant spatial shift in the center of mass of the DCE plume. The center of mass of the DCE plume in 2003 (pre-remediation) was 30-35 meters to the right and 5 meters above the center of mass of the DCE plume in 2006.

Subsequent cross-correlation surfaces between post-remediation sampling events (Figures 34-36) show larger regions with high spatial correlation and the scale of special shifting between observations is significantly less than the pre-remediation post remediation comparison in Figure 31.

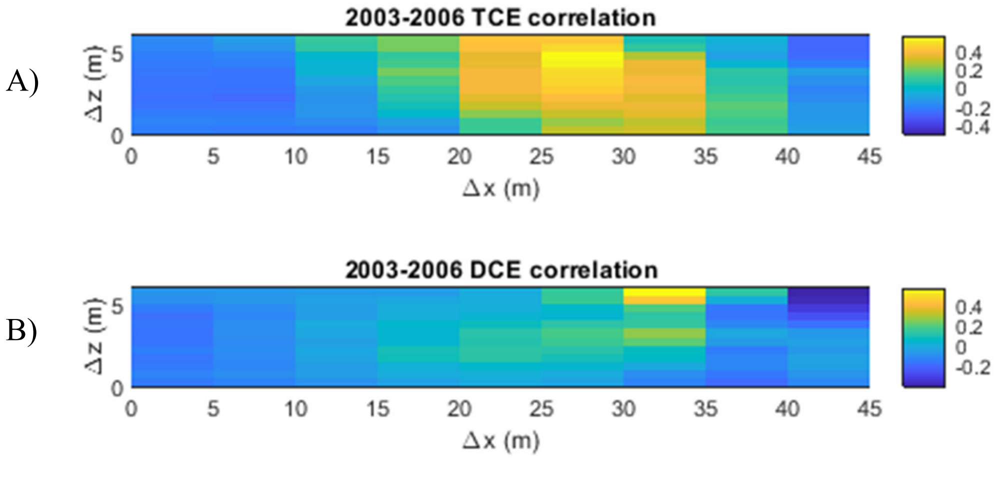


Figure 33. Cross-correlation Surfaces Between 2003 and 2006 PFM Fluxes.

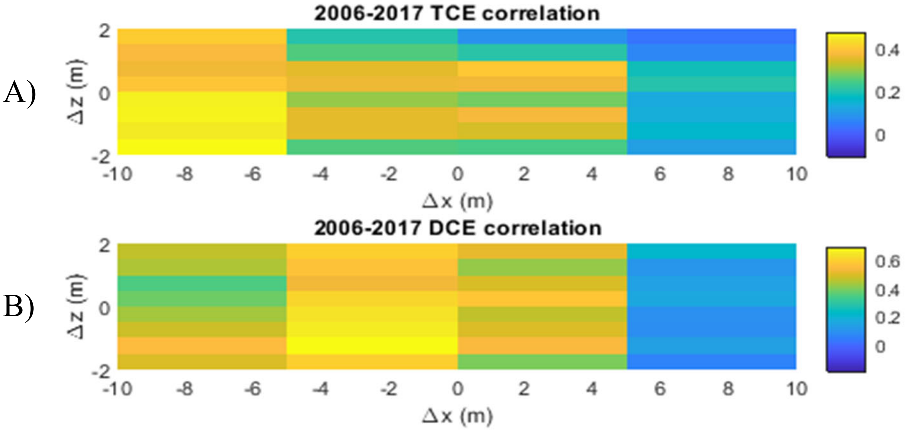


Figure 34. Cross-correlation Surfaces Between 2006 PFM and 2017 BMLS Fluxes.

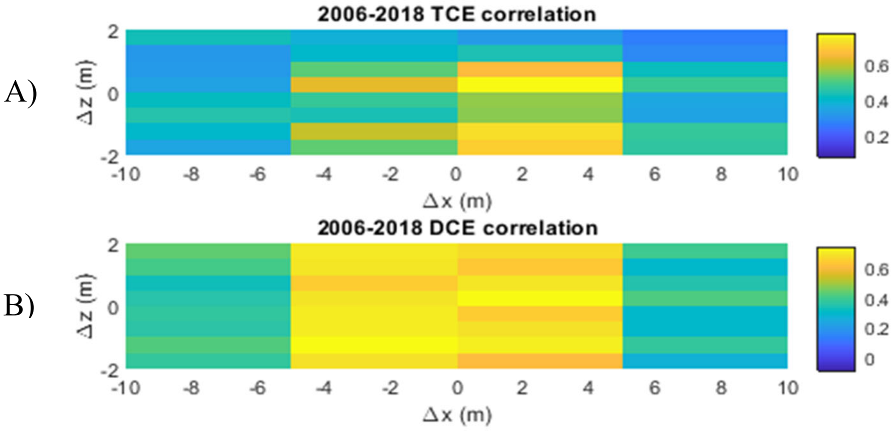


Figure 35. Cross-correlation Surfaces Between 2006 PFM and 2018 BMLS Fluxes.

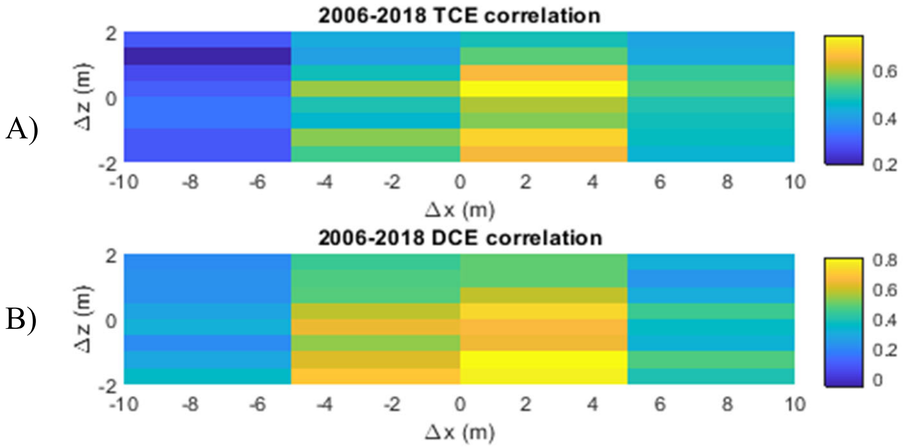


Figure 36. Cross-correlation Surfaces Between 2006 PFM and 2018 PFM Fluxes.

5.8.3 TIME SERIES ANALYSIS RESULTS: NAPL AREA 1 SHALLOW WELLS

5.8.3.1 Comparison of 2003 PFM (pre-remediation) to 2006 PFM (post-remediation).

The results of the stochastic analysis are best summarized through review of the cumulative distribution functions (CDFs) of the simulated contaminant discharges (100 realizations) and maps of the mean simulated fluxes. Figure 37 compares the TCE fluxes and resulting contaminant mass discharge through the flux transect for the 2003 (pre-remediation) and 2006 (post-remediation) sampling events. In Figure 37A it can be seen that the 2003 (pre-remediation) simulated TCE discharge was significantly higher than the 2006 (post-remediation) discharge, and the difference is very close to the 2003 value (indicating that the 2006 values are orders of magnitude lower than the 2003 values). Similarly, in Figures 37 B and C the mean simulated flux magnitudes vary by three orders of magnitude which is similar to the variation in pre- and post-remediation measured fluxes (Figure 20). Also, the spatial shift in the center of mass of the contaminant plume as indicated in the cross-correlation surface (Figure 33) is clearly evident in Figures 37 B and C.

Another beneficial outcome of this method is because it is based upon a symmetric probability distribution, so the median CDF value is equal to the mean. As such, in Figure 37A the CDF at 0.5 corresponds to the mean simulated TCE mass discharge through the flux transect. It follows that for the 2003 (pre-remediation) case the simulated mean TCE mass discharge was approximately 0.788 kg/day (read from Figure 37A using the 2003 line) which compares well with the value of 0.784 kg/day estimated from observed fluxes (Figure 21).

The information provided in Figure 37 can be summarized as follows: between the 2003 (pre-remediation) and 2006 (post-remediation) sampling events the flux magnitudes were decreased by two orders of magnitude, with a significant shift in the center of mass of the plume approximately 25 meters to the left and 5 meters downward within the transect. It is estimated that remedial efforts reduced the TCE mass discharge by approximately 0.775 kg/day (read from Figure 37A using CDF mean value (0.5) and the Difference line).

Figure 38 provides similar comparisons between 2003 (pre-remediation) and 2006 (post-remediation) fluxes and mass discharge for DCE. It can be seen that although the magnitude of DCE fluxes and discharge were considerably less than that for TCE, there was still a significant decrease in DCE flux magnitude (two orders of magnitude) from 2003 to 2006, and a similar spatial shift in the center of mass of the plume is also evident. The information provided in figure 38 can be summarized as follows: between the 2003 (pre-remediation) and 2006 (post-remediation) sampling events the flux magnitudes were decreased by an order of magnitude, with a significant shift in the center of mass of the plume approximately 35 meters to the left and 5 meters downward within the transect. It is estimated that remedial efforts reduced the DCE mass discharge by approximately 0.147 kg/day (read from Figure 38A using CDF mean value (0.5) and the Difference line).

Figure 39 represents the CDF in terms of relative (percent) TCE discharge reduction between 2003 and 2006. The figure indicates that there is extremely high probability that the TCE discharge was reduced by more than 99%. Similarly, Figure 40 indicates that there is very high probability (>95%), that the DCE mass discharge was reduced by 95 to 97.5% between 2003 and 2006.

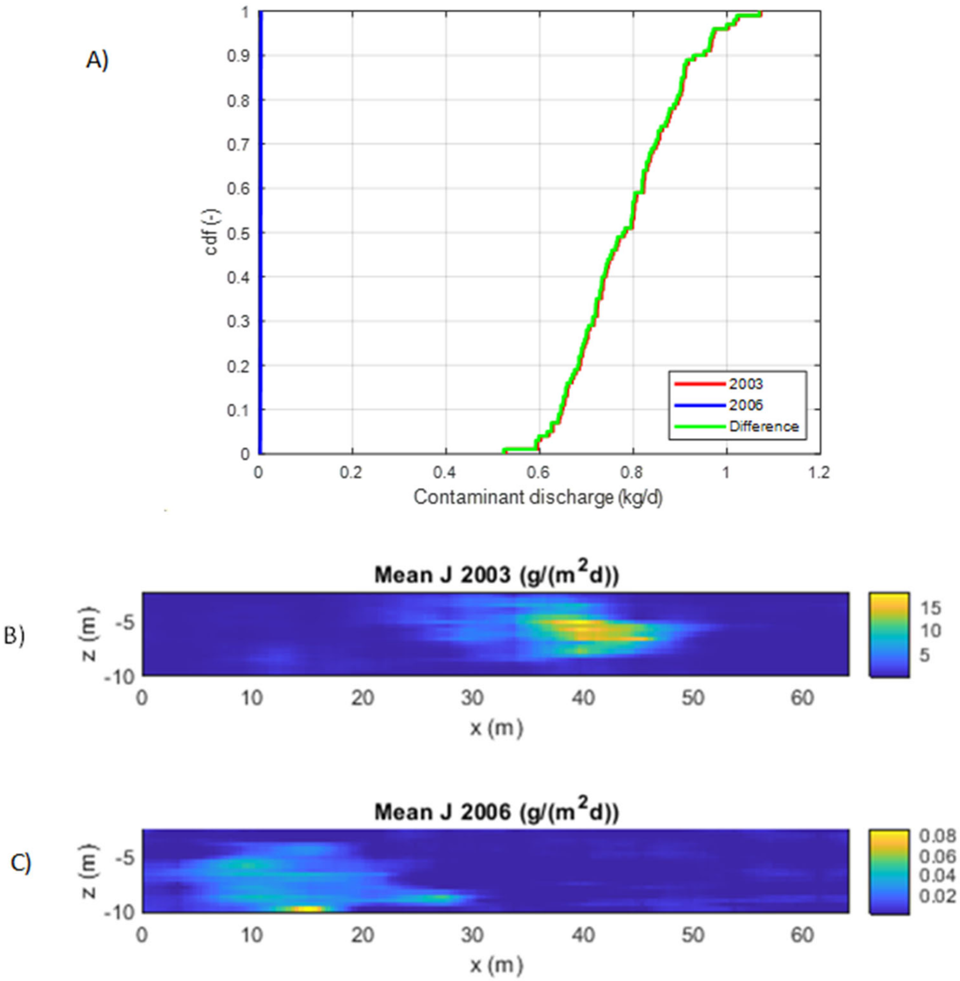


Figure 37. **Simulated TCE Fluxes and CDFs of Simulated TCE Discharges and Discharge Difference Between 2003 and 2006.**

A) CDFs of simulated TCE discharges (100 realizations) and of discharge difference between 2003 and 2006.

B) Map of 2003 mean simulated TCE fluxes.

C) Map of 2006 mean simulated TCE fluxes.

(It is important to note the significant difference in flux magnitudes between figures B and C).

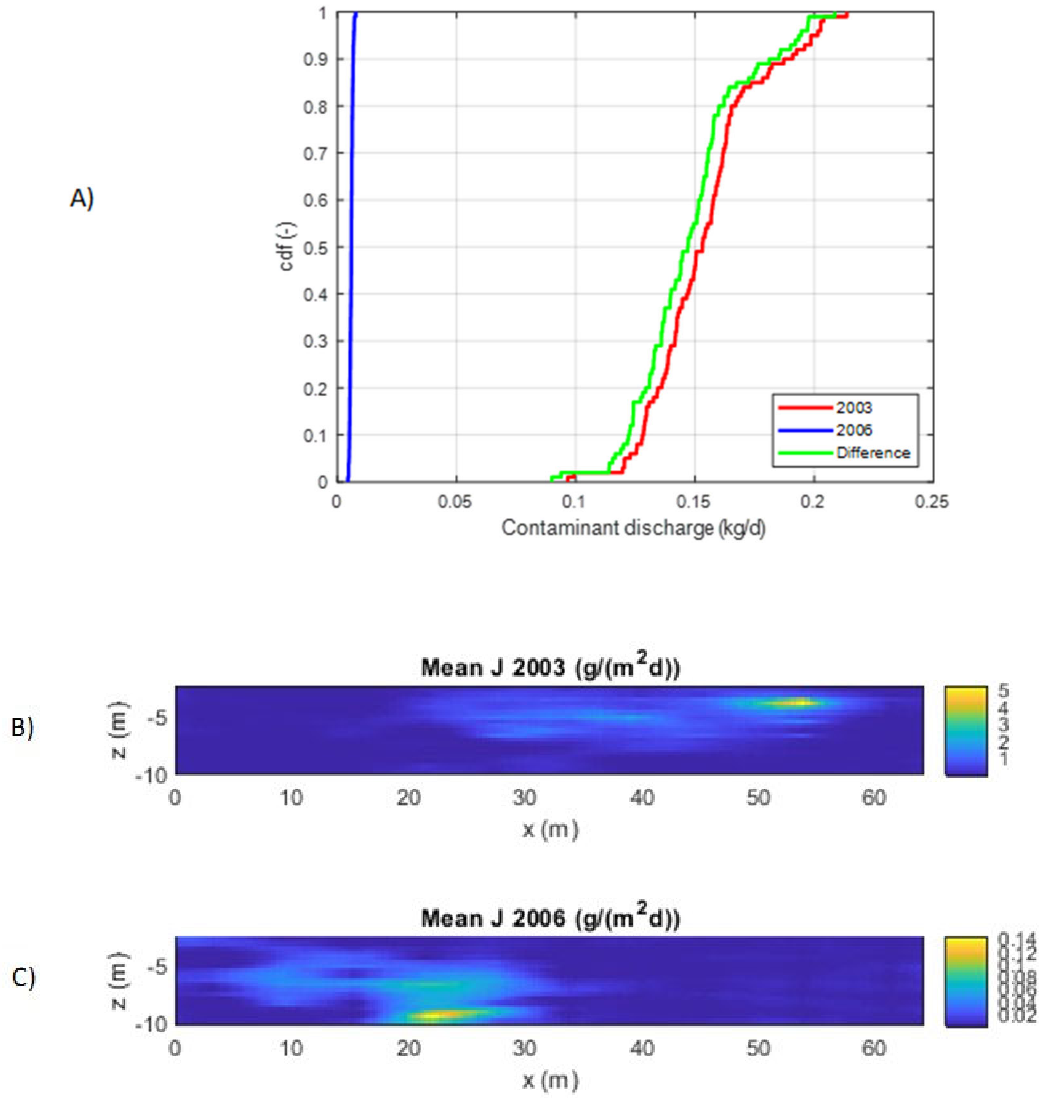


Figure 38. Simulated DCE Fluxes and CDFs of Simulated DCE Discharges and discharge Difference Between 2003 and 2006.

A) CDFs of simulated DCE discharges (100 realizations) and of discharge difference between 2003 and 2006.

B) Map of 2003 mean simulated DCE fluxes.

C) Map of 2006 mean simulated DCE fluxes.

(It is important to note the difference in flux magnitudes between figures B and C).

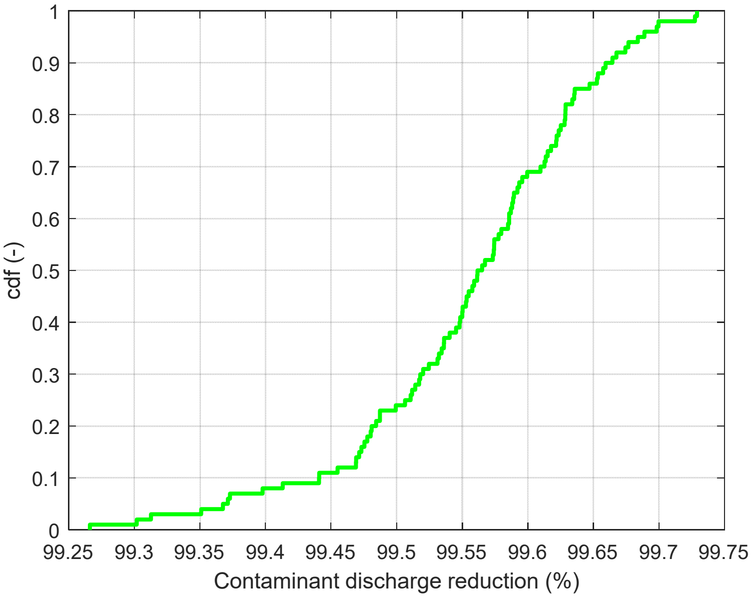


Figure 39. Alternative CDF Representation in Terms of Relative (Percent) TCE Discharge Reduction Between 2003 and 2006.

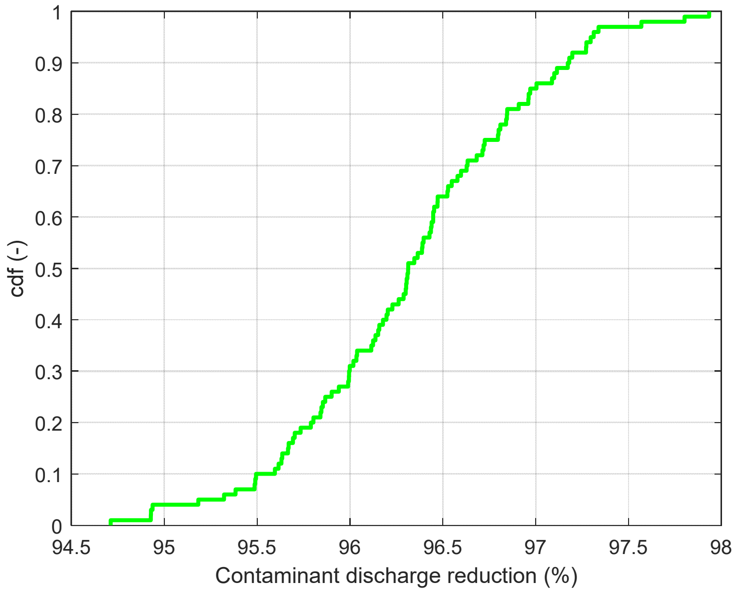


Figure 40. Alternative CDF Representation in Terms of Relative (Percent) DCE Discharge Reduction Between 2003 and 2006.

5.8.3.2 Comparison of 2006 PFM (post-remediation) to 2017 BMLS (post-remediation).

Figure 41 provides comparison of post-remedial TCE sampling results between 2006 PFM measurements and 2017 BMLS measurements. As noted previously when discussing figures 18-21, the 2017 BMLS measurements indicated a significant increase in TCE fluxes when compared to the initial 2006 post-remediation PFM measurements. (The exact reason for this increase is not certain, but the pump and treat system had been shut down for maintenance prior to this sampling event which could likely lead to an apparent contaminant rebound and an increase in aqueous contaminant concentrations). The discharge increase is also evident in the stochastic analysis as the simulated TCE mass discharge difference in Figure 41 is predominantly negative which indicates a net increase in mass discharge.

The information provided in Figure 41 can be summarized as follows: between the 2006 and 2017 post-remediation sampling events the TCE flux magnitudes and resulting mass discharge through the flux transect appear to have increased due to a predominantly negative difference in mass discharge between 2017 and 2006. There was minimal shift in the center of mass of the plume.

Figure 42 provides comparison for DCE sampling results between 2006 PFM measurements and 2017 BMLS measurements. Unlike the TCE results, there was a certain, but relatively small decrease in DCE fluxes and mass discharge from 2006 to 2017. Figure 42 can be summarized as follows: between the 2006 and 2017 post-remediation sampling events the DCE flux magnitudes and resulting mass discharge decreased and there was a minor shift in the center of mass of the DCE plume to the right within the transect.

Figure 43 represents the CDF in terms of relative (percent) TCE discharge reduction between 2006 and 2017. The figure indicates that there is high probability (approximately 85%) that the discharge increased (due to a predominantly negative discharge reduction) and only a slight probability (approximately 15%) that the discharge decreased.

Figure 44 represents the CDF in terms of relative (percent) DCE discharge reduction between 2006 and 2017. The figure indicates that there is very high probability (>99%), that the DCE mass discharge was reduced by 30 to 80% between 2006 and 20017.

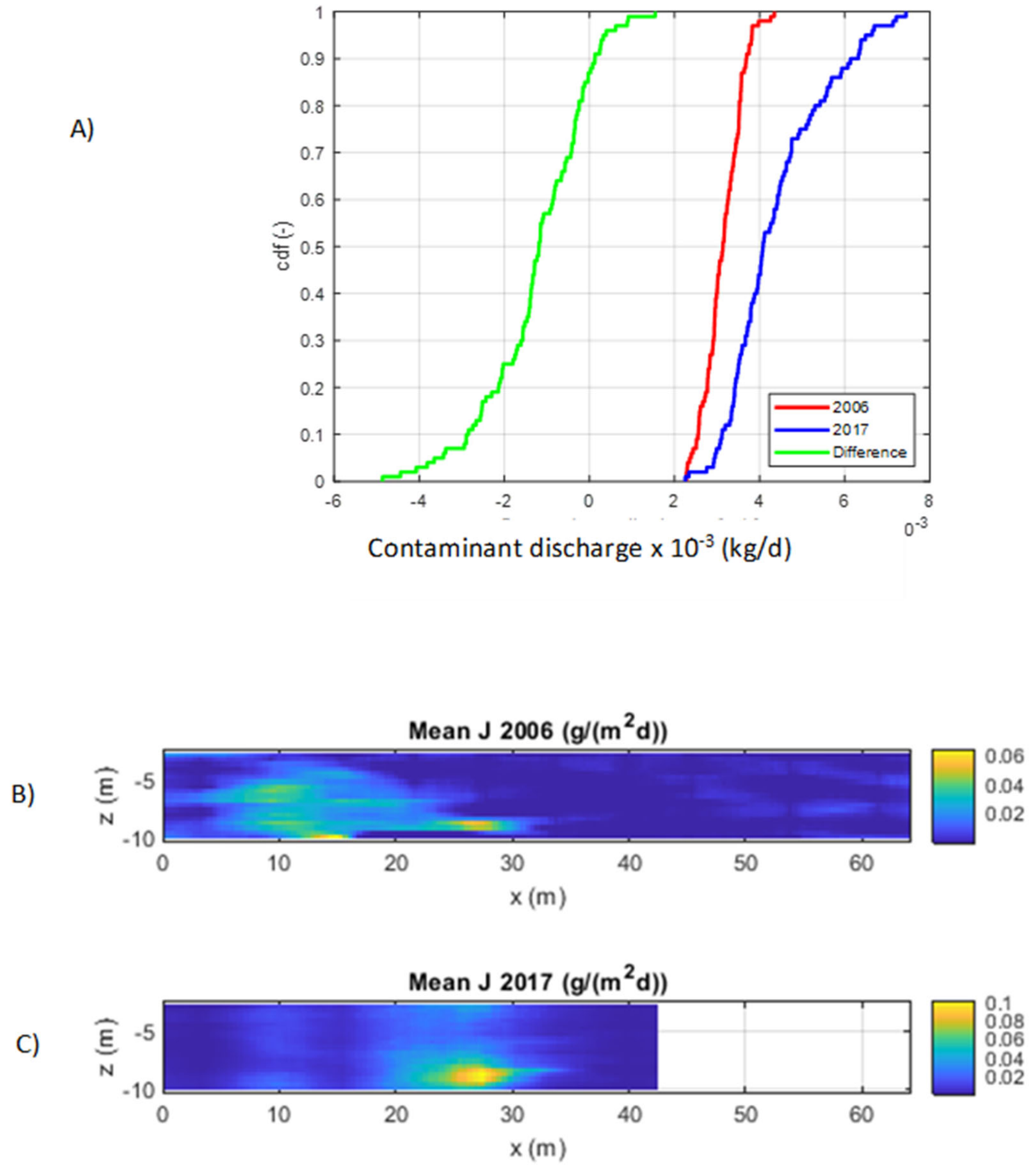


Figure 41. **Simulated TCE Fluxes and CDFs of Simulated TCE Discharges and discharge Difference Between 2006 (PFM) and 2017 (BMLS).**

A) CDFs of simulated TCE discharges (100 realizations) and of discharge difference between 2006 and 2017.

B) Map of 2006 mean simulated TCE fluxes.

C) Map of 2017 mean simulated TCE fluxes.

(Note the difference in flux magnitudes between figures B and C)

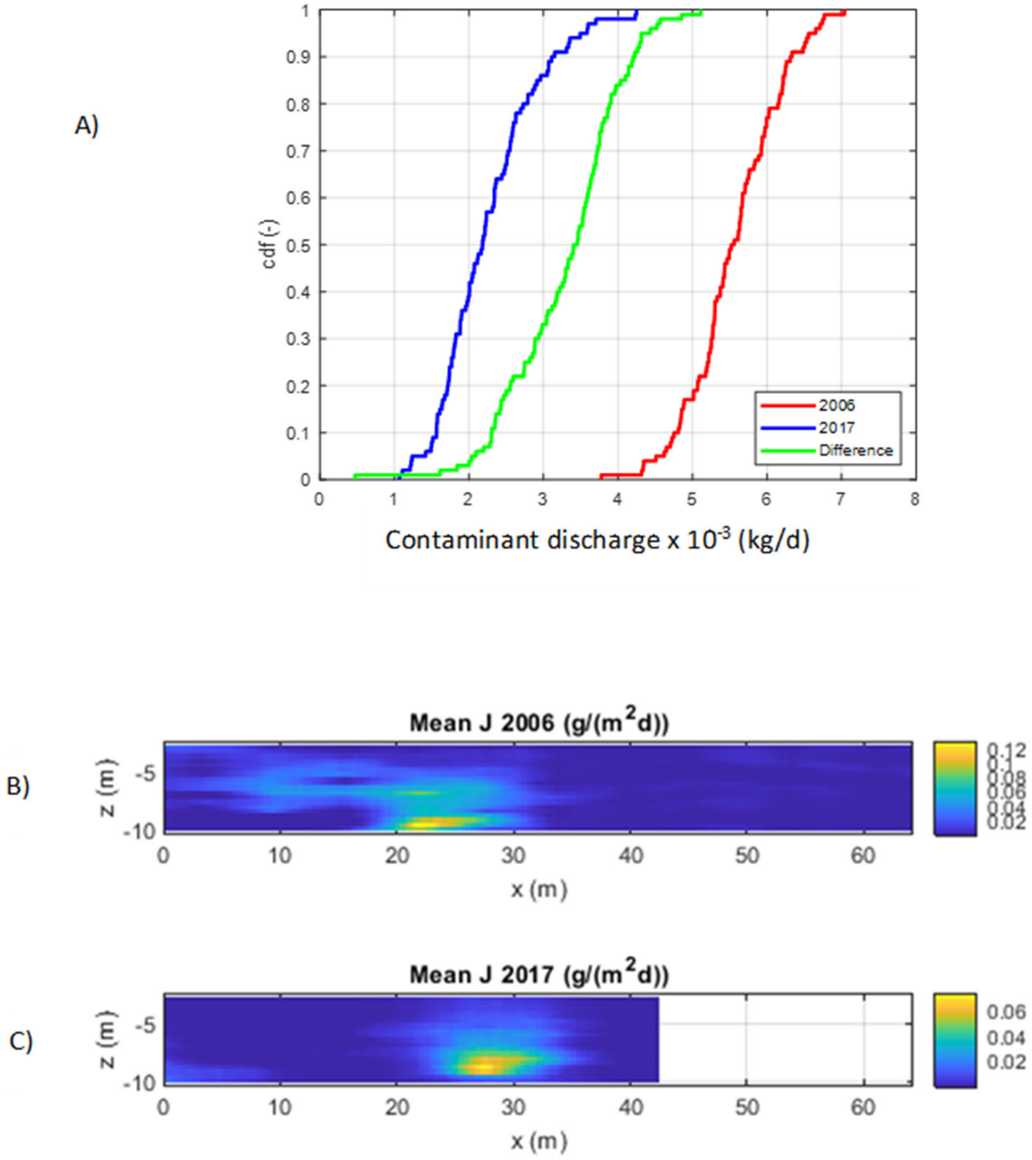


Figure 42. Simulated DCE Fluxes and CDFs of Simulated TCE Discharges and discharge Difference Between 2006 (PFM) and 2017 (BMLS).

A) CDFs of simulated DCE discharges (100 realizations) and of discharge difference between 2006 and 2017.

B) Map of 2006 mean simulated DCE fluxes.

C) Map of 2017 mean simulated DCE fluxes.

(Note the difference in flux magnitudes between figures B and C)

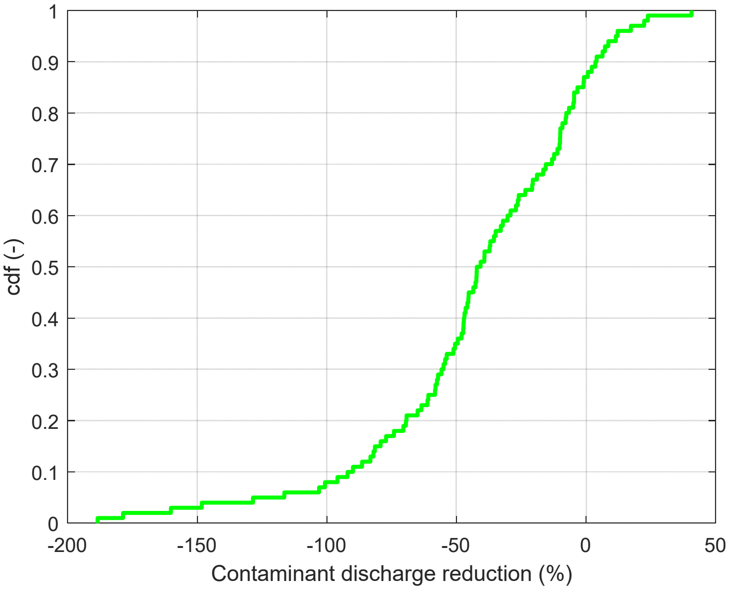


Figure 43. Alternative CDF Representation in Terms of Relative (Percent) TCE Discharge Reduction Between 2006 (PFM) and 2017 (BMLS).

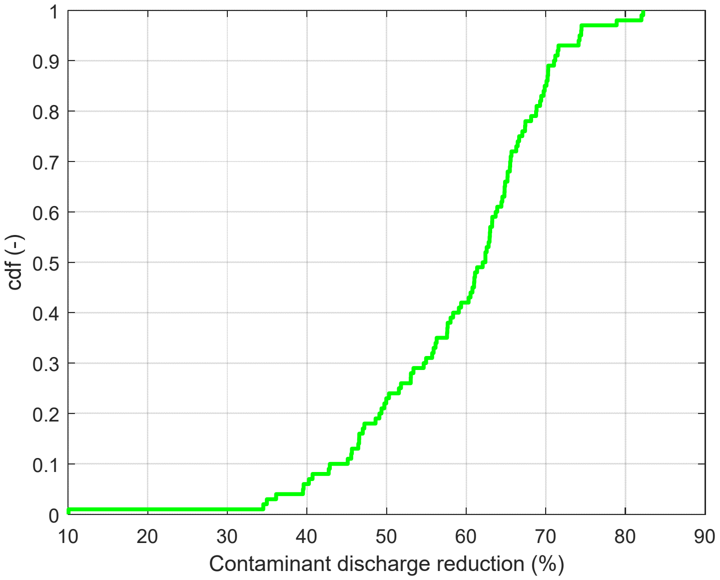


Figure 44. Alternative CDF Representation in Terms of Relative (Percent) DCE Discharge Reduction Between 2006 (PFM) and 2017 (BMLS).

5.8.3.3 Comparison of 2006 PFM (post-remediation) to 2018 BMLS (post-remediation).

Figure 45 provides comparison of post-remedial TCE sampling results between 2006 PFM measurements and 2018 BMLS measurements. Unlike the 2017 BMLS results, the 2018 BMLS results show a definite decrease in TCE flux and resulting discharge from 2006 to 2018.

The information provided in Figure 45 can be summarized as follows: between the 2006 and 2018 post-remediation sampling events the TCE flux magnitudes and resulting mass discharge decreased and there was minimal shift in the center of mass of the plume (possibly slight shift to the right).

Figure 46 provides comparison for DCE sampling results between 2006 PFM measurements and 2018 BMLS measurements. Figure 46 can be summarized as follows: between the 2006 and 2018 post-remediation sampling events the DCE flux magnitudes and resulting mass discharge decreased and there was a minor shift in the center of mass of the DCE plume to the right within the transect.

Figure 47 represents the CDF in terms of relative (percent) TCE discharge reduction between 2006 PFM and 2018 BMLS. The figure indicates a definite discharge reduction as there is high probability that discharge was reduced by between 15 to 78% (mean value approximately 55% discharge reduction).

Figure 48 represents the CDF in terms of relative (percent) DCE discharge reduction between 2006 (PFM) and 2018(BMLS). The figure indicates that there is very high probability (>99%), that the DCE mass discharge was reduced by 86 to 97% between 2006 and 2018.

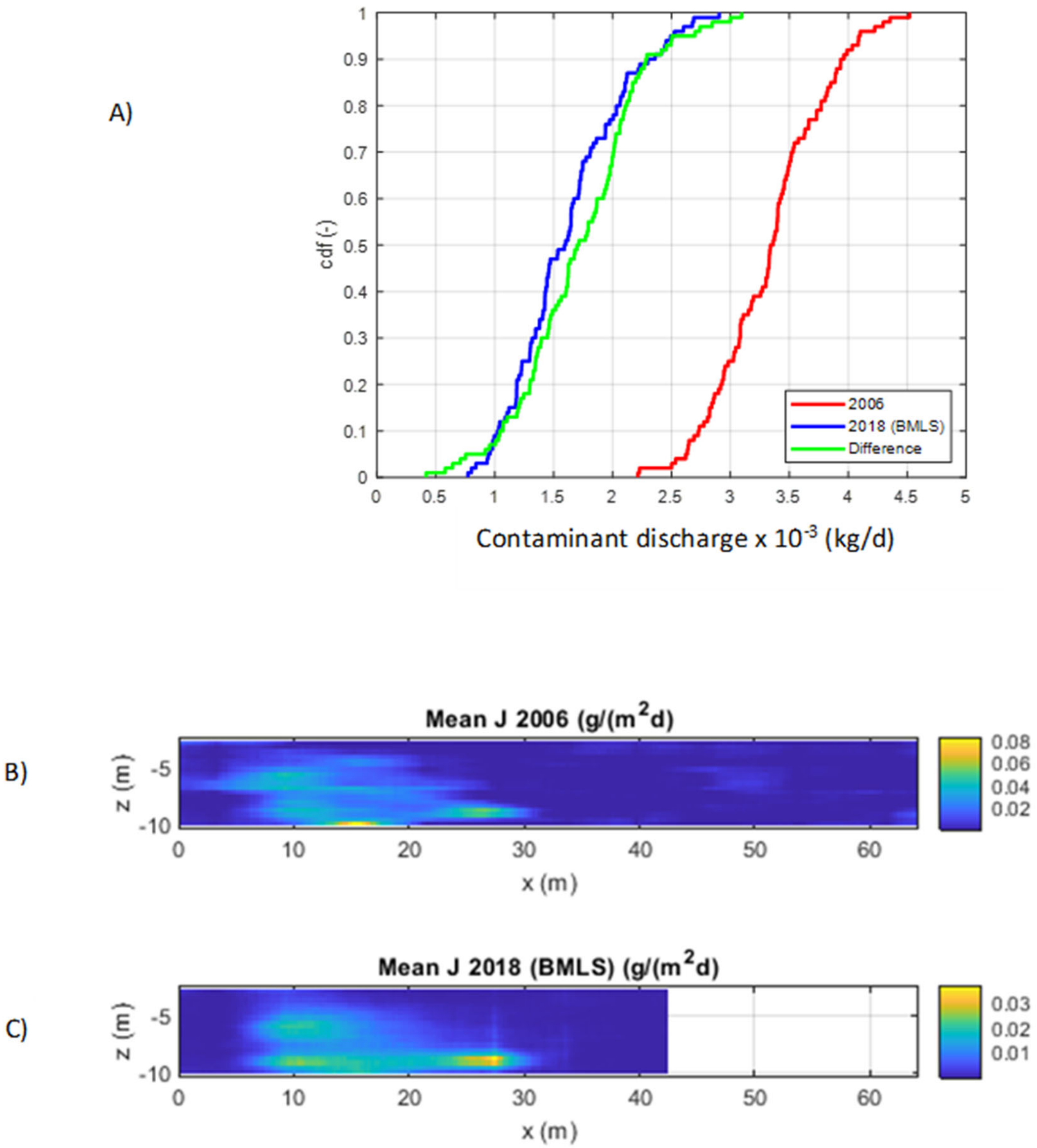


Figure 45. Simulated TCE Fluxes and CDFs of Simulated TCE Discharges and Discharge Difference Between 2006 (PFM) and 2018 (BMLS).

A) CDFs of simulated TCE discharges (100 realizations) and of discharge difference between 2006 (PFM) and 2018 (BMLS).

B) Map of 2006 mean simulated TCE fluxes.

C) Map of 2018 mean simulated TCE fluxes.

(Note the difference in flux magnitudes between figures B and C)

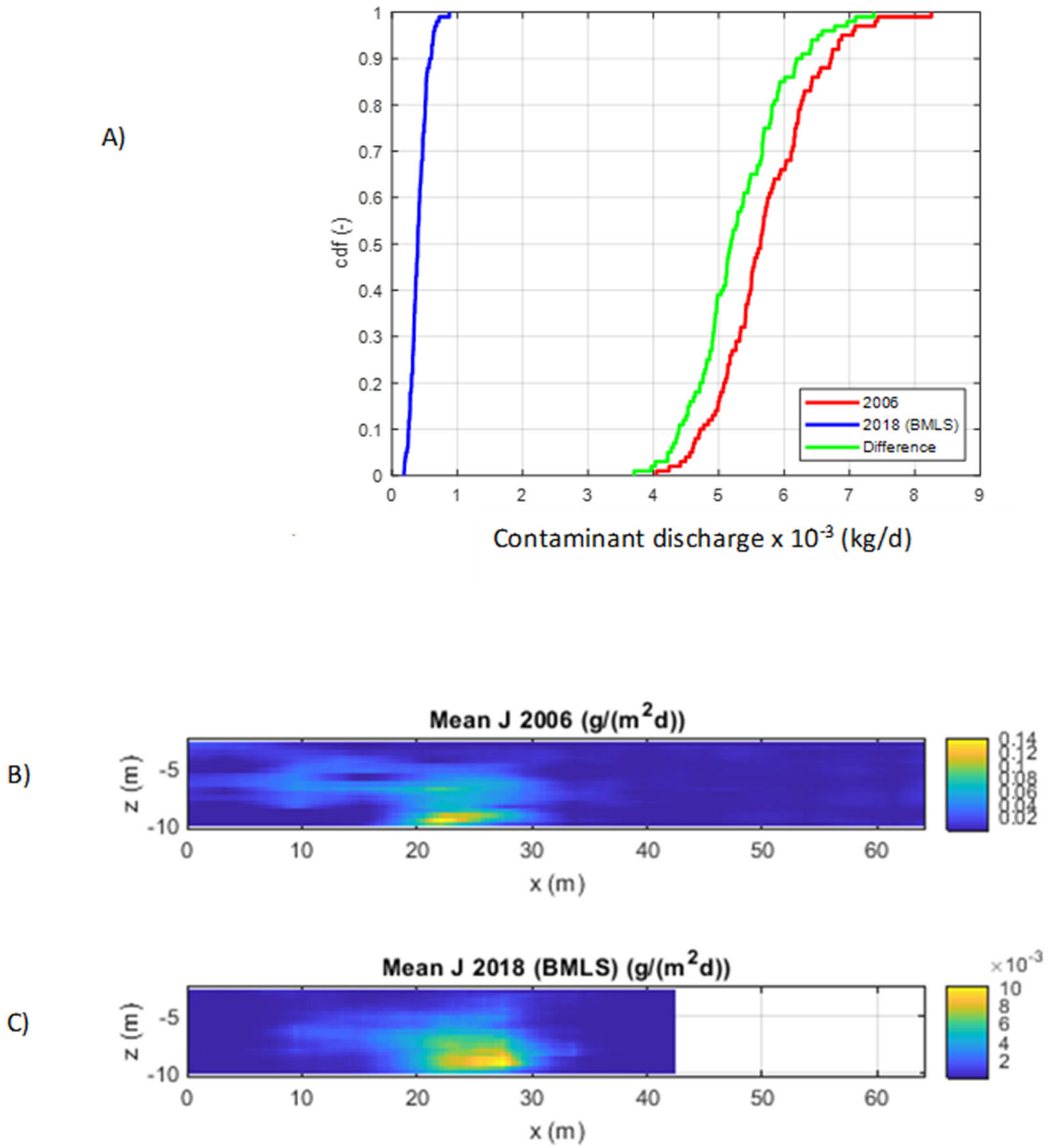


Figure 46. Simulated DCE Fluxes and CDFs of Simulated DCE Discharges and Discharge Difference Between 2006 (PFM) and 2018 (BMLS)

A) CDFs of simulated DCE discharges (100 realizations) and of discharge difference between 2006 (PFM) and 2018 (BMLS).

B) Map of 2006 mean simulated DCE fluxes.

C) Map of 2018 mean simulated DCE fluxes.

(Note the difference in flux magnitudes between figures B and C)

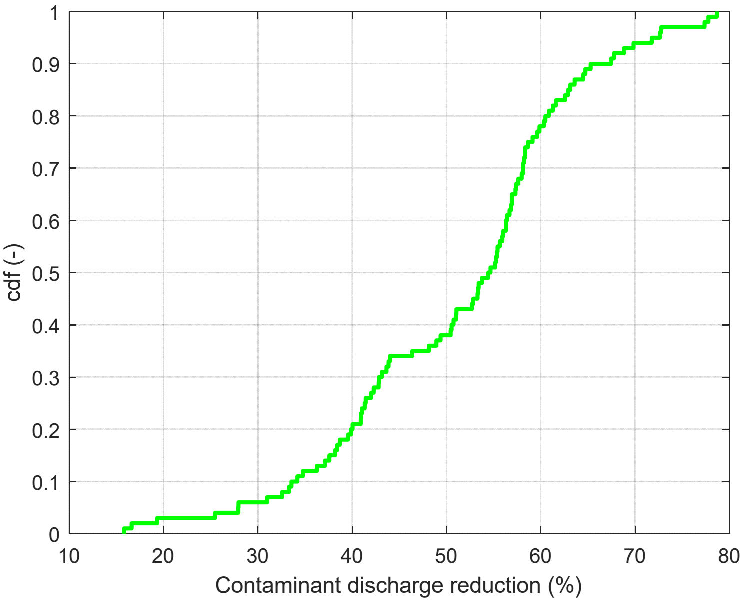


Figure 47. Alternative CDF Representation in Terms of Relative (Percent) TCE Discharge Reduction Between 2006 (PFM) and 2018 (BMLS).

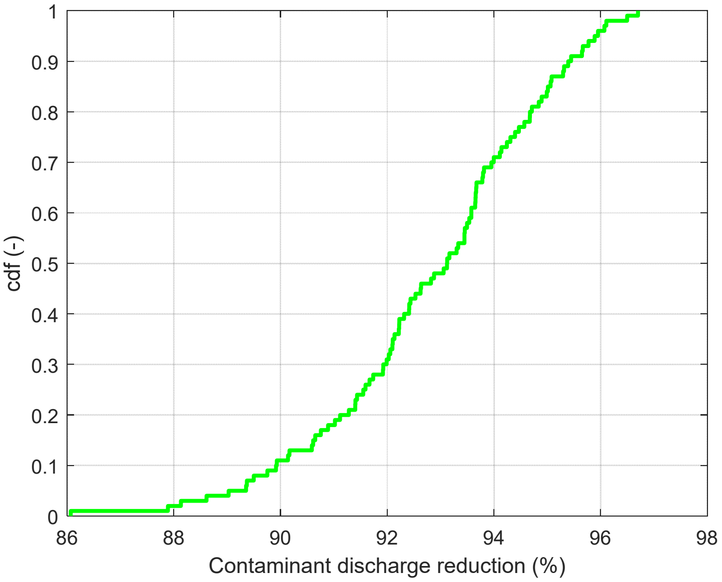


Figure 48. Alternative CDF Representation in Terms of Relative (Percent) DCE Discharge Reduction Between 2006 (PFM) and 2018 (BMLS).

5.8.3.4 Comparison of 2006 PFM (post-remediation) to 2018 PFM (post-remediation).

Figure 49 provides comparison of post-remedial TCE sampling results between 2006 PFM measurements and 2018 PFM measurements. Similar to the 2018 BMLS results, the 2018 PFM results show a definite decrease in TCE flux and resulting discharge. The information provided in Figure 49 can be summarized as follows: between the 2006 and 2018 post-remediation sampling events the TCE flux magnitudes and resulting mass discharge decreased and there was minimal shift in the center of mass of the plume.

Figure 50 provides comparison for DCE sampling results between 2006 PFM measurements and 2018 PFM measurements. Figure 50 can be summarized as follows: between the 2006 and 2018 post-remediation sampling events the DCE flux magnitudes and resulting mass discharge decreased and there was a minor shift in the center of mass of the DCE plume to the right.

Figure 51 represents the CDF in terms of relative (percent) TCE discharge reduction between 2006 PFM and 2018 PFM. The figure indicates a definite discharge reduction as there is high probability that discharge was reduced by between 20 to 73% (mean value approximately 52% discharge reduction).

Figure 52 represents the CDF in terms of relative (percent) DCE discharge reduction between 2006 (PFM) and 2018(PFM). The figure indicates that there is very high probability (>99%), that the DCE mass discharge was reduced by 88.5 to 97.5% between 2006 and 2018.

The 2018 BMLS and PFM results provide very similar results all showing definite TCE and DCE mass discharge reduction since the initial 2006 post-remediation PFM measurements. This suggests that the 2017 BMLS results that indicated potential increases in the TCE mass discharge were most likely an artifact of temporary onsite conditions (such as the pump and treat system being turned off for maintenance) and not likely an indication of a long-term trend.

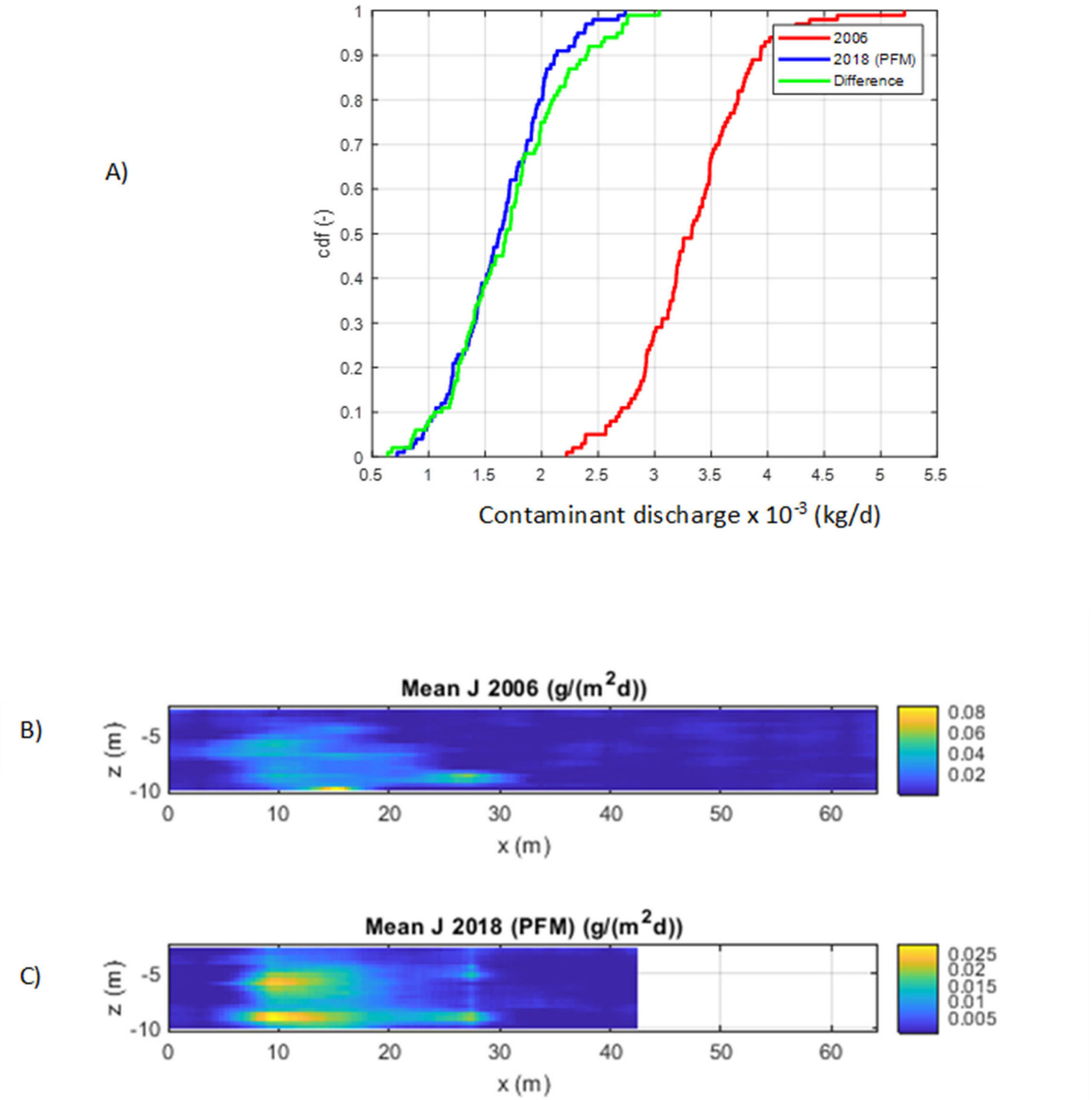


Figure 49. Simulated TCE Fluxes and CDFs of Simulated TCE Discharges and Discharge Difference Between 2006 (PFM) and 2018 (PFM).

A) CDFs of simulated TCE discharges (100 realizations) and of discharge difference between 2006 (PFM) and 2018 (PFM).

B) Map of 2006 mean simulated TCE fluxes.

C) Map of 2018 mean simulated TCE fluxes.

(Note the difference in flux magnitudes between figures B and C)

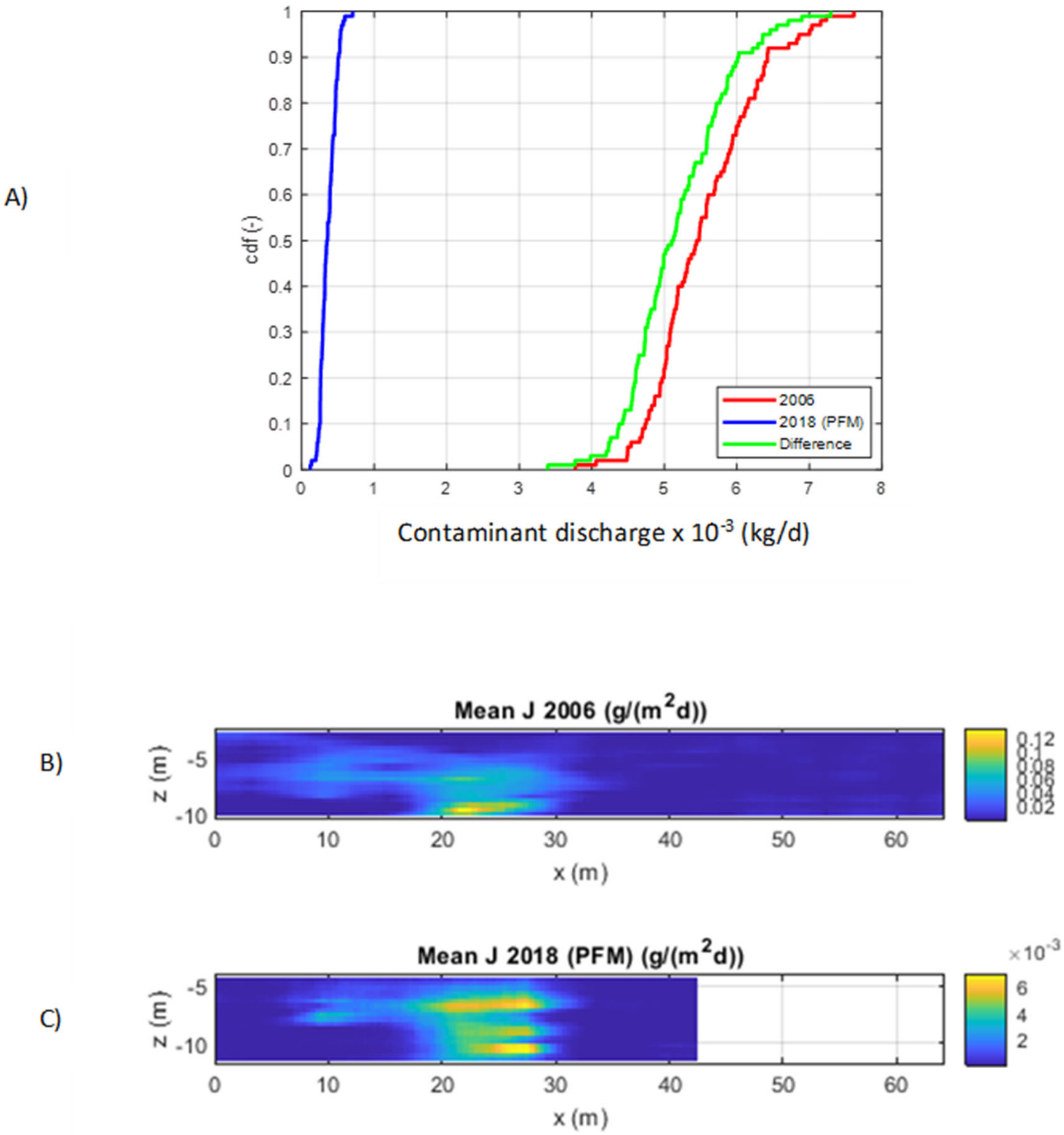


Figure 50. Simulated DCE Fluxes and CDFs of Simulated DCE Discharges and Discharge Difference Between 2006 (PFM) and 2018 (PFM).

A) CDFs of simulated DCE discharges (100 realizations) and of discharge difference between 2006 (PFM) and 2018 (PFM).

B) Map of 2006 mean simulated DCE fluxes.

C) Map of 2018 mean simulated DCE fluxes.

(Note the difference in flux magnitudes between figures B and C)

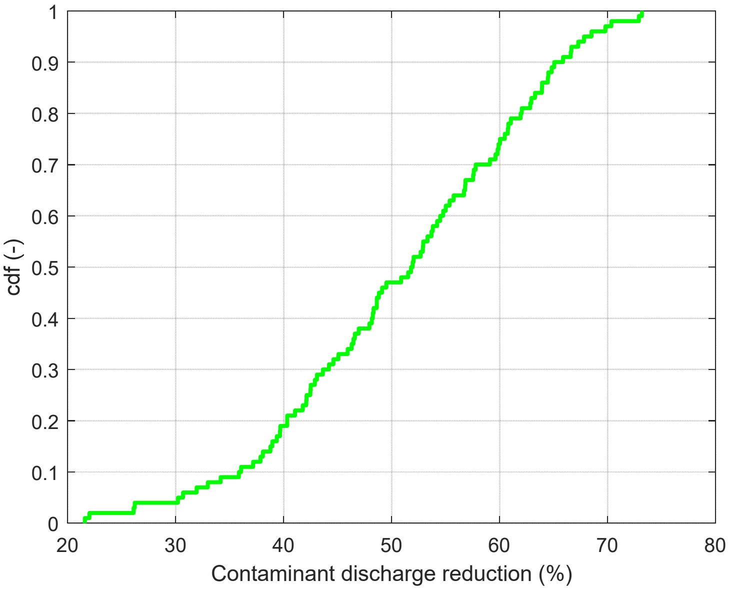


Figure 51. Alternative CDF Representation in Terms of Relative (Percent) TCE Discharge Reduction Between 2006 (PFM) and 2018 (PFM).

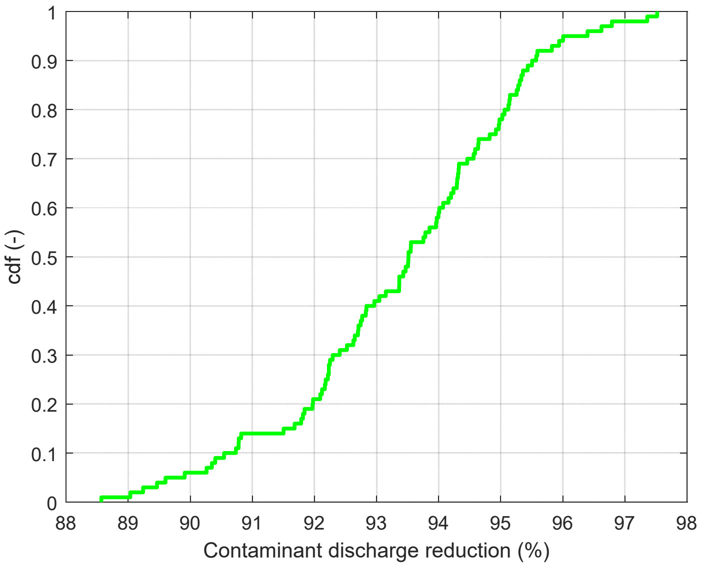


Figure 52. Alternative CDF Representation in Terms of Relative (Percent) DCE Discharge Reduction Between 2006 (PFM) and 2018 (PFM).

5.8.4 TIME SERIES DATA: NAPL AREA 1 DEEP WELLS AND NAPL AREA 3

Pre- and post-remediation data were also collected in the NAPL Area 1 deep well transect and NAPL Area 3 well transects. The stochastic modeling methods discussed in the previous section were not viable for these data because few wells had significant contaminant concentrations beyond 2006, but evaluation of the time series data still provides valuable information about locations with persistent contaminant flux and mass discharge.

5.8.4.1 Time series data: NAPL Area 1 Deep Wells.

The record of TCE and DCE fluxes for the NAPL Area Deep Well transect is summarized in Figures 53 and 54. Figure 53 encompasses the right portion of the transect when looking down-gradient through the transect, while Figure 54 encompasses the left portion. Unlike with the NAPL Area 1 shallow wells, the deep wells did not show a drastic change in contaminant flux from pre-remediation to post-remediation as the initial contaminant levels in the deep wells were significantly lower than the shallow wells. It can be seen that pre-remediation the highest TCE and DCE fluxes were observed in the left side of the transect with well LC208 and LC210 having the highest TCE fluxes and well LC210 having the highest DCE flux (Figure 53).

Post-remediation there was a decrease in contaminant mass fluxes throughout the transect, and the predominant contaminant fluxes appear to be in the proximity of Wells LC208 and LC210. These results are more clearly evident when looking at the estimated TCE and DCE mass discharge in Figures 56 and 57 respectively. It can be seen that for both TCE and DCE the predominant mass discharges are from wells LC208 and LC210. An important thing to note is the significant increase in TCE flux and mass discharge in wells LC208 and LC210 during the final post-remediation (2018) PFM sampling event (Figures 53 and 56). This increase is also evident in the NAPL Area 1 footprint well (NAPL-F11). The PFM-measured Darcy velocities in 2006 and 2018 were similar, but the apparent TCE flux increased by an order of magnitude in LC208 and doubled in LC210 and NAPL-F11 over the same time frame. It is important to note that these higher TCE fluxes in the proximity of LC210 and NAPL-F11 were independently confirmed in a separate study on site as shown in Figure 58, where elevated TCE concentrations were measured in wells NAPL-F11 and LC210.

Initial inspection of the time series data in Figures 53, 55 and 56 makes it appear as if the TCE flux has increased since 2006, but it is important to note that these measured fluxes are influenced by the presence of the pump and treat system, as any changes in the hydraulic gradient will affect the direction of flow through the flux transect. Ideally, for the most accurate flux measurements, groundwater flow should be perpendicular to the flux transect. The flux well transects were initially designed based upon estimated groundwater flow directions for ambient flow conditions on site, but with the operation of the pump and treat system it is likely that flow is not perpendicular to the transect. Time series data of water levels throughout the site indicate significant variability in the local groundwater gradients, and at times the groundwater flow appears to be intersecting the transect at a very shallow angle (closer to parallel rather than perpendicular) which would lead to a decrease in measured mass flux.

Regardless of the flow conditions, what is evident from the measured flux data and independent aqueous water concentrations (Figure 58) is that contemporary TCE concentrations and resulting fluxes are higher in the proximity of well LC208, LC210 and NAPL-Fll which suggests that there is some sort of source material located in this area. The nature of the source material is unknown (free product, contaminated soil, back diffusion, etc.) but these results can help to focus future investigations to identify the location and nature of the source material still present on site.

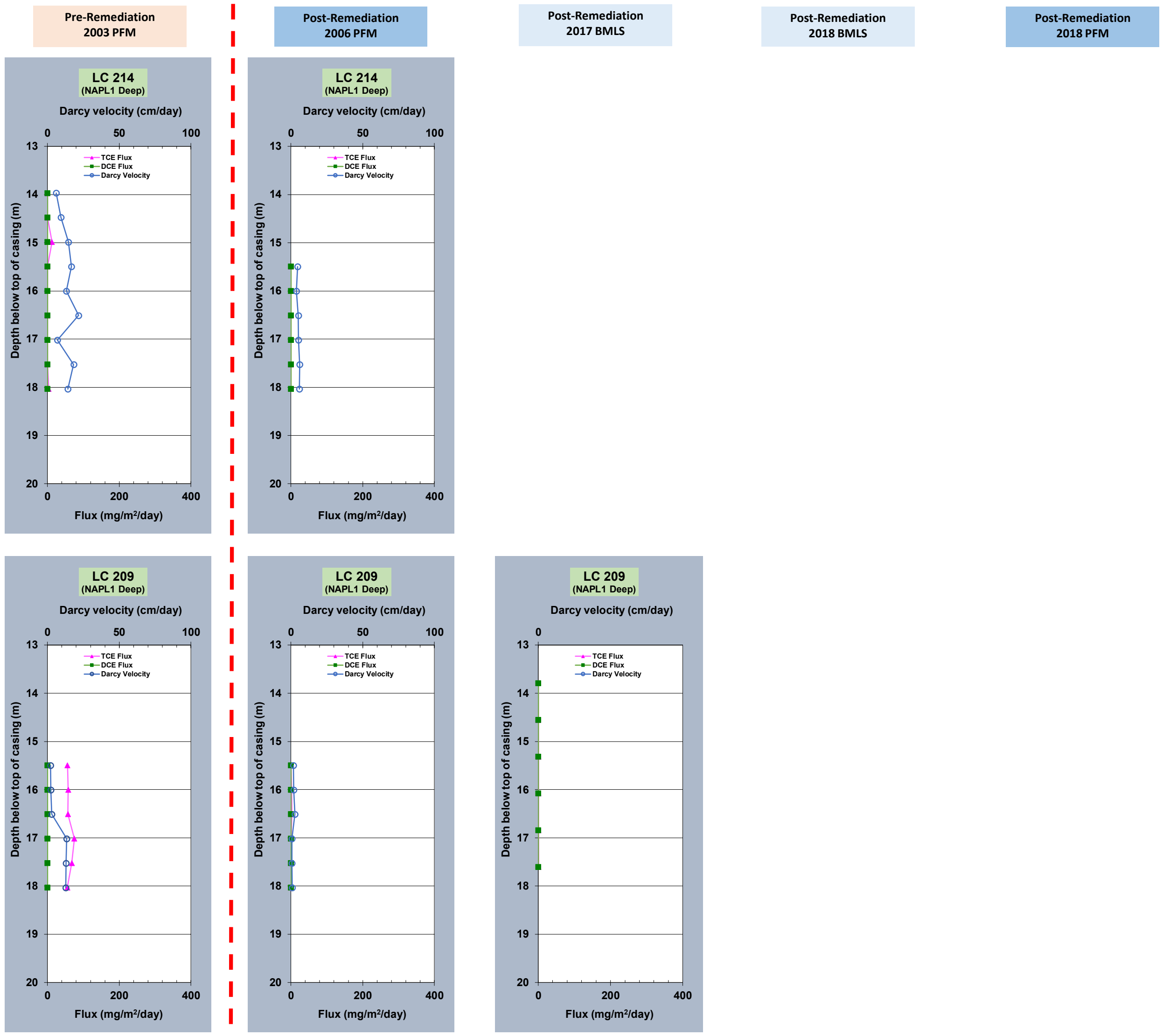


Figure 53. Comparison of Pre- and Post-remedial Fluxes Within the NAPL Area 1 Deep Well Flux Transect (Right Portion of Transect When Looking Down-gradient Through the Transect).

Figure 54. Comparison of Pre- and Post-remedial Fluxes Within the NAPL Area 1 Deep Well Flux Transect (Left Portion of Transect when Looking Down-gradient Through the Transect).

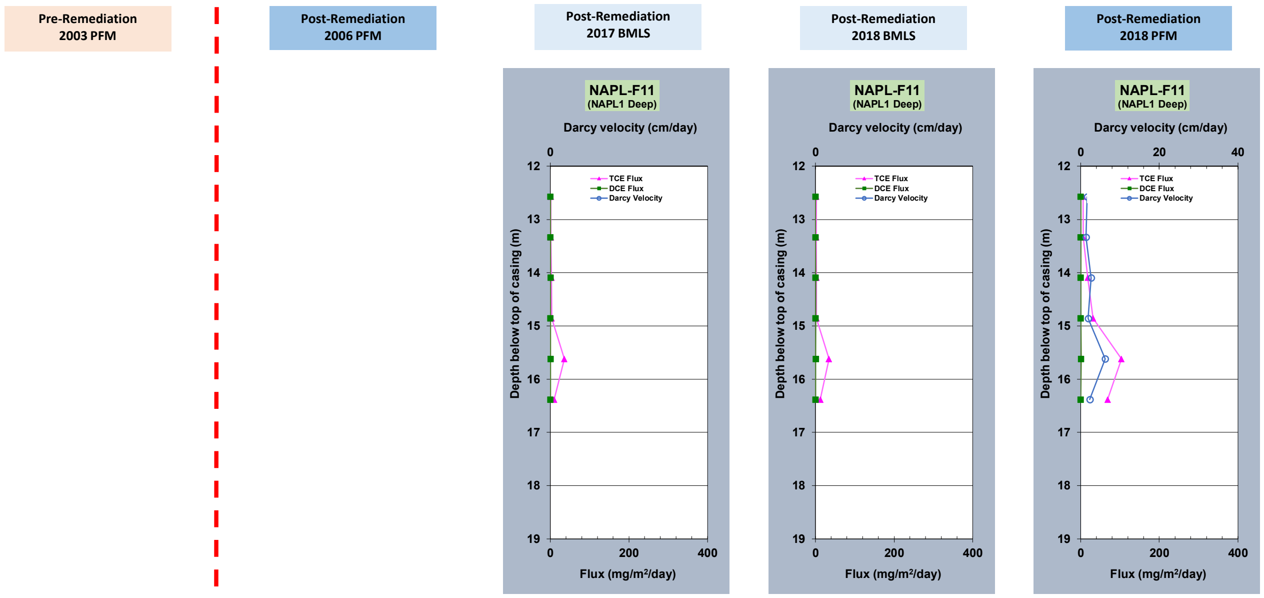


Figure 55. Post-remedial Fluxes Within the NAPL Area 1 Foot Print Well NAPL-F11 Which is Located Up-gradient of Deep Wells LC208 and LC210.

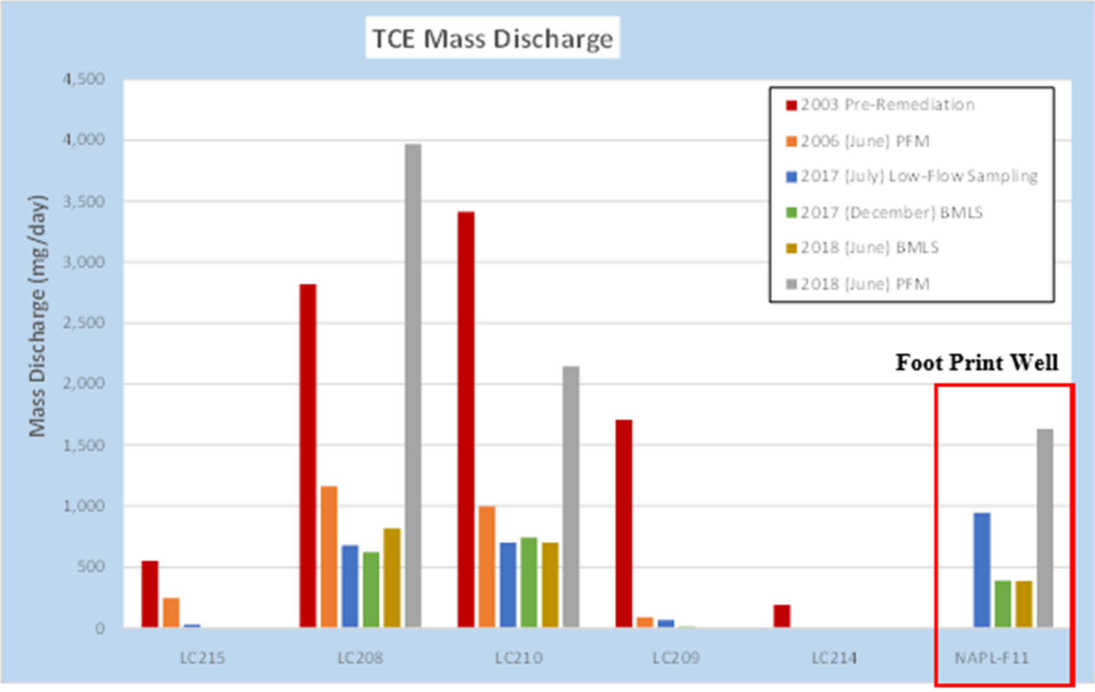


Figure 56. Estimated TCE Mass Discharge Through NAPL Area 1 Deep Well Transect and Foot Print Well.

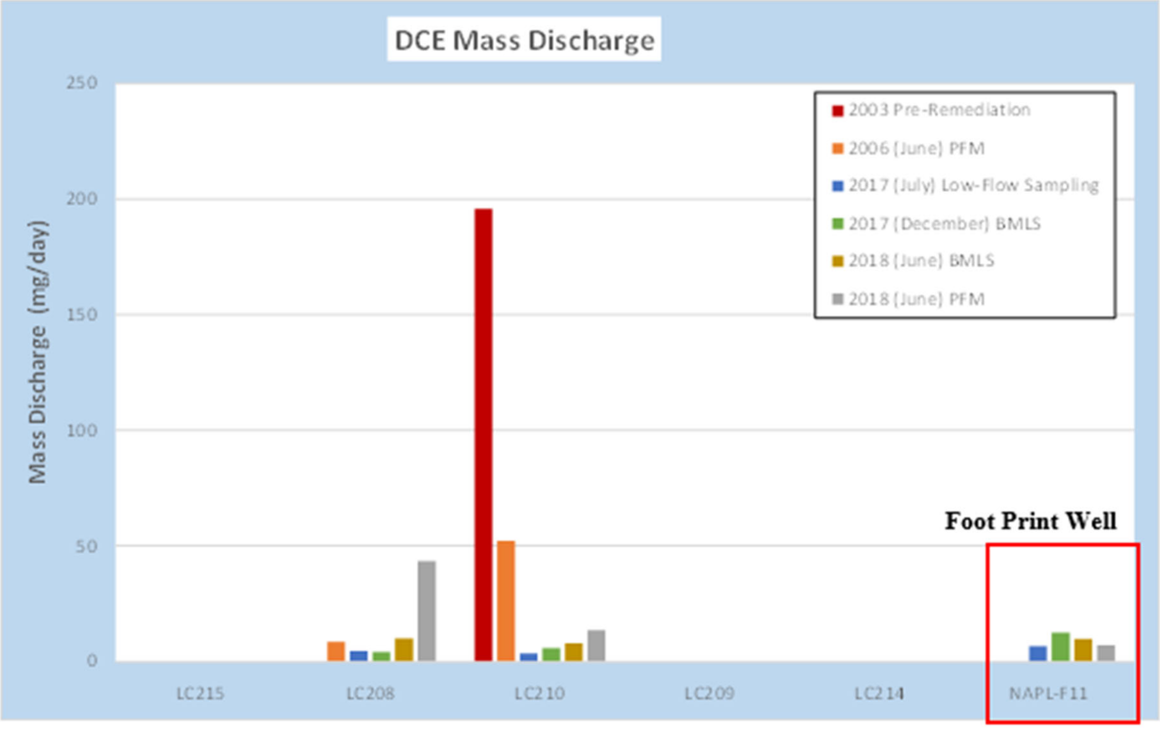


Figure 57. Estimated DCE Mass Discharge Through NAPL Area 1 Deep Well Transect and Foot Print Well.

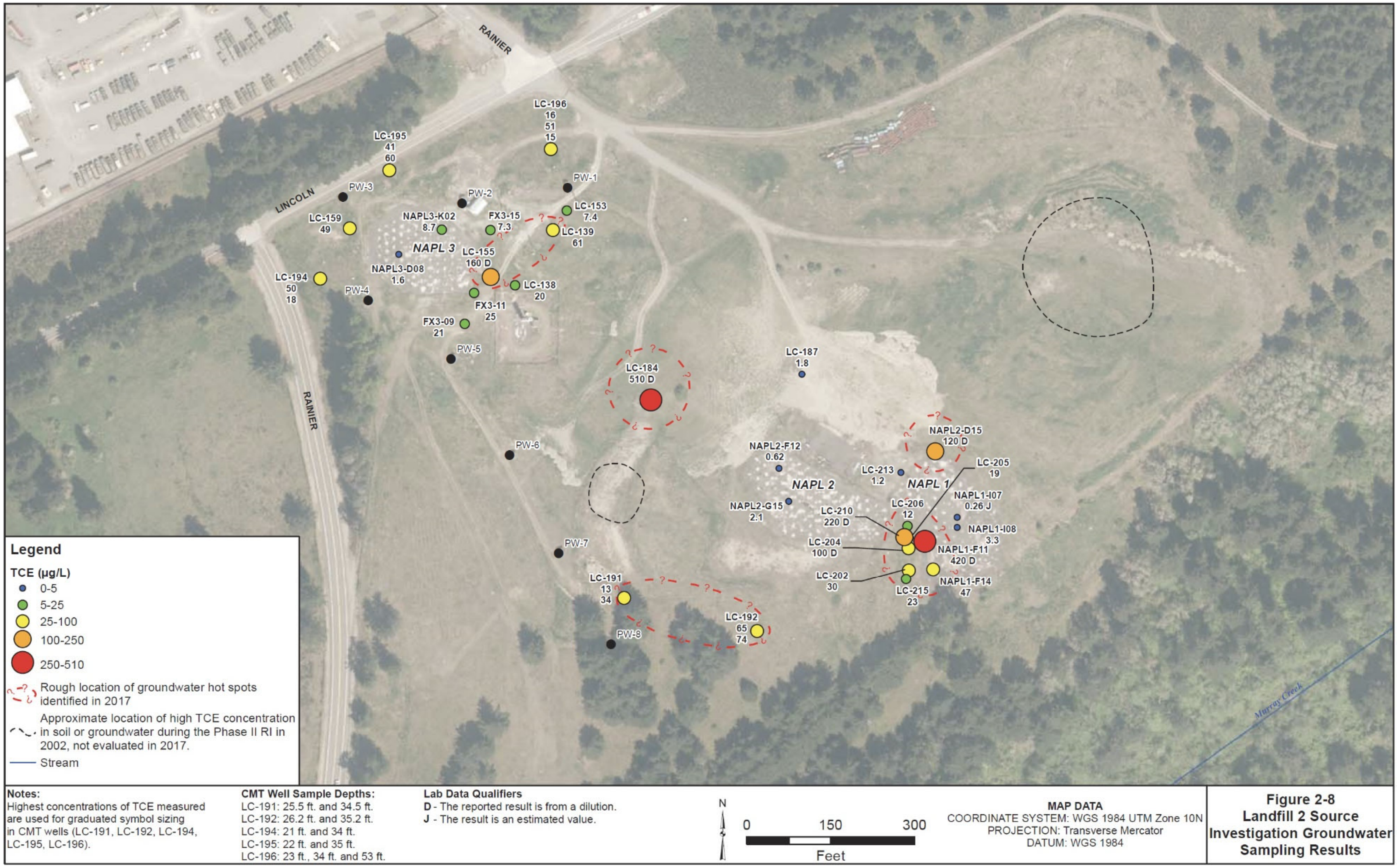


Figure 58. Aqueous TCE Concentrations Observed in 2017 Source Area Investigation

(Adapted from Figure 2-8 of Logistics Center Site Management Improvement Report (Sealaska, 2018c).

5.8.4.2 Time series data: NAPL Area 3.

The record of TCE and DCE fluxes for NAPL Area 3 is summarized in Figures 59 and 60. Figure 59 encompasses the right portion of the transect when looking down-gradient through the transect, while Figure 60 encompasses the left portion. During the initial phase of flux measurements on site in 2006 both an up-gradient and down-gradient transect were installed in NAPL Area 3 (Figure 12). However, during low-flow sampling in 2017 consistently higher contaminant concentrations were measured in the down-gradient transect and as such all subsequent work was focused on the down-gradient transect and footprint well NW EW-1a (Figure 61). Not all wells from the down-gradient transect shown in Figure 12 are represented in these figures. Wells that had minimal TCE and DCE concentrations during the 2017 low-flow sampling event were not included in subsequent sampling.

Unlike NAPL Area 1, pre-remedial flux measurements were not collected in NAPL Area 3. The first PFM flux measurements were performed in 2006, which for this location was technically post-remedial, but active remediation was still being performed on site when the PFM were deployed and soil temperatures were still elevated.

During the 2006 PFM post-remedial measurements, DCE fluxes were significantly higher than TCE fluxes in most NAPL Area 1 down-gradient wells and the predominant contaminant fluxes were in the proximity of flux well FX3-04. By 2017, the contaminant fluxes had decreased significantly (by two orders of magnitude) and TCE fluxes were now equivalent or higher than DCE fluxes in most wells. By the final PFM flux measurement in 2018 Well FX3-04 indicates an increase in TCE flux (Figure 60), while the foot print well NW EW-1a shows an increase in both TCE and DCE fluxes (Figure 61). Although, it is important to note that these fluxes (and aqueous concentrations) are an order of magnitude less than those observed in NAPL Area 1.

These results are also evident in the estimated TCE and DCE mass discharge in Figures 62 and 63 respectively. The 2006 DCE mass discharges were an order of magnitude higher than the TCE discharges throughout the entire transect. But, inspection of the contemporary data (excluding 2006) shows variation in the discharge magnitudes but a definite increase in TCE discharge especially in wells FX3-04 and foot print well NW EW-1a. During the final 2018 PFM measurements the TCE discharge in well FX3-04 was significantly higher than the DCE discharge (Figure 61), while in the foot print well both the TCE and DCE discharges had increased (Figure 62).

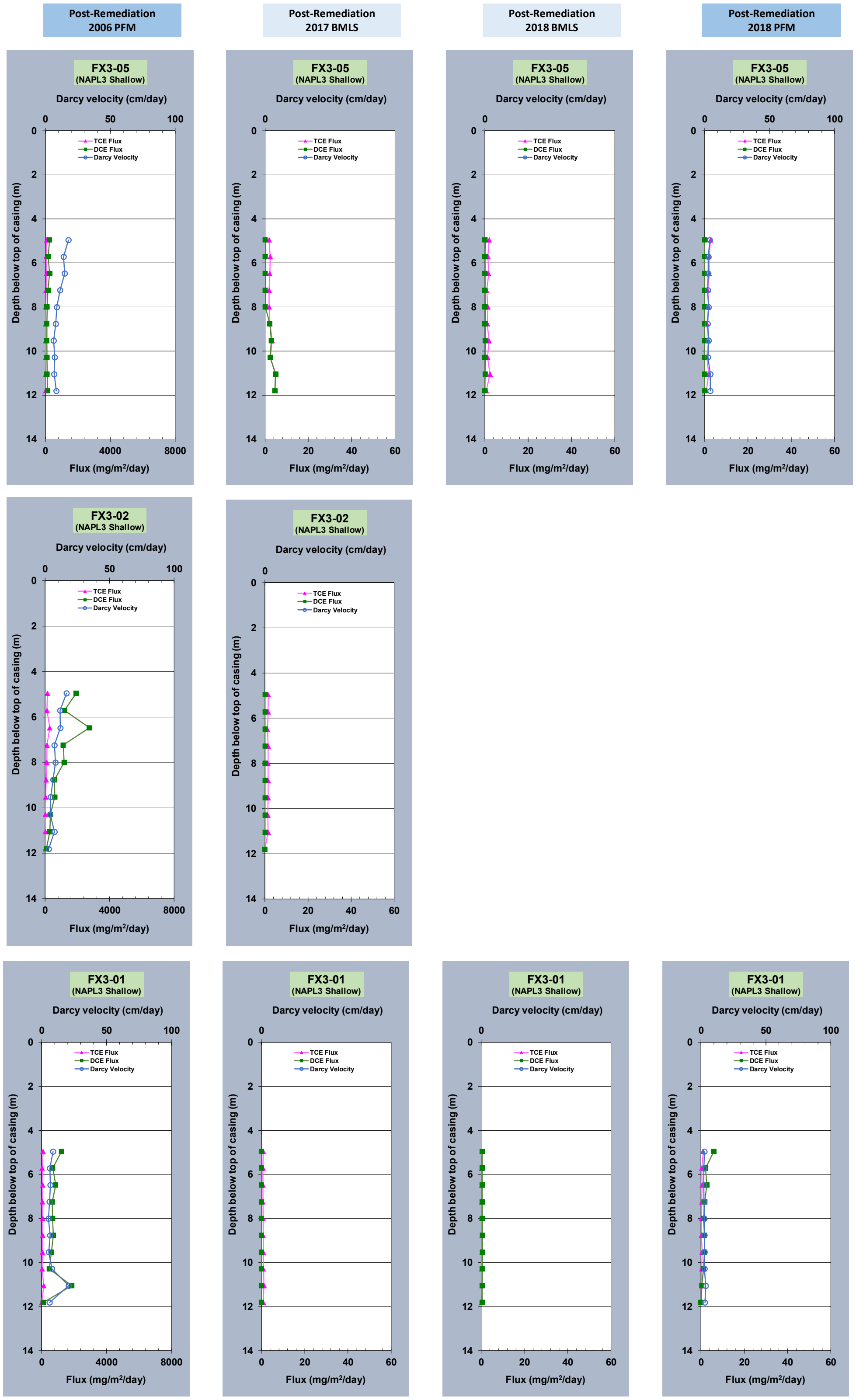


Figure 59. Post-remedial Fluxes within the NAPL Area 3 Flux Transect (Right Portion of Transect when Looking Down-gradient Through the Transect).

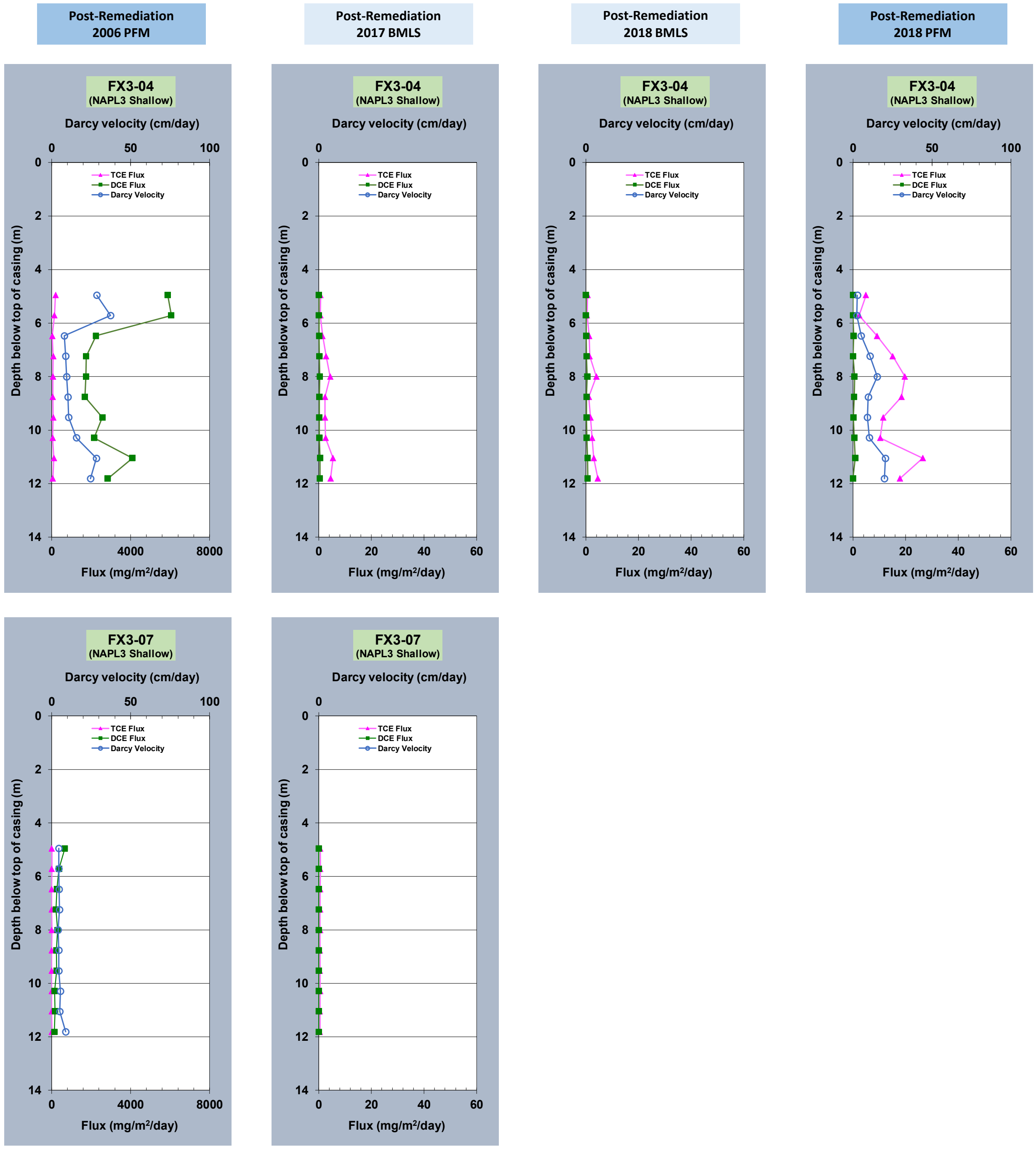


Figure 60. Post-remedial Fluxes Within the NAPL Area 3 Flux Transect (Left Portion of Transect when Looking Down-gradient through the Transect).

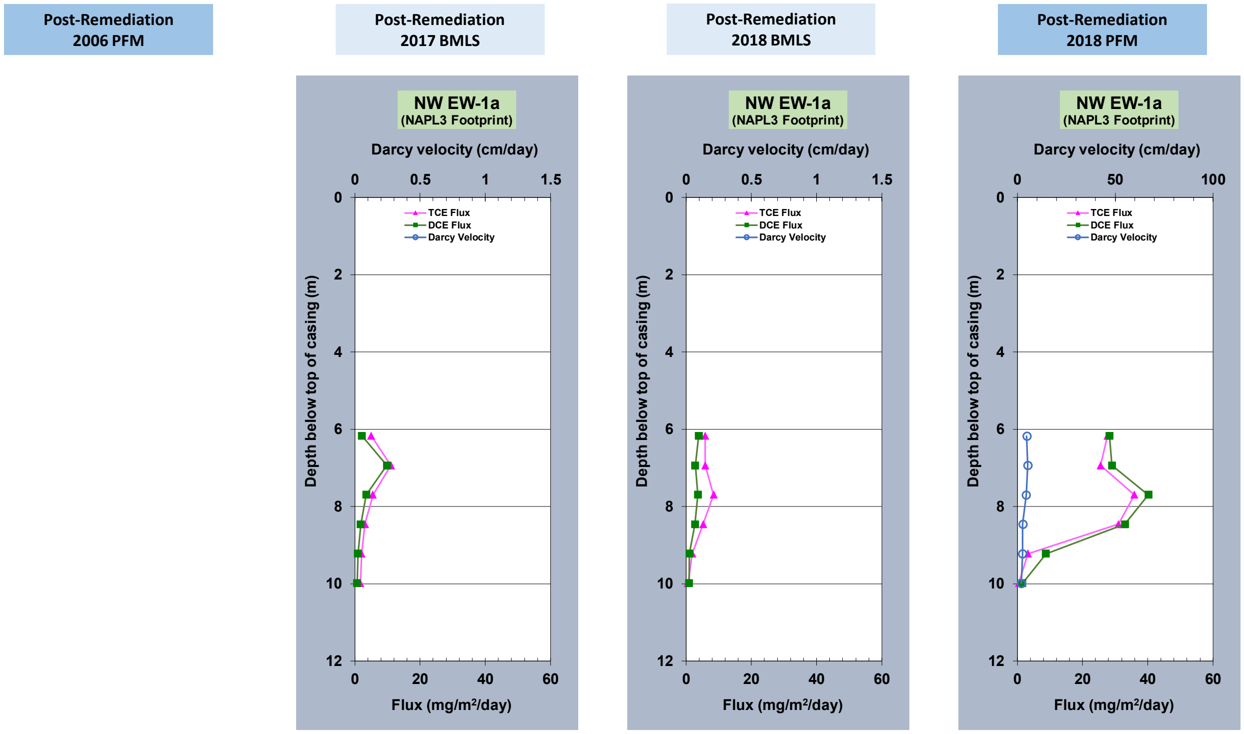


Figure 61. Post-remedial Fluxes within the NAPL Area 3 Foot Print Well NW EW-1.

Figure 62. Estimated TCE Mass Discharge for NAPL Area 3 Flux Transect and Foot Print Well.

A) All post-remediation data.

B) Contemporary data (excluding 2006) for detailed comparison of discharges.

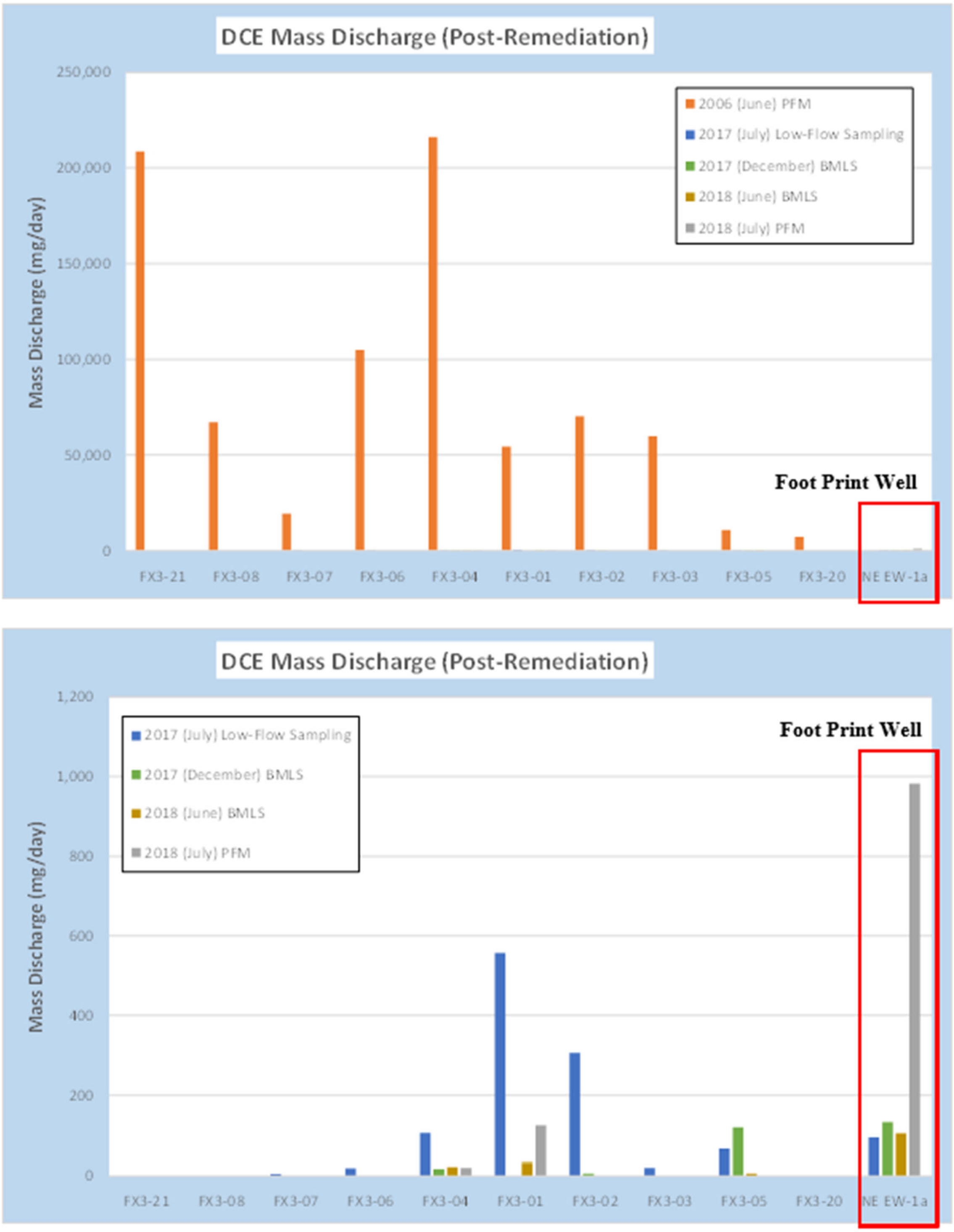


Figure 63. Estimated DCE Mass Discharge for NAPL Area 3 Flux Transect and Foot Print Well.

A) All post-remediation data.

B) Contemporary data (excluding 2006) for detailed comparison of discharges.

5.8.5 SITE CONTAMINANT MASS BALANCE

One of the main benefits of considering site conditions in terms of mass flux and mass discharge at control planes is linking this information to a site wide mass balance. The mass in the source zone can be linked to the mass in the plume through a historical source strength function. While measuring mass quantities in the source is quite challenging using direct measurements, using a mass balance approach can lead to useful estimates for the site.

One approach for source mass estimation, under the assumption of a simple exponential source decay model, makes use of a decay rate (k) estimated from monitoring wells ideally located near the source (Annable et al., 2014):

$$M_{t2} = M_{t1} exp(-(t_2 - t_1)k) = \frac{qAC_{t1}}{k} exp(-(t_2 - t_1)k) \qquad \text{Eq. 5}$$

where M_{t1} and M_{t2} are the source masses [M] at two different times, and C_{t1} is the concentration [ML^{-3}] in the monitoring well at time t_1 [T]. Using equation 5, the present DNAPL source mass (M_{t2}) can be estimated.

Another approach is the power source function model (Park and Parker, 2005; Falta 2008) which in its simplified form for mass discharge is as follows:

$$\frac{MD_S(t)}{MD_0} = \left(\frac{M(t)}{M_0}\right)^{\Gamma} \qquad \text{Eq. 6}$$

where MD_0 is the initial average mass discharge and $MD_s(t)$ is the average mass discharge at time t. Similarly, M_0 is the initial source mass and $M(t)$ is the source mass at time t. The power function exponent (Γ) is a fitting parameter.

5.8.5.1 NAPL Area 1 mass balance.

As mentioned previously, the most complete record of historic flux data has been collected for NAPL Area 1, and we will once again focus our discussion on these data using the 2003 pre-remediation and 2006 post-remediation PFM flux data along with the estimated mass removal during thermal treatment to evaluate the source mass within NAPL Area 1. For application of either model (exponential or power), the 2003 pre-remediation source mass (M_{pre}) is estimated as the mass destroyed/removed by thermal treatment ($M_{thermal}$) plus the estimated 2006 post-remediation mass (M_{post}).

$M_{pre} = M_{thermal} + M_{post}$

Where $M_{thermal}$ is based upon values previously reported (USCE, 2015) and M_{pre} and M_{post} are calculated using PFM-measured mass discharges from 2003 and 2006 respectively.

For application of the exponential source decay model, equation 5 was solved using a multi-component optimization framework to determine the optimal k value that resulted in consistent values for the calculated 2006 source mass and 2003 calibrated source mass. The problem was solved independently using both generalized reduced gradient (GRG) nonlinear and evolutionary solution techniques. Both solution methods converged on the same optimal result:

$k = 0.000308803413798785$

$M_{pre} = 2{,}518.37$ kg

$M_{post} = 18.37$ kg

The optimal k value was then used with mass discharge estimates from the contemporary low-flow sampling, BMLS and PFM measurements to estimate the corresponding apparent source mass for both the shallow and deep well transects within NAPL Area 1. The results are summarized in Table 5.

Table 5. NAPL Area 1 Exponential Source Mass Estimates.

Shallow well transect

2017 Low Flow mass discharge	0.0014	kg/day
2017 Low Flow estimated source mass	4.68	kg
2017 BMLS mass discharge	0.0027	kg/day
2017 BMLS estimated source mass	8.85	kg
2018 BMLS mass discharge	0.0011	kg/day
2018 BMLS estimated source mass	3.60	kg
2018 PFM mass discharge	0.0010	kg/day
2018 PFM estimated source mass	3.37	kg

Deep well transect

2017 Low Flow mass discharge	0.0015	kg/day
2017 Low Flow estimated source mass	4.76	kg
2017 BMLS mass discharge	0.0014	kg/day
2017 BMLS estimated source mass	4.44	kg
2018 BMLS mass discharge	0.0015	kg/day
2018 BMLS estimated source mass	4.90	kg
2018 PFM mass discharge	0.0061	kg/day
2018 PFM estimated source mass	19.76	kg

For application of the power source function model, equation 6 was solved using a multi-component optimization framework to determine the optimal Γ value that resulted in consistent values for the calculated 2006 source mass and 2003 calibrated source mass. The problem was solved independently using both generalized reduced gradient (GRG) nonlinear and evolutionary solution techniques. Both solution methods converged on the same optimal result:

$\Gamma = 1.006484114$

$M_{pre} = 2518.66$ kg

$M_{post} = 18.66$ kg

The optimal Γ value was then used with mass discharge estimates from the contemporary low-flow sampling, BMLS and PFM measurements to estimate the corresponding apparent source mass for both the shallow and deep well transects within NAPL Area 1. The results are summarized in Table 6.

Table 6. NAPL Area 1 Power Source Mass Estimates.

Shallow well transect

2017 Low Flow mass discharge	0.0014	kg/day
2017 Low Flow estimated source mass	4.79	kg
2017 BMLS mass discharge	0.0027	kg/day
2017 BMLS estimated source mass	9.03	kg
2018 BMLS mass discharge	0.0011	kg/day
2018 BMLS estimated source mass	3.69	kg
2018 PFM mass discharge	0.0010	kg/day
2018 PFM estimated source mass	3.47	kg

Deep well transect

2017 Low Flow mass discharge	0.0015	kg/day
2017 Low Flow estimated source mass	4.87	kg
2017 BMLS mass discharge	0.0014	kg/day
2017 BMLS estimated source mass	4.55	kg
2018 BMLS mass discharge	0.0015	kg/day
2018 BMLS estimated source mass	5.02	kg
2018 PFM mass discharge	0.0061	kg/day
2018 PFM estimated source mass	20.06	kg

As discussed previously, the estimated mass discharge values are highly dependent upon the groundwater flow conditions at the time of measurement. The hydraulic gradient and resulting groundwater flow direction and magnitude can vary significantly due to both seasonal fluctuations and impacts of the active pump and treat system. It is likely that the variation seen in the estimated source mass values is due to changes in the local hydraulic gradient during the time of measurement. This is why all source mass estimates are labeled as the "apparent" source mass. As such, the results provide a probable range of apparent source mass values depending on the hydraulic gradient and resulting groundwater flow direction. Higher source mass estimates will be observed when the flow direction is most closely perpendicular to the flux well transect, while lower source mass estimates will be observed when the flow direction not perpendicular with the lowest case being for instances of flow parallel to the flux well transect.

Bearing this in mind, the estimated apparent source mass results are very similar for the exponential and power source models. When rounded up to the nearest whole number, the estimated pre-remediation source mass is approximately 2,519 kg and the estimated post-remediation source mass is 19 kg. Similarly, the apparent source mass estimated from contemporary data (Tables 5 and 6) follow similar trends. For both methods the shallow well transect has an apparent source mass within the range of 3 to 9 kg, with the highest value being estimated from the 2017 BMLS mass discharge.

While the deep well transect has an apparent source mass within the range of 4 to 20 kg, with the highest value being estimated from the 2018 PFM mass discharge. When the shallow and deep well transects are combined the total apparent source mass for NAPL Area 1 is in the range of 7 to 29 kg.

The high flux zone is once again apparent within the deep well transect based upon the 2018 PFM data. At first glance, the results may suggest that the 2018 apparent source mass (20 kg) is potentially higher than the estimated post-remediation source mass (19 kg). But, this is unlikely, and because the values are so close what this more realistically suggests is that the source material that is still present within NAPL Area 1 has been present since post-remediation.

The fitting parameter Γ from the power function model has been shown to range from 0.5 to 2.0 for single-component NAPL sources, where the lower and upper values are applicable to pool- and ganglia-dominated sources respectively (Falta et al., 2005a). It has also been suggested that Γ values less than 1.0 are consistent with sites where the contaminant is primarily in high-permeability zones and Γ values greater than 1.0 are consistent with sites where the contaminant is primarily in low-permeability zones (Falta, 2008). The optimal value determined here was $\Gamma = 1.006$ which is somewhat inconclusive with regard to the nature of the source. However, due to the age of the site and the extended period over which the pump and treat system has been active, it is unlikely that the contaminant is solely in a high permeability zone and more likely within a low-permeability zone.

5.8.5.2 Site mass balance.

Estimating a mass balance for the entire EGDY site is a far more complicated task as there is not a consistent flux record for the site as a whole. However, the pump and treat data can be used to provide a rudimentary estimate based upon the contaminant mass removed after thermal treatment ended (post-remediation). The record of TCE mass removed by pump and treat was obtained from publicly available reports (USACE, 2012; USACE, 2017; and USEPA, 2018) and is summarized in Table 7. It should be noted that no data was reported for 2016, but the pump and treat system was active and because the reported values for 2015 and 2017 were the same, it was assumed that the mass removed in 2016 was the same as 2015 and 2017 (for calculation purposes).

Table 7. TCE Mass Removed by Pump and Treat System.

Year	TCE Mass Removed (lb)	TCE Mass Removed (kg)
2007	329	149.23
2008	246	111.58
2009	129	58.51
2010	141	63.96
2011	108	48.99
2012	119	53.98
2013	71	32.21
2014	61	27.67
2015	85	38.56
2016	85	38.56
2017	85	38.56
Total	1459	662

* No data available--Assumed same as 2015 and 2017

The historical TCE mass removed by the pump and treat system (Table 7) was used with the exponential decay source model in a combinatorial optimization framework to determine the optimal decay rate (k) and initial 2007 (post-remedial) source mass (M_{post}) by minimizing the sum of the squared differences between observed and model-calculated mass removed values over a ten year period (2007 to 2017). The optimal site wide results are summarized below and shown in Figure 64.

Site wide estimates (2007 post-remediation):

k = 0.000556853

M_{post} = 161.60 kg

The estimated decay rate for the site (k = 0.000556853) is greater than the estimated value for NAPL Area 1 (k = 0.000308803), which seems appropriate as there are more observations distributed over a larger area and likely more distant from the source zones.

The exponential decay source model can be applied to shorter and shorter time frames in order to estimate the apparent initial source mass for years 2007-2012. The results are summarized in Table 8 where the apparent source mass decreases from 161.60 kg to 49.62 kg. After this point, the solution approaches an asymptotic limit (linear solution) that no longer provides practical results as the estimated source mass is underestimated and significantly lower than the observed mass removed by the pump and treat system.

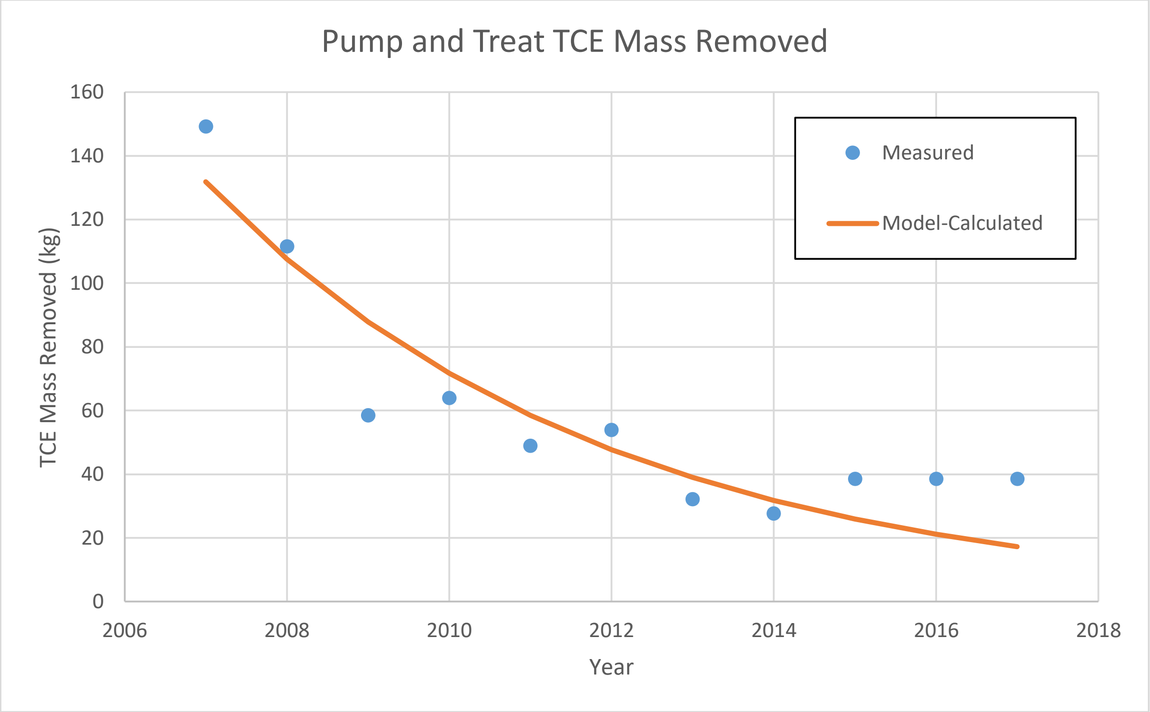


Figure 64. Comparison of Measured and Model-calculated TCE Mass Removed by Pump and Treat.

Table 8. Comparison of Reported TCE Mass Removed and Estimated Apparent Source Mass.

Year	TCE Mass Removed (kg)	Estimated Apparent Source Mass (kg)
2007	149.23	161.60
2008	111.58	104.25
2009	58.51	65.63
2010	63.96	68.23
2011	48.99	55.21
2012	53.98	49.62

It is important to note that the mass balance and resulting apparent source mass estimates are simply estimates, which provide a general indication of the relative proportion of contaminant mass within NAPL Area 1 and the site as a whole. The results indicate that post-remediation the apparent TCE mass remaining within the EGDY site was on the order of 162 kg (rounded from 161.60 kg in Table 8) while the apparent TCE mass within NAPL Area 1 was on the order of 19 kg. Which suggests that the NAPL Area 1 2006 post-remediation contaminant source mass was approximately 12% of the total source mass present on site. Over the following 10 years, through operation of the pump and treat system the contaminant mass on site was steadily reduced to an apparent source mass on the order of 50 kg (rounded from 49.62 kg in Table 8), which has remained relatively constant from 2013 to 2017. Within NAPL Area 1, the apparent source mass post-remediation appears to have decreased significantly between the 2006 and 2017 measurements, but the contemporary data suggest the apparent source mass from 2017 to 2018 to be on the order of 8.72 kg to 23.53 kg (sum of shallow well and deep well estimates from Table 6). Which suggests that the NAPL Area 1 contemporary post-remediation contaminant source mass is approximately 17% to 47% of the total source mass present on site. It is important to recall that the range in contemporary mass flux values and resulting source mass estimates is due to variations in groundwater flow directions with respect to the flux well transects. As such, it is likely that he higher source mass estimates are representative of actual site conditions.

6.0 PERFORMANCE ASSESSMENT

6.1 DATA ANALYSIS METHODS

Quantitative demonstration of the proposed performance objectives is contingent upon rigorous statistical comparison of the methods applied. For this purpose, classic regression analyses are conducted, but these are not sufficient on their own. To augment analysis, statistical methods from Bland and Altman (1986) were applied. These methods are briefly described in the following paragraphs.

When comparing two technologies or methods (e.g., A and B) for measuring a parameter of interest (i.e., contaminant flux), Bland and Altman (1986) recommend first plotting the difference $\Delta = a - b$ between measurements of the same parameter given by two methods against their mean

$(a + b)/2$; where a and b are actual measurements of same parameter using methods A and B respectively. The plot allows one to investigate lack of agreement between methods A and B and to investigate any possible relationship between the measurement error and the mean of the two measurements (which is the best estimate of the unknown true value). Sometimes, the distribution measurement errors vary proportionately with the mean (as with log normally distributed random variables like concentration).

Assuming no relation between the difference (Δ) and the mean, the lack of agreement between methods or the bias is estimated from the mean difference ($\bar{\Delta}$) and the standard deviation of the differences (s). If differences are normally distributed (Gaussian), 95% of differences will lie between these limits of agreement:

$$\bar{\Delta} \pm 1.96(s)$$

If the distribution of difference is not normal but skewed, other methods exist for determining asymmetric confidence intervals (Willink 2005).

Because the above limits of agreement are estimates for the population, standard errors and confidence intervals are used to assess the precision of the above estimated limits of agreement. Again, assuming normality the standard error (S_E) of the mean difference ($\bar{\Delta}$) is:

$$S_E = \sqrt{s^2/n}$$

where n is the number of samples. For the limits of agreement, the standard error (S_{EL}) of

$\bar{\Delta} - 1.96(s)$ and $\bar{\Delta} + 1.96(s)$ is approximately:

$$S_{EL} = \sqrt{3s^2/n}$$

Confidence intervals (e.g. the 95% confidence interval) are calculated using an appropriate value of t (e.g. for $\alpha = 0.05$) obtained from t-distribution tables and assuming n -1 degrees of freedom. The confidence interval on the mean difference is:

$$\bar{\Delta} \pm t(S_E)$$

Whereas confidence intervals on the lower and upper limit of agreement are:

$$\bar{\Delta} - 1.97s \pm t(S_E)$$

$$\bar{\Delta} + 1.97s \pm t(S_E)$$

Since true contaminant flux and source mass values are not actually known for most real world systems, an alternative means of assessing performance is measurement agreement between different methods (Bland and Altman, 1986). The above approach is used to assess BMLS performance and source model results.

6.2 FIELD DEMONSTRATION RESULTS

In this section, the statistical analysis methods presented in section 6.2 are used to evaluate quantitative results for all results summarized in sections 5.8. The discussion of results is organized based upon the performance objectives (Table 1).

6.2.1 PERFORMANCE OBJECTIVE: ACCURACY OF CONTAMINANT FLUX MEASUREMENTS

Evaluation of the accuracy of contaminant flux measurements is based upon comparison of contaminant fluxes measured with BMLS and PFM. Comparisons are made for two contaminants: TCE and DCE.

The measured TCE and DCE flux values for both technologies are compared in figures 65 and 67 respectively. Statistical analysis of the results is summarized in figures 66 and 68 which compare the average contaminant flux for each technology to the difference between measured fluxes. The mean difference for TCE flux is 14.94 mg/m^2/day with a standard error of 9.09 mg/m^2/day and limits of agreement between 106.43 to -76.56 mg/m^2/day corresponding to a 95% confidence interval (Bland and Altman, 1986). Results indicate reasonably good agreement between the two technologies with the BMLS estimating TCE fluxes on average 14.94 mg/m^2/day lower than PFM.

The mean difference for DCE flux is 1.77 mg/m^2/day with a standard error of 1.37 mg/m^2/day and limits of agreement between 15.51 to -11.98 mg/m^2/day corresponding to a 95% confidence interval (Bland and Altman, 1986). Results indicate good agreement between the two technologies with the BMLS estimating DCE fluxes on average 1.77 mg/m^2/day lower than PFM.

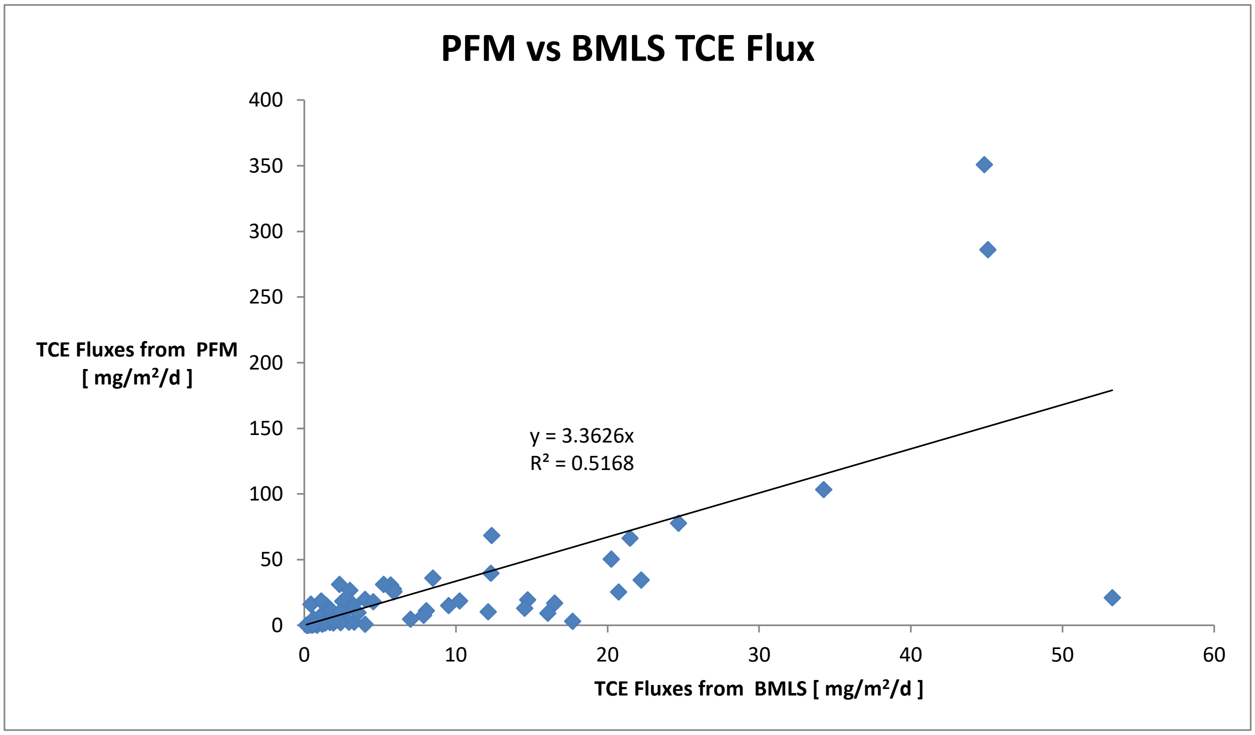


Figure 65. Comparison of TCE Flux by PFM and BMLS.

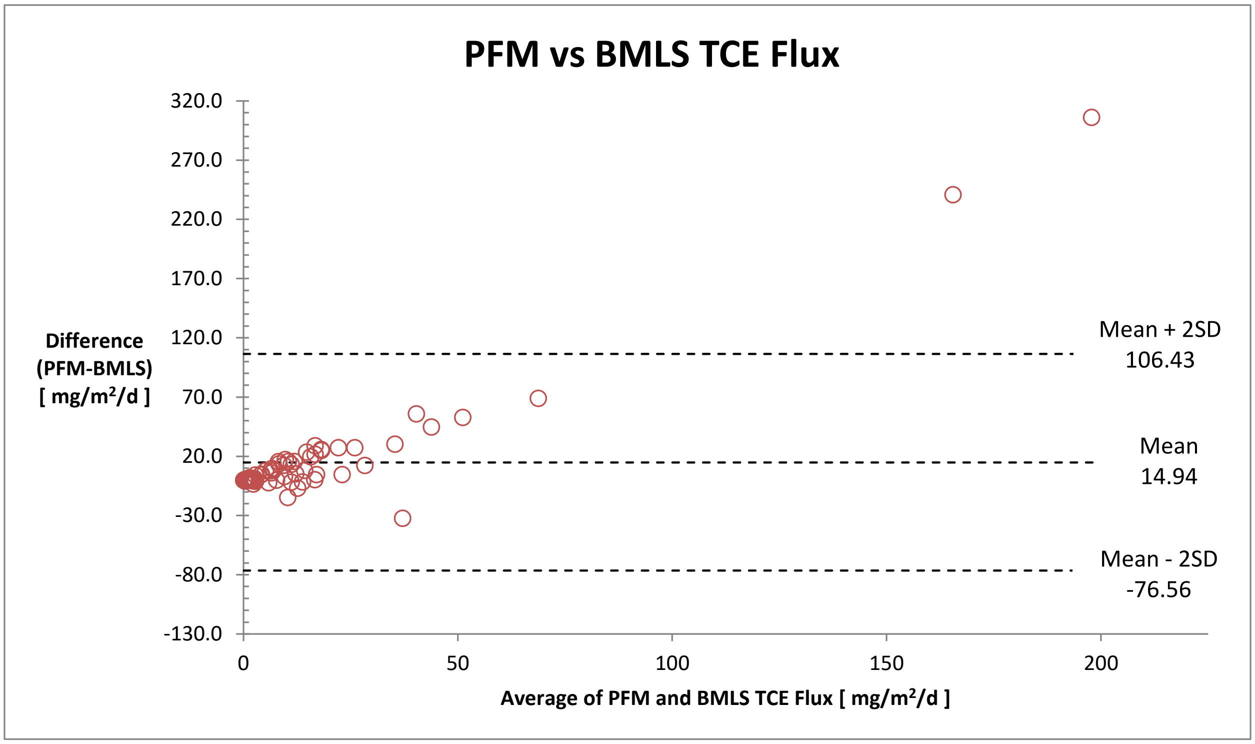


Figure 66. Summary of Statistical Analysis for TCE Flux from PFM and BMLS.

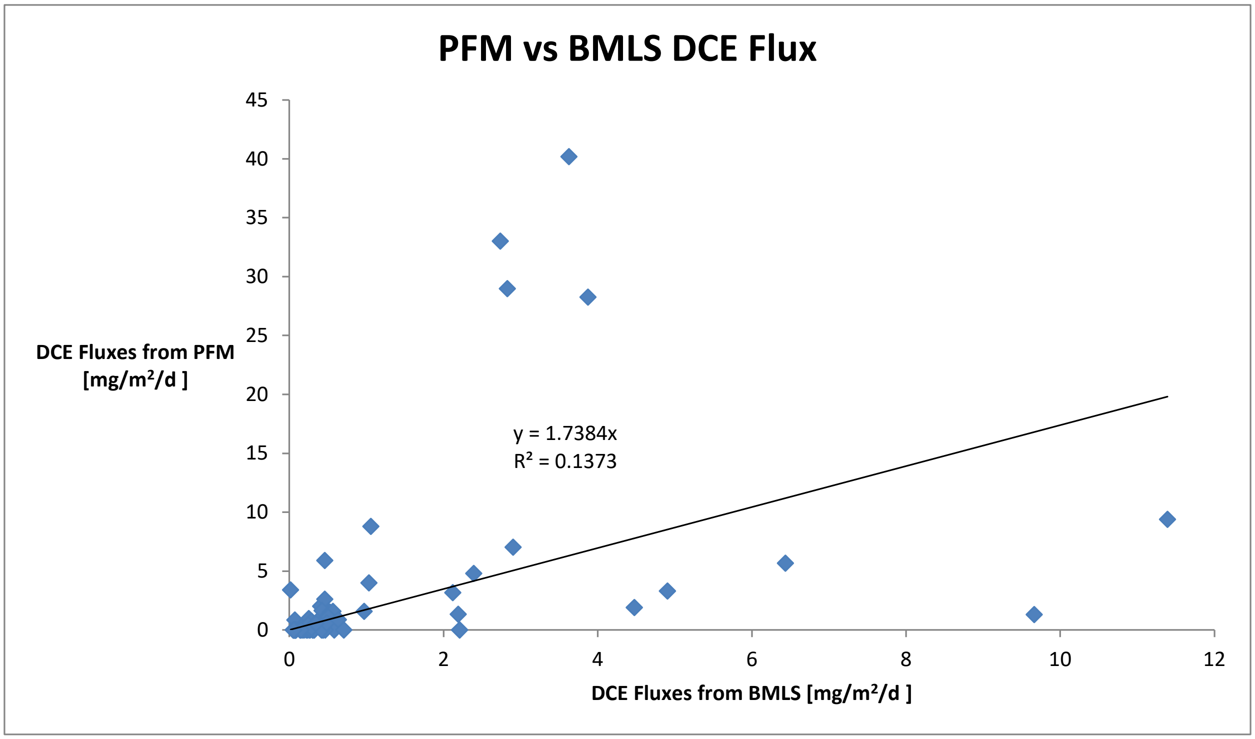


Figure 67. Comparison of DCE Flux by PFM and BMLS.

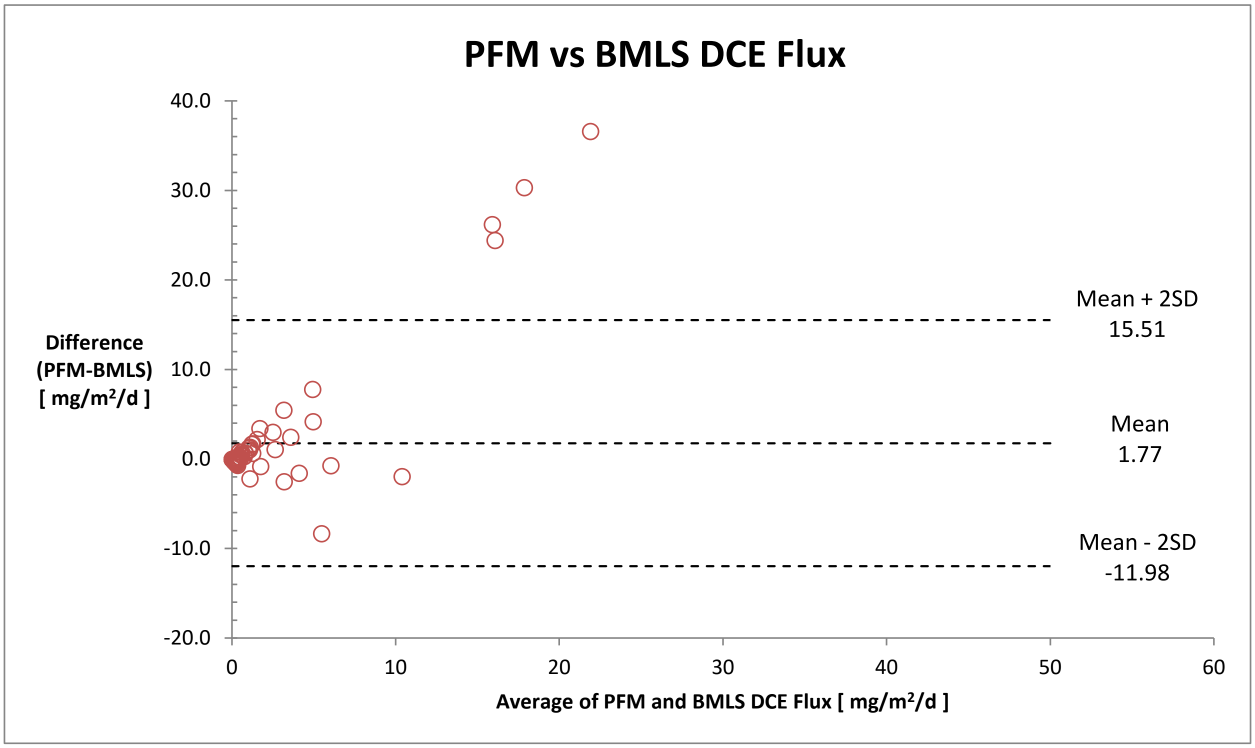


Figure 68. Summary of Statistical Analysis for DCE Flux from PFM and BMLS.

6.2.2 PERFORMANCE OBJECTIVE: ACCURACY OF SOURCE MODEL RESULTS

Evaluation of the accuracy of source model results is based upon comparison of estimated source mass values calculated with an exponential source model and power source model. The estimated source mass for both methods are compared in figure 67 and statistical analysis of the results is summarized in figure 68 which compare the average source mass estimated with each method to the difference between estimates. The mean difference for estimated source mass is 0.16 kg with a standard error of 0.05 kg and limits of agreement between 0.3210 to -0.0059 kg corresponding to a 95% confidence interval (Bland and Altman, 1986). Results indicate good agreement between the two methods with the exponential model estimating source mass values on average 0.16 kg lower than PFM.

6.2.3 PERFORMANCE OBJECTIVE RESULTS

Evaluation of the quantitative performance objectives (Table 9) establishes good agreement between BMLS measures and those provided by PFM. It is important to note that the standard error for TCE mass flux was 9.09 mg/m^2/day which was close to the established performance objective limit. However, this higher standard error was due solely to 4 measurements within well LC208. As discussed in previously in section 5 of this report there was a significant change in conditions between the BMLS and PFM sampling events in 2018 with a noticeable difference in measured fluxes. If these four measurements from LC208 are removed from the analysis the standard error is reduced to 3.21 mg/m^2/day.

The quantitative performance objective analysis also showed excellent agreement between the exponential source decay model and power model (Table 9) with a standard error of only 0.05 kg.

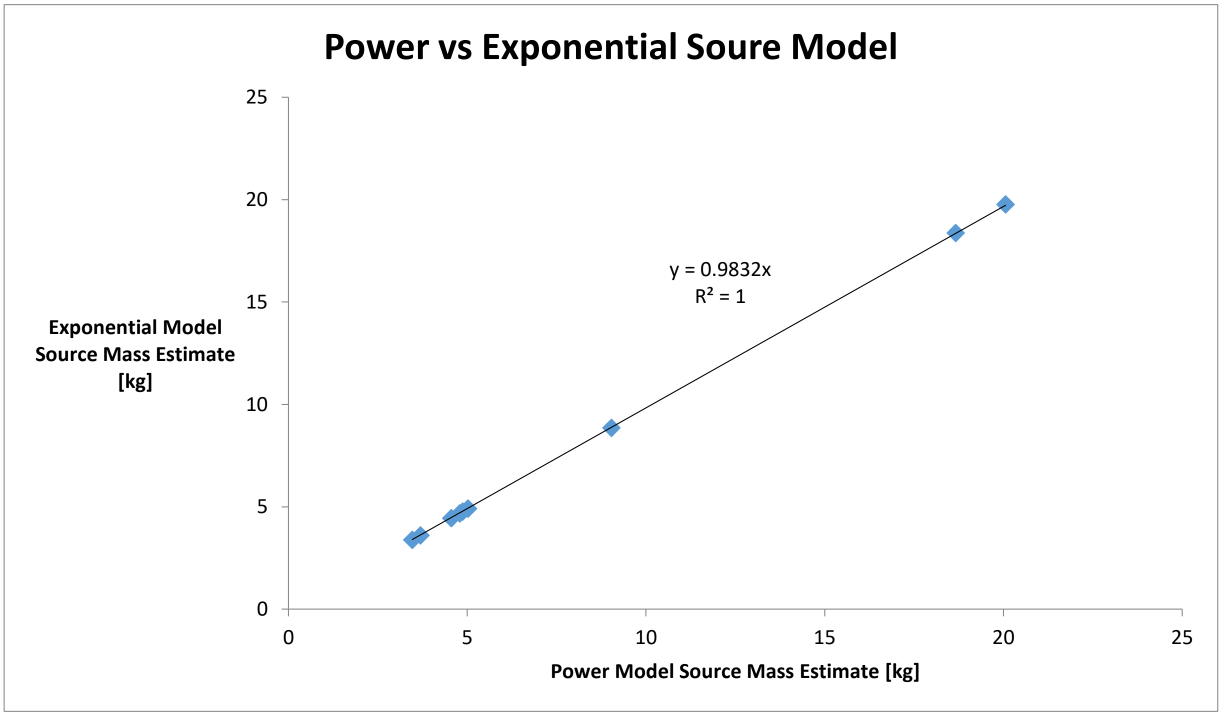


Figure 69. Comparison of Results for Estimated Source Mass Using Power Model and Exponential Model.

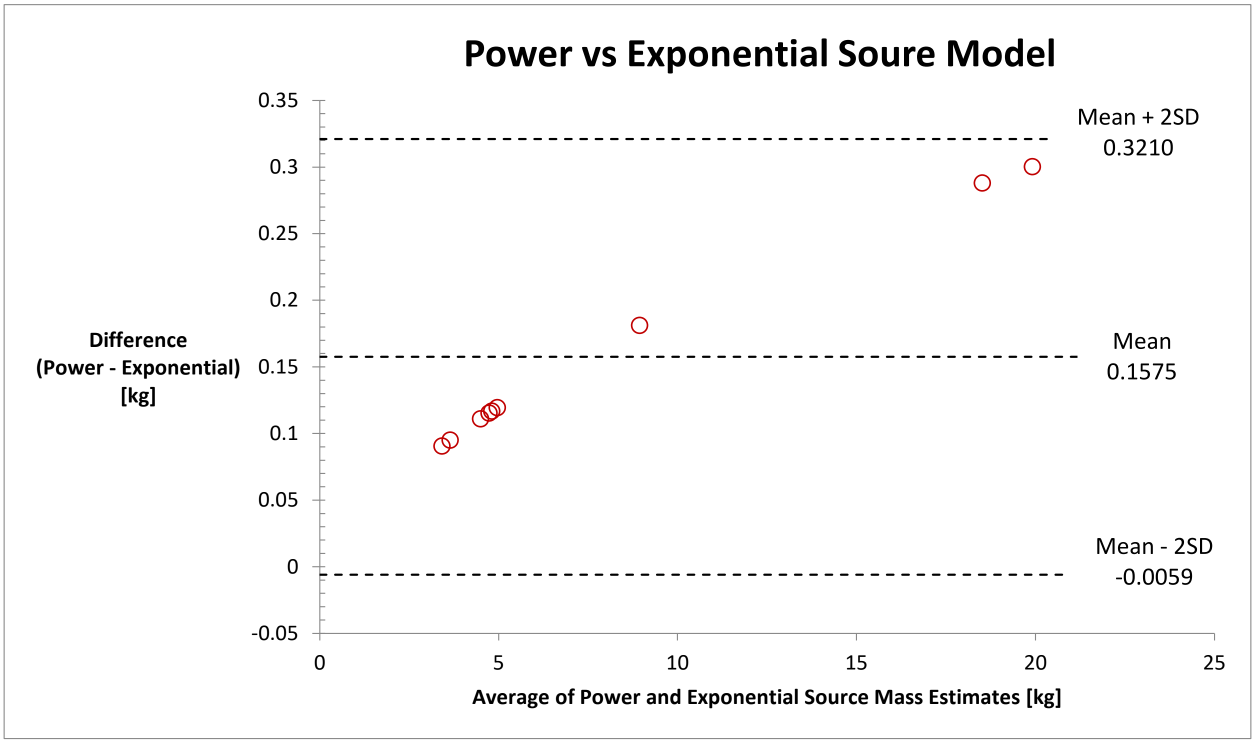


Figure 70. Summary of Statistical Analysis of Estimated Source Mass Using Power Model and Exponential Model.

Table 9. Summary of Quantitative Performance Objectives with Comparative Results.

Performance Objective		Data Requirements	Success Criteria	Technology Comparison
Quantitative Performance Objectives				Standard Error
1	Accuracy of TCE flux measurements	Measures from PFM and BMLS.	Standard error less than 10 mg/m^2/day within 95% confidence interval	9.09 (3.21*) mg/m^2/day
	Accuracy of DCE flux measurements	Measures from PFM and BMLS.	Standard error less than 10 mg/m^2/day within 95% confidence interval	1.37 mg/m^2/day
2	Accuracy of mass discharge models	Source mass estimates from power model and exponential model.	Standard error less than 10 kg within 95% confidence interval	0.05 kg

* Indicates improved standard error value when removing 4 measurements from well LC208 from analysis.

7.0 COST ASSESSMENT

7.1 COST MODEL

This section identifies the information that can be tracked based upon data obtained during the demonstration that will aid in establishing realistic costs for implementing the technology. A simple cost model for the proposed technology is provided in Table 10.

Table 10. Cost Model

Cost Element	Data to be Tracked
Mobilization	• Personnel required and associated labor • Planning • Contracting • Transportation/Shipping • Permitting • Site preparation
Baseline characterization	• Personnel required and associated labor • Investigation into available site-specific literature • Preliminary site visit • Water level measurements • Contaminant sampling and analysis • Shipping • Analytical laboratory costs • Residual Waste Handling
PFM and BMLS	• Personnel required and associated labor • Capital Equipment Purchase • Operator Labor • Operator Training • Raw Materials • Consumables, Supplies • Sample Shipping • Sampling and Analysis • Analytical laboratory costs • Residual Waste Handling
Demobilization	• Personnel required and associated labor • Planning • Contracting • Transportation/Shipping

7.2 COST DRIVERS

7.2.1 COST ELEMENT: Mobilization

Mobilization encompasses required personnel and associated labor, planning, contracting, transportation/ shipping requirements, permitting to secure regulatory approval for alcohol tracer use, and site preparation. Data were tracked in an Excel spreadsheet and included the following cost parameters: transportation and shipping, and labor related costs. The scale of mobilization will depend on the number of wells to be characterized.

7.2.2 COST ELEMENT: Baseline Characterization

Baseline characterization encompasses required personnel and associated labor, a preliminary site visit, water level measurements, contaminant sampling and analysis, sample shipping, analytical laboratory costs, and residual waste handling. Data were tracked in an Excel spreadsheet and included the following cost parameters: sample shipping costs, labor related costs, sample analysis, analytical laboratory costs, and the costs of residual waste handling. The scale of mobilization will depend on the number of wells to be characterized.

7.2.3 COST ELEMENT: PFM and BMLS

Deploying, retrieving, and sampling the PFM and BMLS will encompass required personnel and associated labor, capital equipment purchases, operator labor, operator training, raw materials, consumables, supplies, sampling, sample shipping, sample analysis, analytical laboratory costs, and residual waste handling. Data were tracked in an Excel spreadsheet and included the following cost parameters: the cost to train operators to build, deploy, extract, and sample PFM, materials costs to constructs PFMs, the costs of consumables such as PFM sorbents, fabrics, and tracers, all costs associated with PFM sampling (e.g., vials, preservatives, labor, etc.), sample shipping costs, sample analysis, analytical laboratory costs, and residual waste handling costs. The scale of mobilization will depend on the number of wells to be characterized.

7.2.4 COST ELEMENT: Demobilization

Demobilization encompasses required personnel and associated labor, planning, contracting, transportation/shipping requirements. Data were tracked in an Excel spreadsheet and included the following cost parameters: transportation and shipping, and labor related costs. The scale of mobilization will depend on the number of wells to be characterized.

7.3 COST ANALYSIS

The intent of this project is to provide a more cost-efficient method for long-term flux-based monitoring of contaminated sites. The cost analysis compares the cost of a one-year effort to collect monthly flux data for two scenarios. For the first scenario total cost is based upon all monthly measurements being collected using PFM, while the total cost of the second scenario is based upon one initial PFM and BMLS deployment, with all subsequent monthly measurements being performed with BMLS. For the second scenario, the initial deployment allows for BMLS baseline measurements using PFM measured fluxes and observed water levels. All subsequent monthly flux measurements are then calculated based upon BMLS-measured aqueous fluxes and Darcy velocities (specific discharges). If the site has relatively consistent hydraulic gradient conditions, the Darcy velocity that was initially measured using PFM can be used for contaminant flux calculations. While, for cases where the hydraulic gradient varies significantly the hydraulic gradient can be adjusted based upon observed water levels and aquifer hydraulic conductivity using the initial PFM-measured Darcy velocities as a baseline.

For both scenarios the cost model is designed assuming that the effort involves flux measurements in two well transects consisting of 4 wells within each transect (total of 8 wells). The well saturated flow depth within each well is assumed to be 10 feet. PFM and BMLS will be constructed with vertical sampling intervals of 2.5 feet resulting in 5 samples per well. One sample will be collected from each sample interval along with standard QA/QC samples (dupes every 10 samples).

The cost breakdown for scenario 1 and 2 are outlined in Tables 11 and 12 respectively. The cost of the initial deployment for scenario 2 (combined PFM and BMLS measurements) is twice the cost of the initial deployment for scenario 1 (just PFM measurements). However, the cost of the subsequent BMLS monthly sampling events for scenario 2 is four times less than the monthly sampling events using PFM. Over a one-year sampling campaign scenario 2 provides a savings of \$368,742 (scenario 2 total cost of \$228,705 and scenario 1 total cost of \$597,447). For longer sampling campaigns, the savings with scenario 2 would continue to increase. The outcome is a reliable flux-based long-term monitoring strategy using both PFM and BMLS while providing significant savings over a method using just PFM.

Table 11a. Scenario 1: PFM Flux Based Monitoring.

Initial trip to provide training of onsite staff for PFM deployment, retrieval, and sampling followed by 11 monthly PFM deployments performed by onsite staff.

Site details

2	Number of transects
4	Number of wells per transect
2	Number of PFM per well
2	Number of sample intervals per PFM
16	Total Number of PFM
32	Total number of interrogation Intervals
1	samples per PFM interval
3	QA/QC samples
35	Total Number of Samples
12	PFM Deployments

Cost Breakdown

Deployment 1

Mobilizaton and Demobilization

Travel

2	Number of round trips
2	days & nights per trip
$350	Airline ticket per trip
$70	Rental car per day (minivan)
$140	Rental car total
$120	Hotel per night
$240	Hotel per trip
$100	Fuel per trip
$36	Perdiem (per person per day)
$72	Perdiem per trip
$902	Travel Total

$300	shipping of equipment, supplies and samples

$1,120	Salary and Benefits costs (2 trips with 2 x 8-hour work days at $35/hour. Includes trainging of onsite staff for PFM deployment, retrieval and sampling)
$2,322	**Total for mobilization and demobilization**

PFM Costs

Device costs

$1,078	Unit cost per PFM: 2-inch with 2 x 2.5 ft sample intervals (includes construction of PFM, shipping, and data analysis)
$17,248	Total PFM device cost

Sample analysis costs

$250	Unit cost per TCE and DCE sample analysis (CVOC EPA method 82602C)
$8,750	Total TCE and DCE sample analysis
$200	Unit cost per alcohol tracer analysis (EPA method 8015C)
$7,000	Total alcohol tracer analysis
$15,750	Total sample analysis

$32,998	**PFM Total**

$35,320	Direct Cost Deployment 1
$17,660	IDC

$52,980	**Total Cost Deployment 1**

Table 11b. Scenario 1: PFM Flux Based Monitoring (continued).

Deployments 2-11

PFM Costs

	Device costs
$1,078	Unit cost per PFM: 2-inch with 2 x 2.5 ft sample intervals (includes construction of PFM, shipping, and data analysis)
$17,248	Total PFM device cost
	Sample analysis costs
$250	Unit cost per TCE and DCE sample analysis (CVOC EPA method 82602C)
$8,750	Total TCE and DCE sample analysis
$200	Unit cost per alcohol tracer analysis (EPA method 8015C)
$7,000	Total alcohol tracer analysis
$15,750	Total sample analysis
$32,998	**PFM Total**
$32,998	Direct cost
$16,499	IDC
$49,497	Unit cost per deployment
$544,467	**Total Cost Deployments 2-11**
$597,447	**Total Cost**

Table 12a. Scenario 2: PFM-BMLS Flux Based Monitoring.

Initial trip to provide training of onsite staff for PFM and BMLS deployment, retrieval, and sampling followed by 11 monthly BMLS deployments performed by onsite staff.

Site details

2	Number of transects
4	Number of wells per transect
2	Number of PFM per well
2	Number of sample intervals per PFM
16	Total Number of PFM
32	Total number of interrogation Intervals
1	samples per PFM interval
3	QA/QC samples
35	Total Number of Samples
12	PFM Deployments

Cost Breakdown

Deployment 1

Mobilizaton and Demobilization

Travel

2	Number of round trips
2	days & nights per trip
$350	Airline ticket per trip
$70	Rental car per day (minivan)
$140	Rental car total
$120	Hotel per night
$240	Hotel per trip
$100	Fuel per trip
$36	Perdiem (per person per day)
$72	Perdiem per trip
$902	Travel Total
$300	shipping of equipment, supplies and samples
$1,120	Salary and Benefits costs (2 trips with 2 x 8-hour work days at $35/hour. Includes trainging of onsite staff for PFM deployment, retrieval and sampling)
$2,322	**Total for mobilization and demobilization**

PFM Costs

Device costs

$1,078	Unit cost per PFM: 2-inch with 2 x 2.5 ft sample intervals (includes construction of PFM, shipping, and data analysis)
$17,248	Total PFM device cost

Sample analysis costs

$250	Unit cost per TCE and DCE sample analysis (CVOC EPA method 82602C)
$8,750	Total TCE and DCE sample analysis
$200	Unit cost per alcohol tracer analysis (EPA method 8015C)
$7,000	Total alcohol tracer analysis
$15,750	Total sample analysis
$32,998	**Total PFM Cost Deployment 1**

Table 12b. Scenario 2: PFM-BMLS Flux Based Monitoring (continued).

BMLS Costs	
Device costs	
$800	Unit cost for water level loggers (pressure transducers)
$2,400	Total cost for 3 water level loggers (pressure transducers)
$250	Unit cost per BMLS: 2-inch with 2 x 2.5 ft sample intervals (includes construction of BMLS, shipping, and data analysis)
$25,000	Total BMLS device cost
Sample analysis costs	
$100	Shipping samples to lab
$230	Unit cost per TCE and DCE sample analysis (CVOC by EPA method 8260B)
$0	Total TCE and DCE sample analysis
$27,500	**Total BMLS Cost Deployment 1**
$62,820	Direct Cost
$31,410	IDC
$94,230	**Total Cost Deployment 1**
Deployments 2-11	
BMLS Costs	
Sample analysis costs	
$100	Shipping samples to lab
$230	Unit cost per TCE and DCE sample analysis (CVOC by EPA method 8260B)
$8,050	Total TCE and DCE sample analysis
$8,150	**BMLS Total**
$8,150	Direct Cost
$4,075	IDC
$12,225	Unit cost per deployment
$134,475	**Total Cost Deployments 2-11**
$228,705	**Total Cost**

8.0 IMPLEMENTATION ISSUES

8.1 ENVIRONMENTAL CHECKLIST

Depending on site conditions, permits may be required for permission to release small quantities of food-grade tracers into the aquifer. A standard list of tracers is available, and no issues have been experienced with previous permit requests.

8.2 OTHER REGULATORY ISSUES

Continuous contact with appropriate site managers is strongly recommended through the duration of all testing to avoid issues with any site-specific regulations.

8.3 END-USER ISSUES

The BMLS and PFM technologies currently function through deployment of custom-built devices designed with specified interrogation zones based upon site conditions. Devices are typically deployed in 2-inch, 4-inch and 6-inch wells. Deployment, retrieval and sampling is straightforward and has been demonstrated to field technicians from the United States Environmental Protection Agency (US EPA), United States Geological Survey (USGS) and United States Department of Energy (US DOE) who experienced minimal issues with methodology transfer.

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Harald Klammler	University of Florida	Email: haki@gmx.at	Modeling/Statistical Analysis
Jaehyun Cho	University of Florida	Phone: 352-392-9537 Fax: 352-392-3394 Email: jaehyunc@ufl.edu	Laboratory/field/analytical
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APPENDIX B STANDARD OPERATING PROCEDURE FOR ANALYSIS OF ALCOHOL TRACERS

SCOPE AND APPLICATION

1. This SOP describes the analytical procedures utilized by the University of Florida for analysis of alcohols used as partitioning tracers in both lab and field studies in order to quantify the amount and distribution of residual non-aqueous phase liquids (NAPLs) present in the saturated zone.
2. This SOP was written by R.D. Rhue, Soil and Water Science Department, University of Florida, Gainesville, Fl. It is a modification of SOP-UF-Hill-95-07-0010-v.2, prepared by D.P. Dai, H.K. Kim, and P.S.C. Rao, Soil and Water Science Department, University of Florida. The SOP of Dai, Kim, and Rao was modified from a protocol provided to them by Professor Gary Pope at the University of Texas-Austin.
3. The alcohol tracers used in the UF lab and field studies are ethanol, n-butanol, n-pentanol, n-hexanol, n-heptanol, 2,2-dimethyl-3-pentanol, and 6-methyl-2-heptanol.
4. The method involves gas chromatography (GC) analysis for alcohol concentrations in aqueous samples. A flame-ionization detector (FID) is used to quantify the analyte concentrations in the sample. The method has been found to provide reliable and reproducible quantitation of alcohols for concentrations > 1 ug/mL. This value may be considered the minimum detection level (MDL). The standard calibration curve for FID response has been found to be linear up to 3,000 ug/mL for ethanol.
5. Samples selected for GC-FID analysis may be chosen on the basis of preliminary screening which will provide approximate concentration ranges and appropriate sample injection volumes, standard concentrations, etc.

PURPOSE

The purpose of this SOP is to insure reliable and reproducible analytical results for alcohols in aqueous samples for laboratory-based or on-site (field-based) GC-FID analyses, and to permit tracing sources of error in analytical results.

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

Sample Containers: Field samples will be collected in 5-mL glass sample vials (Fisher Catalog # 06-406-19F) with teflon-faced septa caps. Glass vials and caps are not reused.

Sample Collection: Each field sample vial will be completely filled with liquid, such that no gas headspace exists, and capped. The vials will not be opened until the time for analysis.

Transportation and Storage: Field samples will be stored in coolers containing "blue ice", and later stored in refrigerators in a trailer located on the site. Samples may be subjected to on-site GC analysis, and/or shipped back to UF labs; samples will be packed in coolers and shipped via overnight air express (e.g., FedEx). The samples will be stored in the cold storage room or refrigerator at 4C, until GC analysis. After sub-sampling, the samples are returned to cold storage.

For lab studies, samples will be collected directly in 2 mL GC vials whenever possible and stored in a refrigerator if analysis is expected to take more than a day.

2. Sub-sampling and Dilution

Field samples will be sub-sampled into 2-ml vials for automated GC analysis. Disposable, Pasture glass pipets (Fisher Catalog # 13-678-20B) will be used to transfer samples from 5-mL sample vials to the 2-mL GC vials.

For samples needing dilution prior to GC analysis, a dilution of 1:10 should be sufficient. Dilutions will be made using double-distilled, deionized water.

3. Apparatus and Materials

Glassware: Disposable micro-pipets (100 uL; Fisher Catalog # 21-175B; 21-175F) and Class A volumetric pipets (1 or 2 mL) are required for sample dilution.

Disposable Pasteur glass pipets (Fisher Catalog # 13-678-20B) are required for sub-sampling.

GC vials (2-mL) with Teflon-faced caps (Fisher Catalog # 03-375-16A) are required for GC analysis.

Volumetric class A pipets and volumetric class A flasks are required for preparations of the calibration standards.

Gas Chromatograph System: An analytical GC system with a temperature-programmable oven, auto-injector capable of on-column injection, and either an integrator or a PC-based data acquisition/analysis software system are required. Also required are other accessories, including analytical columns and the gases required for GC-FID operation.

A Perkin Elmer Autosystem with an FID and an integrated autosampler will be used for analysis of field and laboratory samples. The Perkin Elmer system will be linked to an IBM-compatible PC loaded with Turbochrom (version 4.01) software.

A J&W Scientific DB-624 capillary column (30m X 0.53mm, 3□m film thickness) will be used. Zero-grade air and ultra-high purity hydrogen will be used for the FID. Ultra-high purity nitrogen or helium will be used for carrier gas.

4. Reagents

Deionized, Double-Distilled Water: Deionized, double distilled water is prepared by double distillation of deionized water in a quartz still. This water will be referred to as reagent water.

Alcohols: Certified ACS grade alcohols will be purchased from Fisher Scientific and used as received.

5. Standard Solutions

Stock Standard Solution: Analytical standards will be prepared from reagent chemicals by the laboratory. Stock standards each contain a single alcohol dissolved in reagent water and stored in 20 mL glass vials (Fisher Catalog # 03-393-D) with teflon-lined caps. These stock solutions will be kept in a refrigerator at 4 C. Fresh stock standards will be prepared every six months.

The procedure for making stock standard solutions is essentially that given in the Federal Register, Rules and Regulations, Thursday, November 29, 1979, Part III, Appendix C, Section 5.10, "Standard Stock Solutions". The only modification of the procedure for the current study is that reagent water is used as the solvent in place of methanol.

Calibration Standards: Calibration standards will be prepared by diluting the stock standards in reagent water. Each calibration standard will contain each of the alcohols listed above. Five concentrations will be prepared that cover the approximate concentration range utilized in the partitioning tracer experiments.

6. QC blank Spike/Matrix Spike

Two 1 mL aliquots of the sample to be spiked will be transferred to clean vials. To one vial, 1 mL of reagent water will be added. To the second vial, 1 mL of a calibration standard will be added. The spike recovery will be calculated using the difference between the two measured concentrations and the known spike concentration.

7. Quality Control

GC injector septa will be changed every 80 to 100 injections, or sooner if any related problems occur.

Injector liner will be cleaned or changed every 80 to 100 injections or sooner if any related problems occur.

A method blank will be included in every 50 samples

A complete set of calibration standards (5) will be run at the beginning of each day and after every fiftieth sample.

One standard and a blank will be included in every 25 samples.

A sample spike and a blank spike will be included in every 50 samples.

8. Instrumental Procedures

Gas Chromatography: For J&W DB-624 Column:

Injection port temperature 200C

FID detector temperature 225C

Temp Program: Isothermal at 60C for 0 min; Ramp to 120C at 5 C/min.

9. Sample Preparation

Sub-sampling: Field samples will be transferred from the 5 mL sample vials to the 2 mL GC vials and capped with open-top, teflon-lined septa caps.

Dilution: Samples will be diluted if chromatographic peak areas for any of the alcohols exceed those of the highest calibration standard. One mL of sample will be added to an appropriate amount of reagent water to make the dilution.

10. Sample Analysis

Analysis: The samples will be allowed to reach ambient temperature prior to GC analysis.

Sample vials (2 mL) will be loaded onto the Perking Elmer GC auto-injector. A one uL injection volume will be used for both samples and standards.

Analyte Identification: Analyte identification will be based on absolute retention times. The analytes of interest should elute at their characteristic retention times within □0.1 minute for the automated GC system.

Analyte Quantitation: When an analyte has been identified, the concentration will be based on the peak area, which is converted to concentration using a standard calibration curve.

11. Interferences

Contamination by carry-over can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carry over, the injector syringe should rinsed with reagent water between samples.

Potential carry-over will be checked by running a highly concentrated sample, but one still within the standard concentration range, followed by a blank. A negligible reading for the blank will insure that carry-over has been minimized.

12. Safety

The main safety issue concerning the use of the GC at a field site relates to the compressed gases. The FID gases (hydrogen and air) form explosive mixtures. It is important to keep this in mind at all times, and be aware of the hazard potential in the event of an undetected hydrogen leak. All gas connections will be properly leak tested at installation.

High-pressure compressed-gas cylinders will be secured to a firm mounting point, whether they are located internally or externally.

Gas cylinders should preferably be located outside the trailer on a flat, level base, and the gas lines run inside through a duct or window opening. If the gases are located outside, then some form of weatherproofing for the gauges will be necessary. As a temporary measure, heavy-duty polyethylene bags, secured with tie-wraps, have been used successfully; this may not be very elegant but it is very effective for short-term use of the GC. A more permanent protective housing must be built if the GC is located at the trailer for an extended time period.

The main operating drawback to locating the gas cylinders externally is that it is not easy to monitor the cylinder contents from inside. The gas which could be used up most quickly is air for the FID, particularly if two instruments are hooked up to the same supply and they are running continuously. A reserve cylinder of air should be available at all times to prevent down time.

If it is not possible to arrange external citing easily, the gas cylinders should be secured to a wall inside the trailer.

It is a good laboratory operating practice to make sure the flame is attended at all times.

When it is necessary to change the injection liner on the GC, the detector gases should be shut off.

The column must be connected to the detector before igniting the flame.

The trailer should be kept well ventilated when using the GC.

Reference to the Materials Safety Data Sheets (MSDS) will be made for information on toxicity, flammability, and other hazard data

APPENDIX C STANDARD OPERATING PROCEDURE FOR ANALYSIS OF TARGET ANALYTES IN GROUNDWATER SAMPLES

SCOPE AND APPLICATION

1. This SOP describes the analytical procedures utilized by the Department of Environmental Engineering Sciences, University of Florida, for analysis of target analytes in groundwater samples from both lab and field studies. This analysis provides characterization of existing site and lab column aqueous contamination both before and following flushing technology applications.
2. This SOP was written by M.D. Annable, Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL. It is a modification of SOP-UF-Hill-95-07-0012-v.2, prepared by D.P. Dai and P.S.C. Rao, Soil and Water Science Department, University of Florida.
3. The selected constituents are benzene, toluene, o-xylene, 1,1,1-trichloroethane, 1,3,5,-trimethylbenzene, 1,2-dichlorobenzene, decane, and naphthalene.
4. The method involves gas chromatography (GC) analysis for target analyte concentrations in aqueous samples. Headspace analysis with a flame-ionization detector (FID) is used to quantify the analyte concentrations in the sample. The method has been found to provide reliable and reproducible quantitation of the above constituents for concentrations > 5 ug/L. This value may be considered the method detection level (MDL).
5. Samples selected for GC-FID analysis may be chosen on the basis of preliminary screening which will provide approximate concentration ranges and appropriate sample injection times, and standard concentrations, etc.

PURPOSE

The purpose of this SOP is to insure reliable and reproducible analytical results for soluble NAPL constituents in aqueous samples for laboratory-based GC-FID analyses, and to permit tracing sources of error in analytical results.

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

Sample Containers: Field samples will be collected in 20-mL glass sample vials (Fisher Catalog # 03-340-121) with teflon-faced rubber backed caps. Glass vials and caps are not reused.

Sample Collection: Each field sample vial will be completely filled with liquid, such that no gas headspace exists, and capped. The vials will not be opened until the time for analysis.

Transportation and Storage: Field samples will be stored in coolers containing "blue ice", and later stored in refrigerators in a trailer located on the site. Samples will be sent to UF labs packed in coolers and shipped via overnight air express (e.g., FedEx). The samples will be stored in the cold storage room or refrigerator at 4C, until GC analysis. After sub-sampling, the samples are returned to cold storage.

For lab studies, samples will be collected directly in 20 mL Headspace vials whenever possible and stored in a refrigerator if analysis is expected to take more than a day.

2. Sub-sampling and Dilution

Field samples will be sub-sampled placing 10-ml into 20-ml headspace vials containing 2 g of sodium chloride for automated GC analysis. Pipets will be used to transfer samples from 20-mL sample vials to the 20-mL GC headspace vials.

3. Apparatus and Materials

Glassware: Glass pipets are required for sub-sampling.

GC headspace vials (20-mL) with Teflon-faced caps are required for GC analysis.

Volumetric class A pipets and volumetric class A flasks are required for preparations of the calibration standards.

Gas Chromatograph System: An analytical GC system with a temperature-programmable oven, headspace sample injection system, and either an integrator or a PC-based data acquisition/analysis software system are required. Also required are other accessories, including analytical columns and the gases required for GC-FID operation.

A Perkin Elmer Autosystems with an HS40 Auto-headspace sampler and a FID will be used for analysis of field and laboratory samples. The Perkin Elmer system will be linked to an IBM-compatible PC loaded with Turbochrom (version 4.01) software.

A J&W Scientific DB-624 capillary column (50m X 0.53mm, 3μm film thickness) will be used. Zero-grade air and high purity hydrogen will be used for the FID. Ultra-high purity nitrogen or helium will be used for carrier gas.

4. Reagents

Deionized, Double-Distilled Water: Deionized, double distilled water is prepared by double distillation of deionized water in a quartz still. This water will be referred to as reagent water.

5. Standard Solutions

Stock Standard Solution: Analytical standards will be prepared from reagent chemicals by the laboratory. Stock standards will each contain a single analyte dissolved in methanol and stored in 20 mL glass vials (Fisher Catalog # 03-393-D) with teflon-lined caps. These stock solutions will be kept in a refrigerator at 4 C. Fresh stock standards will be prepared every six months. The procedure for making stock standard solutions is essentially that given in the Federal Register, Rules and Regulations, Thursday, November 29, 1979, Part III, Appendix C, Section 5.10, "Standard Stock Solutions".

Calibration Standards: Calibration standards will be prepared by diluting the stock standards in water. Each calibration standard will contain each of the eight analytes listed above. Five concentrations will be prepared that cover the approximate concentration range from 0 to 20 mg/L.

6. QC blank Spike/Matrix Spike

Two 1 mL aliquots of the sample to be spiked will be transferred to clean vials. To one vial, 1 mL of reagent water will be added. To the second vial, 1 mL of a calibration standard will be added. The spike recovery will be calculated using the difference between the two measured concentrations and the known spike concentration.

7. Quality Control

A method blank will be included in every 50 samples

A complete set of calibration standards (5) will be run at the beginning of each day and after every fiftieth sample.

One standard and a blank will be included in every 25 samples.

A sample spike and a blank spike will be included in every 50 samples.

8. Instrumental Procedures

<u>Gas Chromatography</u>: For J&W DB-624 Column:

Headspace sample temperature	90C
Injection needle temperature	100C
Transfer line Temperature	110C
FID detector temperature	225C
Carrier gas pressure	8psi

Temp Program: Isothermal at 50C for 0 min; Ramp to 200C at 5 C/min; hold for 10 min.

9. Sample Preparation

<u>Sub-sampling</u>: Field samples will be transferred from the 20 mL sample vials to the 20 mL GC headspace vials and capped with open-top, teflon-lined septa caps.

<u>Dilution</u>: Samples will be diluted if chromatographic peak areas for any of the analytes exceed those of the highest calibration standard. One mL of sample will be added to an appropriate amount of reagent water to make the dilution.

10. Sample Analysis

<u>Analysis</u>: Sample headspace vials (20 mL) will be loaded onto the Perking Elmer HS40 auto-sampler. Samples will be pressurized for 1 min followed by a 0.1 minute injection time and a withdrawal time of 0.5 minute.

Analyte Identification: Analyte identification will be based on absolute retention times. The analytes of interest should elute at their characteristic retention times within ±0.1 minute for the automated GC system.

Analyte Quantitation: When an analyte has been identified, the concentration will be based on the peak area, which is converted to concentration using a standard calibration curve.

11. Interferences

Contamination by carry-over can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carry over, the injector needle should purged with carrier gas between samples.

Potential carry-over will be checked by running a highly concentrated sample, but one still within the standard concentration range, followed by a blank. A negligible reading for the blank will insure that carry-over has been minimized.

12. Safety

The main safety issue concerning the use of the GC relates to the compressed gases. The FID gases (hydrogen and air) form explosive mixtures. It is important to keep this in mind at all times, and be aware of the hazard potential in the event of an undetected hydrogen leak. All gas connections will be properly leak tested at installation.

High-pressure compressed-gas cylinders will be secured to a firm mounting point, whether they are located internally or externally.

When it is necessary to change the injection liner on the GC, the detector gases should be shut off.

The column must be connected to the detector before igniting the flame.

Reference to the Materials Safety Data Sheets (MSDS) will be made for information on toxicity, flammability, and other hazard data.

APPENDIX D STANDARD OPERATING PROCEDURE FOR EXTRACTION OF ANALYTES FROM FLUX DEVICE SORBENTS

SCOPE AND APPLICATION

1. This SOP describes the procedures used by the Department of Environmental Engineering Sciences, University of Florida, for extraction of target analytes (including tracers) from sorbents used in flux devices inserted in monitoring wells.
2. This SOP was written by M.D. Annable, Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL.
3. The selected constituents are TCE, PCE, and alcohol tracers:

Methanol
Ethanol
2-propanol (IPA)
2-methyl-1-propanol (IBA)
2-methyl-2-propanol (TBA)
n-propanol
n-butanol
n-pentanol
n-hexanol
n-heptanol
3-heptanol
n-octanol
2-octanol
2,4-dimethyl-3-pentanol
2-ethyl-1-hexanol
3,5,5-trimethyl-1-hexanol
6-methyl-2-heptanol
2,6-dimethyl-2-heptanol
n-decane

Potential Sorbents include:

Liquid (mixed in a sand matrix at a pore volume saturation of 10%)
Tetradecane
Heptadecane

Hexadecane

Solid

Activated Carbon

Surfactant modified zeolytes

4. The method involves liquid extraction in 20 or 40 ml VOA vials using organic solvents.

PURPOSE

The purpose of this SOP is to insure reliable and reproducible analytical results. Extracted constituents will be quantified suing analytical methods described in other SOPs.

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

Sample Containers: Field samples will be collected in 20-mL or 40-ml glass sample vials (Fisher Catalog # 03-340-121) with teflon-faced rubber backed caps.

Sample Collection: Each field sample vial will be partially filled with the extraction solvent (alcohol IPA, IBA, etc. or Methylenechloride) using a pipet or repeating volume dispenser. Typically 10 or 20-ml of solvent will be used.

Transportation and Storage: Field samples will be stored in coolers containing "blue ice", and later stored in refrigerators in a trailer located on the site. Samples will be sent to UF labs packed in coolers and shipped via overnight air express (e.g., FedEx). The samples will be stored in the cold storage room or refrigerator at 4C, until GC analysis. After sub-sampling, the samples are returned to cold storage.

For lab studies, samples will be collected directly in 20 mL Headspace vials whenever possible and stored in a refrigerator if analysis is expected to take more than a day.

2. In the laboratory, samples will be rotated for a minimum of 8 hours on a rotator (Glas-Col model RD 4512).

3. Sub-sampling and Dilution

Field samples will be sub-sampled into 2 ml GC vials. Pipets will be used to transfer samples from 20-mL sample vials to the 2-mL GC vials.

4. Apparatus and Materials

Glassware: Glass pipets are required for sub-sampling.

Safety

Gloves and eye protection will be worn during all extraction activities.

Reference to the Materials Safety Data Sheets (MSDS) will be made for information on toxicity, flammability, and other hazard data.

APPENDIX E QUALITY ASSURANCE PROJECT PLAN (QAPP)

E.1 Purpose and Scope of the Plan

This Quality Assurance plan is written to cover activities associated with testing the Flux Meter at the Canadian Forces Base Borden site. The plan focuses on field installation, sampling and processing of data from the Flux Meters.

E.2 Quality Assurance Responsibilities

The responsibility for QA will be shared by Kirk Hatfield and Mike Annable at the University of Florida. During field activities one of the PI's will be present to oversee QA procedures. Other personnel present during field sampling activities will include graduate students or post-doctoral researchers from the University of Florida, Purdue University, and the University of Waterloo.

E.3 Data Quality Parameters

This section discusses measures to be taken to ensure the representativeness, completeness, comparability, accuracy, and precision of the data.

Accuracy

Accuracy is defined as the closeness of the results to the true value.

The percent recoveries of surrogates, QC check standards, and matrix-spiked analytes are used to evaluate the accuracy of an analysis. The percent recovery represented by X can be calculated using the following equations:

For surrogates and QC check standards:

$$X = \frac{SSR}{SA} \times 100$$

For matrix spikes:

$$X = \frac{SSR - SS}{SA} \times 100$$

where:

SSR = Spiked sample result

SS = Sample result

SA = Spike added from spiking mix

The mean percent recovery (X) is defined by:

$$\overline{X} = \frac{\sum_{i=1}^{N} X_i}{N}$$

where:

X_i = The percent recovery value of a spike replicate

N = Number of spikes

Precision

Precision is a measure of the mutual agreement among individual measurements of the same parameters under prescribed similar conditions.

The analytical precision is determined using results from duplicate or replicate analyses of samples and from matrix spike results for a given matrix. The Relative Percent Difference (RPD) is used to evaluate the precision of duplicate analyses. Relative Percent Difference is defined in the following equation:

$$\%RPD = \frac{2(X1 - X2)}{\overline{x}} \, x \, 100$$

X1 = First duplicate value

X2 = Second duplicate value

When replicate analyses are performed, precision is measured in terms of the Standard Deviation (SD) which is defined in the following equation:

$$S = \sum_{i=1}^{N} \left[\frac{(X_i - \overline{X})^2}{N - 1} \right]^{\text{‰}}$$

where:

X_i = The recovery value of a spike replicate

X = Arithmetic average of the replicate values

N = Number of spikes

Completeness

Completeness is defined as the percent of parameters falling within acceptance criteria and the results subsequently reported. A goal of 95 percent completeness has been set for all samples.

The general requirement of this quality assurance program is to analyze a sufficient number of standards, replicates, blanks, and spike samples to evaluate results adequately against numerical QA objectives.

E.4 Calibration Procedures, Quality Control Checks, and Corrective Action

The focus of the following section is to describe initial and continuing calibration procedures for analytical instrumentation, duplicate and control testing and data reduction, validation, and reporting.

Supplies and Quality Control Materials

All supplies (i.e., glassware, chemicals, reagents) used will be of the best possible quality to ensure proper instrument calibration and avoid contamination. All reagents used are prepared from Analytical Reagent Grade (AR) chemicals or higher purity grades, unless such purity is not available. The preparation of all reagents will be documented, including source, mass, and dilutions. Each reagent will be clearly labeled with the composition, concentration, date prepared, initials of preparer, expiration date, and special storage requirements, if any.

Reagents

Reagent solutions are stored in appropriate glass, plastic, or metal containers. Reagents are stored under conditions designed to maintain their integrity (refrigerated, dark, etc.). Shelf life is listed on the label and the reagent is discarded after it has expired. Dry reagents such as sodium sulfate, silica gel, alumina, and glass wool are either muffled at 400°C or extracted with solvent before use for organic chemical analyses. Water used in the laboratory is glass distilled or deionized, and periodically checked for purity. In addition, water used in the organics area is carbon-filtered or purchased as HPLC grade. All organic solvents used are either glass-distilled or pesticide grade. Solvents and reagent solutions are checked for contamination by employing reagent blanks, before use in any analysis.

Quality Control Reference Materials

All Quality Control Reference Materials are acquired only from authorized vendors or sources commonly used by U.S. EPA Regional Laboratories.

Standards Traceability

When standard reference materials arrive at the laboratory, they are registered in a bound log book, "Standards Notebook for Neat Materials and Primary Solutions." An example of a logging sequence is used to illustrate this process.

(1-S-XXX-12-4) (label and log sequence)

Where:

1 = Notebook log number
S = Standard Notebook--"Neat and Primary Standards"
XXX = Receiving analyst's initials
12 = Notebook page
4 = Entry number on notebook page

All working standards prepared at the site lab are logged in the "Standards Notebook for Intermediate and Working Standards." A similar labeling convention has been adopted for classifying these working standard materials. An example is given below.

1-W-XXX-6-5 (label and log)

Where:

1 = Number of notebook
W = Standards notebook - "Intermediate and Working" Standard
XXX = Analyst's initial
6 = Page Number
5 = Page entry number in sequence

Instrument Calibration

Every instrument used to analyze samples must pass the calibration criteria established in the appropriate SOP. Initial calibration criteria for instrument linearity, sensitivity, resolution, and deactivation must be met before samples can be analyzed. Sustained performance is monitored periodically during sample analyses by the use of continuing calibration check standards.

GC Section

Initial Calibration

The linear calibration range of the instrument must be determined before the analysis of any samples. Gas chromatographic conditions used for sample analyses are used during calibration.

The calibration is performed in accordance with the SOP derived from the methods used. For most GC analyses, a 5-level calibration is run. The concentrations of the standards must bracket the linear range of the instrument. Calibration using fewer than 5-levels is done only when specifically allowed by the method.

Relative Retention Times and Relative Response Factors

Instrument calibration and sample analysis must be performed using appropriate internal standards to establish relative retention times (RRT) and relative response factors (RRF) where required. Internal standards appearing in a chromatogram will establish primary search windows for those target compounds nearby in the chromatogram. RRT are calculated using this equation:

$$RRT = \frac{RT^{target}}{RT^{is}}$$

The RRF may be calculated as follows:

$$\text{Absolute Response Factor} = \text{RF} = \frac{\text{Area}}{\text{Amount}}$$

Note: <u>Amount</u> in this equation refers to the mass (e.g. ug) of compound mixed into the solution injected.

Each calibration standard is analyzed and the RRF is calculated for each analyte according to the following equation:

$$RRF = \frac{A_s \, x \, C_{is}}{A_{is} \, x \, C_s}$$

A_s = Area of analyte

A_{is} = Area of internal standard

C_{is} = Concentration of internal standard

C_s = Concentration of analyte

Note: Certain data processors may calculate the RRF differently.

The standard deviation (SD) and the % coefficient of variation (CV) of RRFs for the compounds are calculated using the following equations:

$$S = \sum_{i=1}^{N} \left[\frac{(RRF_i - RRF_m)^2}{N - 1} \right]^{‰}$$

Where:

RRF_i = Individual RRF

RRF_m = Mean RRF

N = Number of RRFs

and

$$\%CV = \frac{S \, x \, 100}{RRF_m}$$

Coefficient of Variation

The %CV of each compound must be less than 30 percent. This criterion must be achieved for the calibration to be valid.

If the %CV is less than 20 percent, the RRF of the compound can be assumed to be invariant, and the average RRF can be used for calculations.

If the %CV is between 20 percent and 30 percent, calculations must be made from the calibration curve. Both the slope and the intercept of the curve must be used to perform calculations.

Initial Calibration Verification

The calibration curve must be validated further by analyzing a QC check sample. The QC check sample must be obtained from EPA, another vendor, or it must be from another lot number. The QC check sample verifies the validity of the concentrations of the standards used to obtain the initial calibration.

All analytes in the QC check standard must be recovered within 80 to 100 percent. If any analyte exceeds this criterion, then a new calibration curve must be established. All sample results for a target analyte can be reported only from valid initial calibrations.

Continuing Calibration

The working calibration curve or RRF for each analyte must be verified daily by the analysis of a continuing calibration standard. The ongoing daily continuing calibration must be compared to the initial calibration curve to verify that the operation of the measurement system is in control.

The continuing calibration check must be performed during each day of analysis to verify the continuing calibration of the instrument. A day is defined as 24 hours from the start run time of the last valid continuing calibration. Generally, a continuing calibration check sample is injected every 10 samples.

Verification of continuing calibration is performed by the analysis of a midpoint standard containing all of the analytes of interest. Verification of continuing calibration of the measurement system is done by calculating the percent difference (%D) of the continuing calibration RRF from the mean RRF from the initial calibration curve using the following equation:

$$\%D = \frac{(RRF_m - RRF) x 100}{RRF_m}$$

Where:

RRF_m = The mean relative response factor from the initial calibration curve

RRF = The relative response factor from the continuing calibration standard

The %D must meet the acceptance criteria established in the appropriate SOP. If these criteria are exceeded, a new calibration curve must be established.

Other Calibrations

Weekly calibrations are performed for equipment such as balances, thermometers, ovens, incubators, and dissolved oxygen (D.O.) meters that are required in analytical methods, but which are not recorded in a dedicated QA instrument log.

Balances

Balances are checked with Class S weights on a daily basis. Before a weighing session, the analyst is required to perform at least one calibration check in the range of the material to be weighed. This value is also recorded on the specific balance control chart and must be within the control limit. The criteria for calibration checks are given in Table E.1.

Table E.1. Criteria for Balance Calibration Checks

Class S Weight (grams)	Warning Level (grams)	Control Level (grams)
Analytical Balances		
0.0100	0.0098-0.0102	0.0097-0.0103
0.1000	0.098-0.102	0.097-0.103
1.000	0.995-1.005	0.990-1.010
10.000	9.995-10.005	9.990-10.010
50.00	49.98-50.02	49.95-50.05
Top Loading Balances		
1.00	0.95-1.05	0.90-1.10
10.0	9.9-10.1	9.8-10.2
50.0	49.7-50.3	49.5-50.5

Incubators, ovens, and waterbaths

Temperatures are checked daily with an NBS grade thermometer and necessary adjustments made as required. All temperature readings are recorded and posted on the appropriate equipment.

DO meters

DO meter is calculated daily using a modified Winkler technique. The Winkler solution is titrated against 0.025N sodium thiosulfate.

Conductivity bridges

Conductivity meter is standardized daily against a solution of KCl to obtain a new cell constant.

pH meters

The pH meter is standardized daily using buffers at pH of 4, 7, and 10.

Refrigerators

Refrigerators are maintained at 4°C, with control levels ranging from 1°C to 10°C. A temperature reading is taken each workday morning immediately after unlocking the refrigerator. The temperature reading is recorded and entered on the control chart posted on the door of the refrigerator. If a trend is apparent or if the temperature is outside the acceptable range, the Lab Manager is notified so that corrective action can be initiated if required.

Freezers

Freezers are maintained at -10°C, with control levels ranging from 0°C to -35°C. A temperature reading is taken each workday morning immediately after unlocking the freezer. The temperature reading is recorded and entered on the control chart posted on the door of the freezer. If a trend is apparent, or if the temperature is outside the acceptable range, the Lab Manager is notified so that corrective action can be initiated if required.

Calibration Standards

All calibration standards, including internal standards used in LMG, are obtained from chemical suppliers with certificates of high purity and concentration.

Traceability

All standards are traceable to the National Institue of Standards and Testing (NITS) Standard Reference Materials (SRM) or to the U.S. EPA Reference Standards.

Working Standards

The commercial standards are used as stock standards. Working standards are made from the stock standards at appropriate concentrations to cover the linear range of the calibration curve. The working standards are used for initial calibration curves, continuing calibration checks, and preparation of analyte spiking solutions as appropriate for a particular analysis. All stock and working solutions are uniquely identified, dated, labeled, and initialed.

Standards Logbook

All stock solutions are given a unique code number and are entered into a bound "Primary Standards" logbook. The name of the compound and other pertinent information, including concentration, date of receipt, and analyst's name, are also entered.

Working standards are given a unique code number that allows them to be traced to a specific stock solution. The working standard is entered in a "Working Standards" logbook with analyst's name, date and method of preparation, and other pertinent information.

CORRECTIVE ACTIONS

Laboratory Imposed

Corrective actions will be initiated if the quality control criteria indicate an analysis is out of control.

- Check calculations for accuracy
- Check instrumentation to ensure it is operating properly. Recalibrate if necessary.
- Remake standards and reagents and reanalyze samples.
- Re-prep and re-analyze samples.

The analyst is responsible for initiating corrective actions for analytical problems encountered during analysis of samples. Most problems which occur and are corrected during the analytical run will be explained in the run log or analytical bench sheet for that run. A corrective action report (CAR) may be necessary for some problems encountered, such as complete system failure, chronic calibration failure, or severe matrix interferences.

During data review, the reviewer may initiate corrective actions based on problems or questions arising from the review. A CAR will be initiated.

The Laboratory Manager may initiate corrective actions if a problem is noticed during a QC review of data, a system audit, or a performance audit. A CAR will be initiated.

CARs are signed and dated by Project Manager, and by the Laboratory Manager. CARs will be filed in appropriate department files and in the Lab Manger's files.

Agency Imposed

Any actions deemed necessary by regulatory agencies, such as EPA, will be taken. These actions are most likely to arise from a systems or performance audit, or from data review conducted by the agency.

Corrective Action Reports

Corrective Action Reports

The field laboratory will have a Corrective Action System that ensures the proper documentation and dispositions of conditions requiring corrective action. The system will also ensure that the proper corrective action is implemented to prevent recurrence of the condition.

Situations Requiring Corrective Action Reports

The Corrective Action System applies to all situations that affect data quality. These situations include, but are not limited to, quality control criteria being exceeded, statistically out-of-control events, deviations from normally expected results, suspect data, deviations from the standard operating procedure, and special sample handling requirements. Corrective actions may also be initiated as a result of other QA activities, such as performance audits, systems audits, laboratory/interfield comparison studies, and QA project-related requirements of certifying agencies such as EPA.

Corrective Action Procedures

The procedure requires documenting the condition requiring corrective action on a Corrective Action Report and implementing corrective action based on the results of the investigation performed to determine the cause of the condition (Table E.2).

When a condition requiring corrective action arises, the Corrective Action Report is initiated. The initiator describes the condition requiring corrective action. An investigation, if necessary, is conducted to determine the cause of the condition. A corrective action is recommended based on the results of the investigation. The Corrective Action Report is reviewed by the Project Manager and the Field Site Manager who either approve the recommended corrective action or indicate a different corrective action. The originator has the responsibility of following up to be sure that the corrective action is implemented. Implementation of the corrective action is documented by the Corrective Action Report being signed and dated by the person who implemented the corrective action.

Table E.2. Corrective Actions

QC Activity	Acceptance Criteria	Recommended Corrective Action
Initial instrument blank	Instrument response <MDL response	Prepare another blank, if same response, determine cause of contamination: reagents, environment, instrument equipment failure, etc.
Initial calibration standards	Coefficient of variation >0.99995 or standard concentration value ± 10% of expected value	Reanalyze standards. If still unacceptable, then remake standards
QC Check Standard	± 10% of expected value	Reanalyze standard. if still unacceptable, then remake standards, or use new primary standards if necessary
Continuing calibration Standards	± of expected value	Reanalyze standard. If still unacceptable, then recalibrate and rerun samples from the last cc stnd. Check
Method blank	<MDL	Reanalyze blank. If still positive, determine source of contamination. If necessary, reprocess (i.e., digest or extract) sample set
Initial calibration Standards (GC/MS)	RRF <30%	Reanalyze standards. If still unacceptable, prepare new standards.
Surrogate recovery (GC/MS Semivolatiles)	0 or 1 outside CLP criteria	Re-extract and/or re-analyze
Surrogate recovery (GC/MS volatiles)	0 outside criteria	Re-analyze

Table E.3. Corrective Action Report Criteria for Control Charts

Criteria	Corrective Action
A point outside ±3 standard deviations	Attempt to determine the source of the problem. Verbally report the deviation and results of preliminary investigation to the Field Site Manager, who will decide jointly what action to take. After implementing corrective action, complete the Corrective Action Report and submit it to the Project Manager and the Field Site Manager for approval.
Three consecutive points accuracy outside ± standard deviation	Conduct investigation. Check accuracy of data input, calculations, instrument, standards, etc., to locate the source of the problem. Document results in a Corrective Action Report. Have the report approved by the supervisor. No results can be reported until the Corrective Action Report has been approved. Send a copy of the Corrective Action Report and a copy of the QC chart to the Field Site Manager.
Obvious outlier.	Conduct investigation. Check accuracy of data input, calculations, dilutions, instrument, standard, etc.. present initial findings to the Field Site Manager. They will jointly decide what actions need to be taken. Document the results in a Corrective Action Report and have it approved by the Field Site Manager. No results can be reported until the Corrective Action Report is approved. Send a copy of the Corrective Action report and a copy of the control chart to the Field Site Manager.
Obvious shift in the mean.	Conduct investigation. Check calculations, data entry, standards, instrument, calibrations, etc. Document results in a Corrective Action Report. Have the Corrective Action Report approved by the Field Site Manager. No results can be reported until the report is approved. Send a copy of the Corrective Action Report and a copy of the QC chart to the Field Site Manager.

E.5 Demonstration Procedures

Initiating the flux meter experiments will involve limited field effort. All of the components of the device can be prepared prior to field activities. In the field, the primary activity will be assembly of the flux meters which can be completed with two people in a mater of minutes. Extraction and sub-sampling also required fairly minimal time and personnel. Only the controlled flow flume experiments will require establishing steady flow from one end of the flume using peristaltic pumps. These pumps will be calibrated in the field using simple time and volume measurements. Periodic flow measurements will be made to determine total average flow.

Samples collected at the Borden site will be sent to the University of Florida for analysis. In the laboratory, instrument maintenance will include the following.

Maintenance Schedule

Preventive maintenance, such as lubrication, source cleaning, and detector cleaning, is performed according to the procedures delineated in the manufacturer's instrument manuals.

The frequency of preventive maintenance varies with different instruments. Routine maintenance performed includes cleaning and/or replacement of various instrument components. In general, the frequency recommended by the manufacturer is followed. In addition to the regular schedule, maintenance is performed as needed. Precision and accuracy data are examined for trends and excursions beyond control limits to determine evidence of instrument malfunction.

Maintenance is performed when an instrument begins to degrade as evidenced by the degradation of peak resolution, shift in calibration curves, decreased ion sensitivity, or failure to meet one or another of the quality control criteria. Table E.4 lists routine equipment maintenance procedures and frequency.

Instrument maintenance logbooks are maintained in the laboratory at all times. The logbook contains a complete history of past maintenance, both routine and nonroutine. The nature of work performed, the date, and the signature of the person who performed the work are recorded in the logbook. Preventive maintenance is scheduled according to each manufacturer's recommendation. Instrument downtime is minimized by keeping adequate supplies of all expendable items on hand. Expendable items are those with an expected lifetime of less than one year. Routine instrument preventive maintenance is handled by the instrument operator. Repair maintenance is performed by a full-time electronics technician, or by the manufacturer's service personnel.

Table E.4. PREVENTIVE MAINTENANCE

Instrument	Activity	Frequency
Gas Chromatograph	Change septum Check carrier gas Change carrier gas Change in-line filters Perform ECD wipe test Clean ECO Check system for leaks Clean/replace injection point liner Clean/replace jet tip Service flame photomeric detector	As needed Daily As needed As needed As license requires Return to vendor as needed As needed As needed As needed As needed
IR	Change desiccant Electronics maintenance	Every six months Every six months
UV	Clean and align optics Replace lamp Calibrate	Annually As needed Weekly
pH Meter	Calibrate Check fluid in probe	Daily Daily
D.O. Meter	Clean and replace membrane and HCl solution Calibrate	Daily Daily
Balance	Calibrate Maintenance	Daily Annually
Ovens	Temperature checks	Daily
Refrigerators and Freezers	Temperature checks	Daily
COD Heating Block	Check temperature with NBS thermometer	As needed
Conductivity Meter	Standardize with KCl Check probe visually	Daily Daily

E.6 Calculation of Data Quality Indicators

The focus of this section is to present methods of calculating data quality that will be used for this project.

Control Samples

The laboratory will employ control samples to assess the validity of the analytical results of the field samples. Determination of the validity of field sample results is based on the acceptance criteria being met by the control sample. The acceptance criteria for each type of control sample are delineated in the appropriate SOP. These acceptance criteria are based on the laboratory's statistical process capabilities determined from historical data, and meet the EPA CLP acceptance criteria as a minimum. Often, in-house criteria are more stringent than required by CLP. The control samples are analyzed in the same manner as the field samples. They are interspersed with the field samples at frequencies that are specified by the appropriate SOP.

Method Blank Analyses

A method blank is a "clean" sample (i.e., containing no analyte of concern), most often deionized water, to which all reagents are added and analytical procedures are performed. Method blanks are analyzed at a rate of one per sample lot or at least every 20 samples. The blank is analyzed in order to assess possible contamination from the laboratory or the procedure. If the analyte of interest is found in the blank at above reporting levels, inorganic analysis is suspended until the source of contamination is found and corrective action is taken. The Laboratory Manager is notified when blank results are unacceptably high, and may assist in the investigation.

Surrogate Spike Analyses

For certain analyses such as those performed by GC/MS, each sample and blank is spiked with one or more surrogate compounds before preparatory operations such as purging or extraction. These surrogate standards are chosen for properties similar to sample analytes of interest, but are usually absent from the natural sample.

Surrogate spikes evaluate the efficiency of the analytical procedure in recovering the true amount of a known compound.

The results of surrogate standard determinations are compared with the true values spiked into the sample matrix prior to extraction and analysis, and the percent recoveries of the surrogate standards are determined. Recoveries should meet the upper and lower control limits as specified for each compound. If control limits are exceeded for surrogate standards, the following sequence of actions is taken:

a. The sample is re-injected.

b. Raw data and calculations are checked for errors.

c. Internal standards and surrogate spiking solutions are checked for degradation, contamination, or solvent evaporation.

d. Instrument performance is checked.

e. If a, b, and c fail to reveal the cause of the noncompliance surrogate recoveries, the sample is re-purged or re-extracted.

f. If all the measures listed above fail to correct the problem for laboratory blank surrogate analyses, the analytical system is considered out of control, and the instrument must be recalibrated and examined for mechanical faults.

g. If all the measures listed above fail to correct the problem for field sample surrogate analyses, the deficiency probably is due to sample interferences, and not due to any procedural or mechanical problems in the laboratory. The surrogate spike recovery data and the sample data from both extractions are reported and are flagged. The Laboratory Manager is notified with an exceptions report and the corrective actions taken.

Matrix Spike/Matrix Spike Duplicate Analyses

To evaluate the effect of the sample matrix on the analytical methodology, two separate aliquot samples may be spiked with a standard mix of compounds appropriate to a given analysis. The matrix spike and the matrix spike duplicate (MS/MSD) are analyzed at a frequency of one per lot or one per 20 samples, whichever is more frequent. The percent recovery for each of the spiking compounds is calculated. The relative percent difference (RPD) between the MS/MSD is also calculated.

The observed percent recoveries (%R) and relative percent differences (RPD) between the MS/MSD are used to determine the accuracy and the precision of the analytical method for the sample matrix. If the percent recovery and RPD results exceed the control limits as specified for each spiking compound, the sample is not reanalyzed. Poor recovery in matrix spiked samples does not necessarily represent an analytical system out of control. It is possible that unavoidable interferences and matrix effects from the sample itself preclude efficient recoveries. The poor recovery is documented for the Project Manager.

Internal Standards Analysis

Once an instrument has been calibrated, it is necessary to confirm periodically that the analytical system remains in calibration. The continuing calibration and precision of the organics analytical system are checked for each sample analysis by monitoring the instrument response to internal standards. When internal standard addition is not appropriate to a particular method, other means of accuracy checks, such as standard addition, are used. Results from internal standard analyses are compared to the mean calibrated value. Deviation from this mean beyond a predetermined magnitude, depending on the type of analysis, defines an out-of-control condition. The system must then be brought back into control by:

- Checking the quality of the internal standards and reanalyzing the sample
- Recalibrating the system
- Correcting the malfunctions causing the instrument to fall out of calibration

Duplicate Sample Analyses

Duplicate analyses are performed for cations analyses and upon special request for selected other parameters to evaluate the reproducibility of the method. Results of the duplicate analyses are used to determine the RPD between replicate samples. For each parameter analyzed, at least one duplicate sample is run per group of 20 samples.

The precision value, RPD, is reviewed by the section supervisor and the division manager. If the precision value exceeds the control limit or the established protocol criteria for the given parameter, the sample set is reanalyzed for the parameter in question unless it is determined that heterogeneity of the sample has caused the high RPD.

QC Check Standard Analyses

Analysis of QC check standards is used to verify the preparation process or the standard curve, and is performed with each group of samples. Results of these data are summarized, evaluated, and presented to the section supervisor and the division manager for review.

The results of the QC check standard analysis are compared with the true values, and the percent recovery of the check standard is calculated. If correction of a procedure or instrument repair is done, the check standard is reanalyzed to demonstrate that the corrective action has been successful.

At least twice a year, a QC check standard for each parameter group is analyzed as a double-blind sample. Samples are prepared, submitted, and evaluated by the Laboratory Manager.

Other Quality Control Samples

Under some sampling analysis, additional quality control samples may be required. These may include:

a. **Blank/Spike--**Analyte of interest or surrogate is spiked into blank water rather than into a sample. The blank/spike goes through the entire analytical procedure, and percent recovery is calculated with no likelihood of matrix effect. For many contracts, an externally provided LCS sample (EPA) serves as a blank/spike sample.
b. **Trip Blank--**A sample bottle filled with laboratory blank water travels with the sample kit to the sampling site, and is sent back to the laboratory packed in the same container as any volatile samples collected. Trip blank analyses check for possible volatile contamination during shipping or sampling.
c. **Field Blank--**A field blank can be a sample container filled with laboratory blank water and sent to the sampling site, or it may be filled at the site with purchased distilled water or decontamination water. The field blank analysis checks for possible contamination by the sampling team.
d. **Equipment Rinsates--**After equipment has been cleaned in the field, many contracts require that the equipment be rinsed and the rinsate analyzed for the same parameters requested on the samples. The rinsate analysis proves the equipment has been cleaned properly and will not contaminate the next samples taken.

Control Charts

The laboratory will use control charts to monitor for out-of-control conditions.

Control Charting Process

The control chart program uses a series of Lotus (or equivalent) macros to perform data processing and control charting. These macros also perform statistical decisions on the acceptability of the data.

The control chart used is a variation of the Shewart control chart of averages. The chart plots individual quantitative results against the order of time measurement. The plotted values are compared with control limits determined by the variability about the mean of the standard "in control" process. The control chart estimates the process mean and the variability from a moving window of 50 to 200 samples, depending upon the analytical parameters involved. The mean is estimated from the arithmetic average of the samples in the current window. The variability is estimated as the sample SD of the sample values in the current window. The program calculates the □2 SD and the □3 SD limits and displays them on the chart. The t-statistic is used to estimate the 99.7 percent tolerance limits for the degrees of freedom in the current window. Values outside the t-statistic limits are unconditionally rejected from inclusion in the sample window and automatically documented in a Corrective Action Report (CAR). The CAR prompts the analyst to initiate investigation and corrective action.

When the maximum number of samples has accumulated in the current window, the summary statistics of the mean and SD are written to the long-term data base. The last 20 samples in the old window are then transferred to a new window for continued use in the charting process.

The long-term data base charts the mean □1 SD error bars.

Instrument Detection Limits, Method Detection Limits, and Reporting Limits

Instrument Detection Limits (IDL)

Instrument Detection Limit (IDL) studies are performed for inorganic parameters when an instrument is installed, when major maintenance or repair work has been done, and routinely once per calendar quarter.

To determine IDL, seven consecutive measurements per day are made on a prepared standard solution (in reagent water) of an analyte at a concentration 3 to 5 times the instrument manufacturer's suggested IDL. Each measurement is performed as though it were a separate analytical sample. This procedure is repeated on three nonconsecutive days. The standard deviation is calculated for each set of seven replicates and the average of the standard deviations is obtained. This average is multiplied by 3 to give the instrument detection limit (IDL).

Method Detection Limits (MDL)

The Method Detection Limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. The sample must be carried through the entire method under ideal conditions. MDL is determined according to the method outlined in 40 CFR 136, Appendix B. MDLs are determined at least annually for all parameters. MDL studies are also conducted for new methods introduced in the lab, after major maintenance or modification to an instrument, and as part of the training of new analysts.

To determine MDL, seven replicate analyses are made of analytes spiked into blank water at 1 to 5 times the estimated method detection limit. The spiked samples must be carried through the entire analytical procedure, including any extraction, digestion, or distillation process, for MDL calculation. The SD of these replicates is calculated.

$$MDL = t \times S$$

Where:

t = The student t value for a 99% confidence interval

S = Standard deviation of the replicate analyses

Reporting Limits

In most cases, final report forms list reporting limits rather than either IDL or MDL. Reporting limits are taken from EPA SW846 published limits or from historical data. Matrixes or analyte concentrations which require dilution will change the detection limits for that sample.

E.7 Performance and System Audits

In this section information is provided on performance audits and onsite system audits.

Performance Evaluation Samples

Performance evaluation samples are analyzed throughout the project for all parameters, as a constant check on accuracy and precision for all analyses.

Audits

Internal audits of the laboratory are conducted in two phases. The first phase is conducted by the Laboratory Quality Assurance Coordinator during the fourth quarter of

the year. This is usually a 2-day systems audit which covers all sections of the laboratory. An audit report is issued within 2 weeks of completion. The Field Site Manager has the responsibility for coordinating all responses to the audit finding and for following up on the required corrective action. A follow-up audit is made when deemed necessary by the by the Field Site Manager or the Laboratory Manager. A quality assurance review questionnaire is provided in the Appendix.

The second phase consists of quarterly audits performed by the Field Site Manager. These are half-day or day-long audits, and are concentrated on specific areas that are deemed problem areas by the Field Site Manager. An audit report is issued at the completion of the audit. Responses and follow-up corrective action to the audit findings are required, and are monitored by the Field Site Manager.

All audit reports are issued to management and circulated to all staff. Copies are filed with the Field Site Manager and the Laboratory Manager.

E.8 Quality Assurance Reports

The performance of the field laboratory as assessed by the quality monitoring systems in place is reported by the Field Site Manager to management quarterly and as needed. Copies of all quality reports are maintained in the Field Site Manager and Laboratory Manager files.

Quality assurance reports to management include, but are not limited to, the following:

- Results of performance and systems audits
- Status of corrective actions
- Periodic assessment of data accuracy, precision, and completeness
- Significant QA problems and recommended solutions

In addition to the quarterly reports, a final report summarizing items covered in the quarterly reports is provided by the Field Site Manager to the Project Manager.

E.9 Data Format

Introduction

In order to provide analytical data which is technically sound and defensible, a system of data management will be implemented in the laboratory. All activities which pertain to a sample are documented.

All data generated during the demonstration, except those that are generated by automated data collection systems, will be recorded directly, promptly, and legibly in ink. All data entries will be dated on the day of entry and signed or initialed by the person entering the data. Any change in entries will not obscure the original entry, will indicate the reason for such change, and will be dated and signed or identified at the time of the change.

In automated data collection systems, the individual responsible for direct data input will be identified at the time of data input. Any change in automated data entries will not obscure the original entry. Updated entries will indicate the reason for the change, the date, and the person responsible for making the change.

Data Tracking in the Laboratory

The Field Site Manager is responsible for developing a system for tracking and maintaining sample identity between the collection point, analysis and reporting. This process will be periodically reviewed by the Project Manager.

Analyses and Data Reduction

The Field Site Manager is responsible for the reduction of raw data when such steps are required to produce the correct data format for reporting. Data reduction may be done manually or through one of a number of computer programs used in the laboratory.

Chromatogram Identification

In the GC section computer software is used to identify chromatograms. A system-supplied file name (a hexadecimal date-time) and a user-supplied file name (related to an entry in the injection log) identify each acquisition.

Data Reduction Formulas

Linear regression formulas are used in a computer software system to calculate samples values for many general inorganic parameters and metals analyses. These programs use the general formula for linear regression:

$$Y' = a + bx$$

where:

Y' = The predicted value of y for a selected value of x

a = The value of y when x = 0

b = The slope of the straight line

x = Any value of x selected

Sample values for GC/MS parameters are calculated by systems software using the general formula:

$$\frac{Area_{Target} \ x \ Amount_{IS}}{Area_{IS} \ x \ ResponseFactor}$$

GC data is calculated using either an internal or an external standard. For internal standards:

$$Concentration = \left(\frac{A_x^{sample}}{A_x^{standard}} \right) \left(\frac{A_{IS}^{standard}}{A_{IS}^{sample}} \right) \left(amt_x^{standard} \right) \left(\frac{P}{T} \right) \left(\frac{amt_{IS}^{Sample}}{Amt_{IS}^{standard}} \right)$$

where: P = 1/fraction of extract to which IS is added

For calculations using an external standard:

$$Concentration = \left(\frac{A_x^{sample}}{A_x^{standard}} \right) \left(C_x^{standard} \right) \left(\frac{V}{T} \right)$$

where: C = concentration of x in standard
V = volume of final extract
T = total sample extracted

E.10 Data Storage and Archiving Procedures

Data from GC's will be saved and archived in P&E Turbochrom format. All data will be backed-up on ZIP disks. This data will be batch processed into an Excel .csv file that can be easily converted to an Excel Worksheet. These files will be backed-up and transferred to individuals responsible for calculating flux results. All data related to the project will be organized for rapid retrieval and transfer to other interested parties.