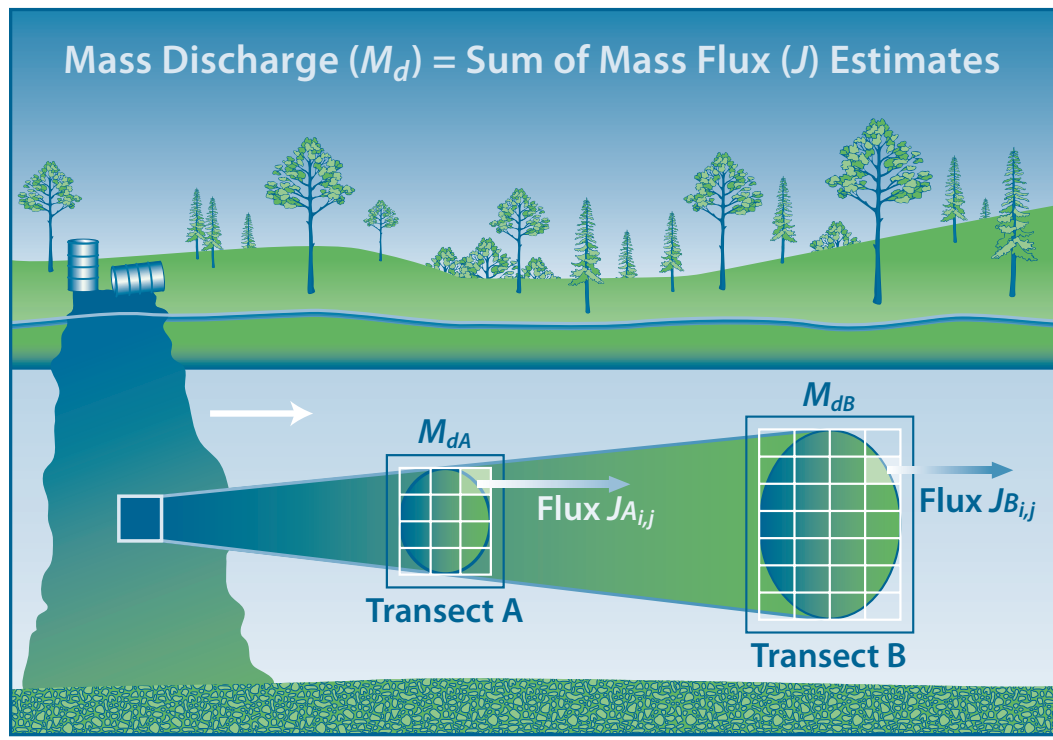


# Technology Overview

## Use and Measurement of Mass Flux and Mass Discharge



August 2010

Prepared by  
The Interstate Technology & Regulatory Council  
Integrated DNAPL Site Strategy Team

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**MASSFLUX-1**

**Use and Measurement of Mass Flux and Mass Discharge**

**August 2010**

**Prepared by  
The Interstate Technology & Regulatory Council  
Integrated DNAPL Site Strategy Team**

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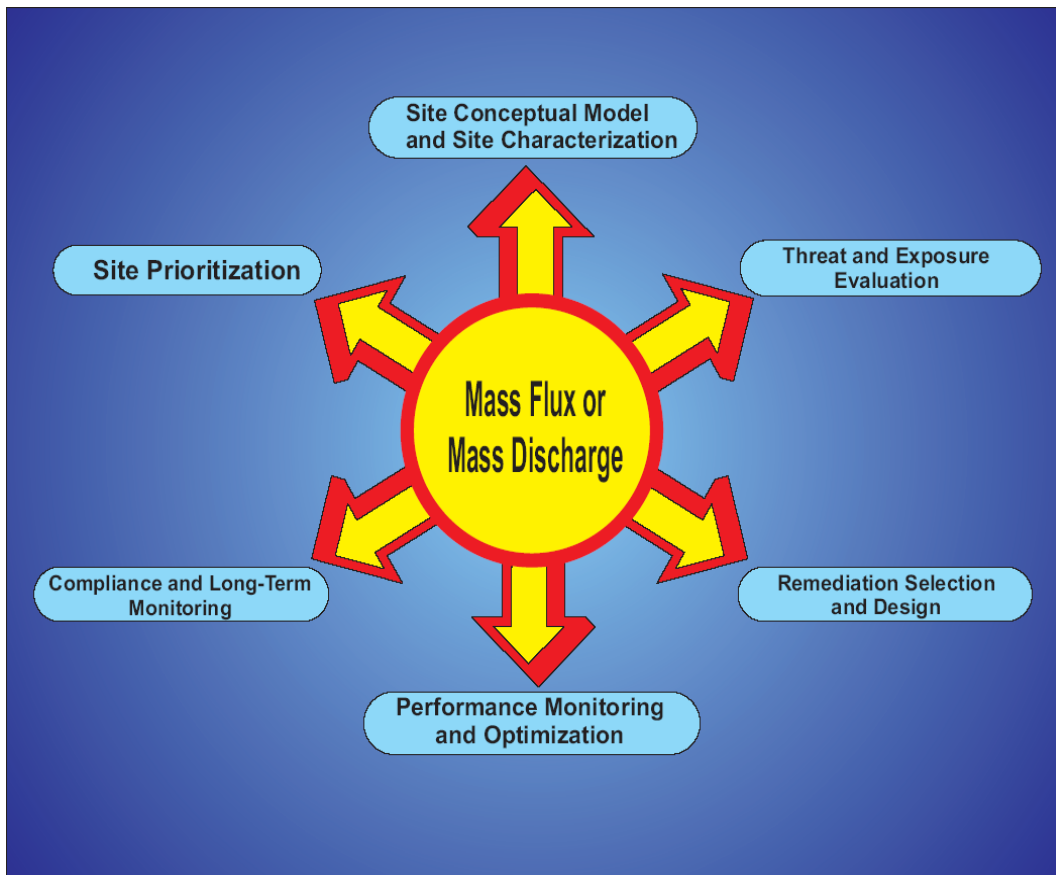
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## EXECUTIVE SUMMARY

Most decisions regarding contaminated groundwater sites are driven by contaminant concentrations. These decisions can be improved by also considering contaminant *mass discharge* and *mass flux*. Mass discharge and flux estimates quantify source or plume strength at a given time and location. Consideration of the strength of a source or solute plume (i.e., the contaminant mass moving in the groundwater per unit of time) improves evaluation of natural attenuation and assessment of risks posed by contamination to downgradient receptors, such as supply wells or surface water bodies.

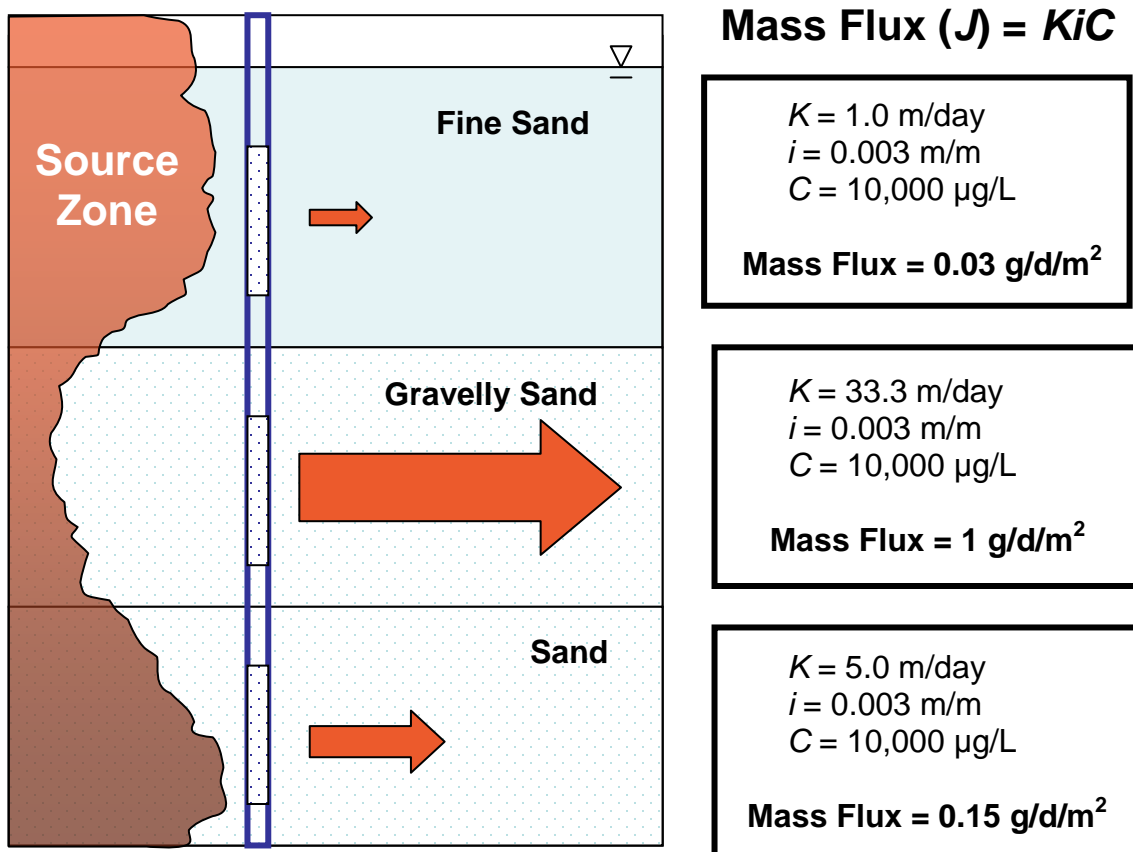
It is important to distinguish between these two terms. *Mass flux* is a rate measurement specific to a defined area, which is usually a subset of a plume cross section. Mass flux is thus expressed as mass/time/area (e.g., g/d/m<sup>2</sup>). *Mass discharge* is an integrated mass flux estimate (i.e., the sum of all mass flux measures across an entire plume) and thus represents the total mass of any solute conveyed by groundwater through a defined plane. Mass discharge is therefore expressed as mass/time (e.g., g/d). In addition to defining the source strength and plume attenuation rate, mass flux estimates can identify areas of a plane through which the majority of the contaminant mass is moving. This information is valuable in virtually all aspects of contaminated site management (Figure ES-1).



**Figure ES-1. Potential applications of mass discharge and mass flux data for contaminated groundwater management.**

Mass discharge is calculated by combining concentration data with the Darcy velocity of groundwater. By evaluating mass discharge at a site and thereby accounting for the combined effects of concentration and groundwater velocity on contaminant movement, managers will have a more complete understanding of the site, which will improve management decisions regarding site prioritization or remedial design and operations. For example, contaminant concentrations alone cannot provide a complete picture of the processes governing plume behavior because groundwater velocity (which varies across a site) is an integral component of plume behavior. However, incorporating mass discharge information into the conceptual site model (CSM) improves remediation efficiency and shortens cleanup times, particularly at sites with multiple source areas or where plumes cross multiple stratigraphic units.

Figure ES-2 provides an example of the benefits of mass flux information for a site with multiple stratigraphic units. In this case, the three stratigraphic layers have identical contaminant concentrations and hydraulic gradients but varying hydraulic conductivities and, therefore, varying groundwater velocities. Considering concentration data suggests only that cleanup of all three layers is equally important. But the mass flux estimates clearly identify the layer that poses the greatest downgradient risk and justify remediation of the gravelly sand first.



**Figure ES-2. Benefit of mass flux assessments for prioritizing treatment zones.** Although the concentrations and groundwater gradient ( $i$ ) are identical, the fluxes and, therefore, the risks differ significantly because of variations in the hydraulic conductivity ( $K$ ). Similar variations in  $K$  are common in most aquifers.



Mass flux and mass discharge estimates can help managers more accurately answer several key questions:

- Is the contaminant plume stable, expanding or contracting?
- How will a proposed remedial action affect the future distribution, transport, and/or fate of the contaminants?
- What will be the risks and exposures at various points in the foreseeable future?
- How much source removal will be needed before transitioning to other technologies, such as in situ bioremediation or allowing monitored natural attenuation to complete the site remediation?

In most cases, mass flux and mass discharge data will not be the only information needed to address these questions. Explicitly considering the mass information can augment the time concentration data (e.g., when evaluating plume stability). A common experience is that measuring mass flux and discharge at a site improves the overall CSM, leading to a better understanding of the potential risks and helping managers identify the highest-priority portions of the site.

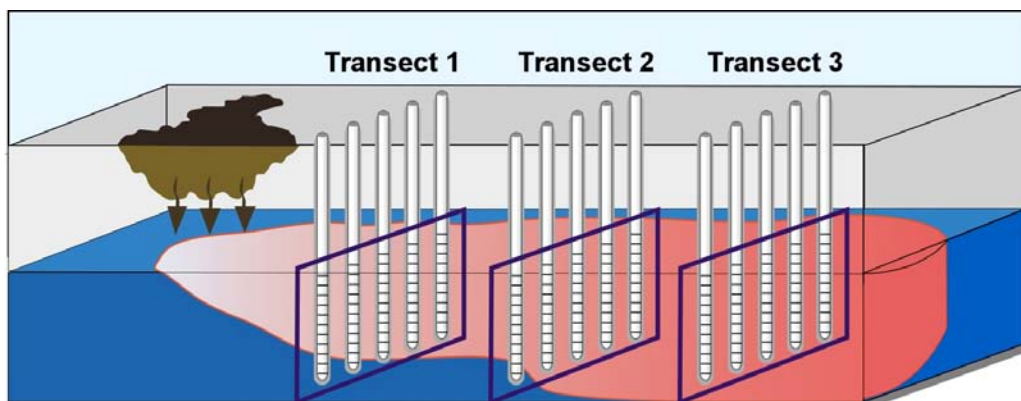
Mass flux and mass discharge estimates do have limitations. Collecting the data necessary to calculate either will increase total project cost. The costs may be relatively low for estimates based on models or mathematical analyses of existing data, but they can be significant for so-called high-resolution mapping (measuring fluxes at relatively close-spaced points along one or more transects, sampling at multiple depth intervals at each sampling point). The uncertainty involved in mass flux and mass discharge estimates can be significant, and it should be quantified where possible. However, it also should be evaluated relative to the concentration data, which may be at least as uncertain. Reliable mass flux and mass discharge estimates often require more detailed characterization of hydraulic conductivity and groundwater flow field than is typically available at most sites. Ultimately, the degree of accuracy required for mass flux or discharge estimates should be determined based on the planned uses of the estimates. In some cases an initial approximation may be sufficient, and higher-resolution measurements can be collected later if necessary.

There are three basic methods to measure mass flux and/or mass discharge:

- **transect methods**, in which individual monitoring points are used to integrate concentration and flow data (Figure ES-3)
- **well capture/pump test methods**, which rely on extracting groundwater and measuring the flow and mass discharge from the wells
- **passive flux meters**, which are recently developed devices to estimate mass flux directly in wells

Mass discharge and flux also may be estimated by analyzing existing site data. Such estimates can be obtained by analyzing flow rates and concentrations (a) along transects oriented perpendicular to isocontours (or along transects using existing monitoring wells) or (b) by using solute transport models that require flow and concentration data as input parameters. Mass discharge data have been determined historically at many sites where soil vapor extraction or

groundwater pump-and-treat systems have been implemented. These data are typically used to evaluate the rate of source depletion, and in some cases asymptotic and mass discharge trends have been used to determine the time to transition to a new technology or management strategy.



**Figure ES-3. Use of multiple well transects to measure mass discharge and mass flux.**  
(Adapted from Einarson and Mackay 2001.)

This technology overview summarizes the concepts underlying mass discharge and flux, their potential applications, and case studies of the uses of these metrics. Review of the case studies showed that mass discharge and flux estimates have been useful for several site management objectives and that evaluating mass discharge and flux can improve CSMs and lead to more efficient remediation. Specific findings from the case study review include the following:

- **Mass discharge and flux data have improved decision making.** For example, they have been used to trigger transition between technologies.
- **Mass discharge and flux data have reduced remediation costs.** For example, mass flux estimates have been used to identify high-priority layers in stratified aquifers, leading to more cost-effective cleanup.
- **Mass discharge and flux data have been used to prioritize sites.** For example, responsible parties have used mass discharge estimates to identify the sites needing further characterization and remediation within regional flow systems impacted by multiple sources.
- **Mass discharge and flux data have been used to predict remediation performance.** Mass discharge, high-resolution mapping, and available analytical tools have provided the basis for estimation of natural attenuation rates, plume responses to source treatment, and remediation time frames.
- **Transect testing has been by far the most common method used, and transects have proven useful for site management.** Use of well transects has provided more credible estimates of natural attenuation rates than the more typical practice of relying on a line of wells along a flow path because transect data are less susceptible to temporal variations in flow direction and strength.

Other uses of mass flux and mass discharge data include risk assessment, particularly when evaluating risks to potential downgradient receptors or when assessing the risks of vapor intrusion into buildings located above contaminated groundwaters. In many cases, this information is used in the underlying models, but its importance is not recognized and the estimates may be highly uncertain.

Key conclusions from this overview of mass flux and mass discharge include the following:

- Mass flux and discharge estimates have proven valuable for contaminated site management and should be used more frequently.
- Use will increase rapidly as the benefits of mass flux and discharge information are more widely recognized.
- A specific estimation method may be better suited to specific site conditions and objectives, so it is important to consider the advantages and limitations of the methods available.
- Useful mass discharge and flux estimates often can be developed from existing site data and/or limited site sampling, often for relatively little cost.
- All methods of mass flux and discharge estimation involve uncertainty that should be recognized and quantified, to the extent practicable, when considering use of the parameters. However, concentration-only data may have similar, or greater, uncertainty.
- Strategies to manage uncertainty include precharacterization and sampling in stages.
- Mass discharge can also have an important role in regulatory decisions and may have advantages over concentration data for some purposes. Examples include deciding when to shift from aggressive treatments to natural attenuation; evaluating dense, nonaqueous-phase liquid (DNAPL) source remediation efforts; or even determining when no further action is required at a site.

This document is intended to foster understanding of mass discharge and mass flux estimates through description of their development and use. In the interest of brevity, this technology overview assumes the reader has a general understanding of hydrogeology, the movement of chemicals in porous media, remediation technologies, and the overall remedial process. Additionally, nothing in this technology overview modifies any existing regulatory requirement of a state or federal agency.

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# USE AND MEASUREMENT OF MASS FLUX AND MASS DISCHARGE

## 1. INTRODUCTION

Many regulatory discussions about sites with groundwater contamination are driven by point-in-time measurements of contaminant concentration—snapshots of contaminant concentrations that may appear to be relatively stable or to show notable changes over time. However, concentration data alone cannot answer all questions critical to contaminant plume assessment or management. Among these questions are the following:

- Is the current distribution of contaminants stable, expanding, or contracting?
- How will a proposed remedial action affect the future distribution, transport, and/or fate of contaminants?
- What will be the risks and exposures at various points of potential exposure throughout the foreseeable future?
- How much source removal will be needed before transitioning to other technologies such as in situ bioremediation or allowing monitored natural attenuation (MNA) to complete the site remediation?
- Which hydrogeologic zones should be targeted by remedial action for maximum benefit?
- What are the options for optimizing existing remedial actions to reduce life cycle costs?

The answers to these questions require an understanding of plume dynamics and specifically the *mass flux* and *mass discharge* of contaminants within the plume. Mass flux (expressed as mass/time/area, e.g., g/d/m<sup>2</sup>) and mass discharge (expressed as mass/time, e.g., g/d) can provide important information about source strength, natural attenuation rates, and possibly the areas of the subsurface through which the majority of the mobile contaminant mass is moving (assuming sufficiently high vertical resolution). The terms “total mass flux” or “integrated mass flux” are used by some authors; both refer to the sum of all of the individual mass flux estimates across an entire plume, which this document terms “mass discharge.” In this overview, we use the terms “mass flux” ( $J$ ) and “mass discharge” ( $M_d$ ).

Nothing in this technology overview on the use and measurement of mass flux and mass discharge supersedes existing regulatory requirements from state or federal agencies. As always, familiarity with state, federal, and local environmental rules is necessary before proceeding with any environmental investigation.

Environmental regulatory standards for contaminants in water do not consider mass flux; they consider only concentrations of contaminants in groundwater in terms of mass per volume. This focus on concentration is understandable since aqueous contaminant concentration is used to determine and regulate the risk to a given receptor exposed to the groundwater at a specific location. This regulatory approach causes site managers to focus primarily on the concentration trends through time and space, relying on data from specific monitoring wells to manage plume remediation or to document performance and compliance. Because mass flux is not needed for concentration-based plume management and additional data must be collected for its calculation, managers typically have not calculated, evaluated, or fully appreciated the value of mass flux for site management.

Over time, recognition of the benefits of mass flux estimates has grown, as a series of quotations shows. First, academic specialists identified a potential application:

Therefore, the ultimate impact of plumes emanating from solvent DNAPL source zones can be evaluated in terms of impact of relatively small annual mass fluxes to the receptor such as water-supply wells or surface waters. In some cases, the fluxes present significant risk to human health and/or the environment, and extensive remedial action is warranted. In other cases, the fluxes are insignificant, and remedial action would provide little or no actual environmental risk reduction. (Pankow and Cherry 1996)

Then, the U.S. Environmental Protection Agency (USEPA 1998) summarized three key reasons for developing mass flux or discharge estimates (here, the word “flux” refers to mass discharge as defined in this document):

1. The reduction in the flux [discharge] along the flow path is the best estimate of natural attenuation of the plume as a whole.
2. The flux [discharge] is the best estimate of the amount of contaminant leaving the source area. This information would be needed to scale an active remedy if necessary.
3. The flux [discharge] estimate across the boundary to a receptor is the best estimate of loading to a receptor.

Next, the complementary values of both mass flux and concentration data in assessment and remediation were recognized:

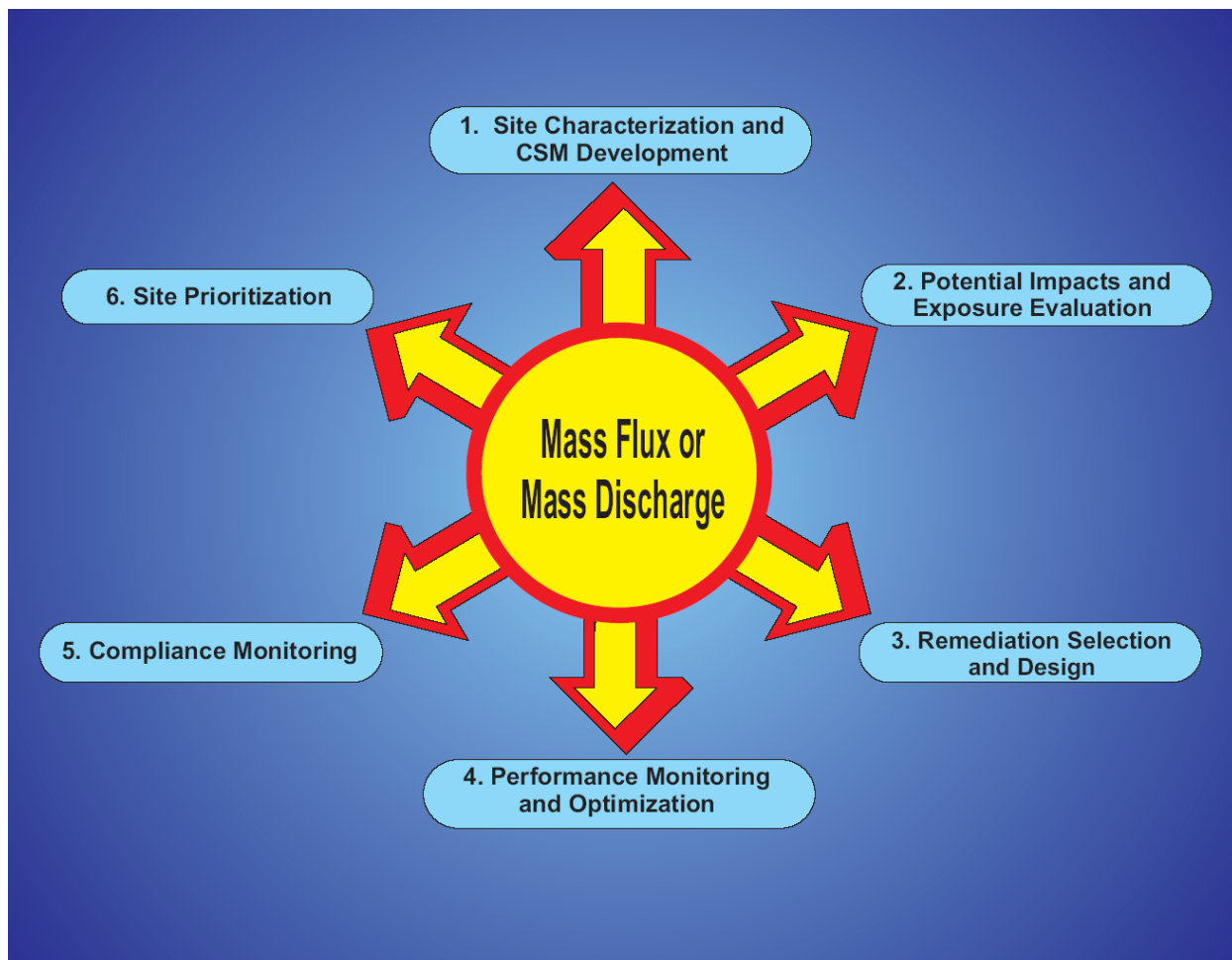
In summary, measurements of mass flux of the contaminants and footprint parameters—not just concentrations—are necessary to document cause-and-effect and to assess long-term sustainability/permanence. Site-characterization and monitoring plans should be proactively designed to accommodate mass flux estimates. (USEPA 2001a)

Mass flux is now being used more frequently to characterize and monitor groundwater contamination (USEPA 2003) due to a growing recognition that mass flux data can provide a more complete measure of the exposure posed by the contaminants than static point concentration estimates alone (Einarson and Mackay 2001; Buscheck, Nijhawan, and O’Reilly 2003). Intense interest in developing and testing better methods to measure and estimate mass flux began when it was identified as one of the most pressing research needs for management of chlorinated solvent sites (SERDP 2004). Recent improvements in mass flux measurement have made the development of sufficiently detailed estimates more practical and economical.

While it is unlikely that mass flux will globally replace point concentrations as the metric for regulatory compliance, it is a powerful tool for developing remedial goals and defining decision points. Mass flux and mass discharge information help managers better understand the impact of a complex plume on the environment and/or receptors, as well as better evaluate the impacts of treatment and whether interim remedial objectives have been achieved. The decision to collect and evaluate mass flux data is site specific. It should consider the reliability of other available data, the uncertainty associated with mass flux estimates, the specific application(s) of the mass



flux data, and the cost-benefit of collecting mass flux data. Figure 1-1 helps illustrate the application of mass flux and mass discharge in the site investigation and remediation process.



**Figure 1-1. Mass flux and mass discharge application within the remedial process.**  
(Numbers preceding applications correspond to those in Table 1-1.)

Mass flux estimates can better characterize a contaminated site than typical monitoring networks (Feenstra, Cherry, and Parker 1996). Typical monitoring plans focus primarily on defining plume boundaries and concentration trends, but chemical concentrations (and groundwater velocities) vary tremendously across a plume, and areas of significant flux may be missed during source and extent delineation. A mass flux calculation requires measurement of the variability in concentrations and velocities within a plane of the plume and therefore is based on a more thorough site characterization. Additionally, mass flux values at different times and places along a plume show the combined impact of all of the physical, chemical, and biological processes acting on the contaminants. The additional understanding of plume dynamics provided by mass flux improves the conceptual site model (CSM), which helps site managers make better remediation decisions (Nichols and Roth 2004, Basu et al. 2006). Prior ITRC documents also have concluded that the addition of mass flux data can result in more credible remediation decisions than concentration data alone (ITRC 2004, 2008a, 2008b). Specifically, mass flux information can improve the understanding and management of contaminated sites several ways:

- Mass flux estimates along transects near source zones can yield critical information about source zone strength, source zone architecture, and the degree of heterogeneity in the aquifer.
- Mass discharge estimates can improve assessment of the potential exposure to a receptor, such as a water supply well or surface water body.
- Mass flux data comparisons over time and space can directly measure the attenuation capacity of the aquifer, delineate the highest contaminant mass and mass flux zones within a plume, and identify the optimal treatment zones within a plume.
- Mass discharge and mass flux estimates can be used to develop remedial goals and performance metrics, select and design remediation systems, monitor remedy performance, and define transition points, in time or space, between technologies.
- Mass discharge can help regulatory agencies and site managers prioritize remediation of multiple sites based on differences in source strength and threats to receptors.

The use of mass flux and mass discharge is increasing and will accelerate as field methods improve and practitioners and regulators become more familiar with their application, advantages, and limitations.

Mass flux characterization is intended to reduce uncertainty, and a cost-benefit analysis should be undertaken before beginning such a characterization. For example, when using mass flux estimates to size a remediation effort, questions such as “How wrong can this estimate be without compromising effectiveness or protectiveness?” should determine the scope and resolution of the mass flux definition. Further, it must be realized that mass flux characterization can increase total project costs without a concomitant rise in data usability.

As with any investigation, integration of mass flux or discharge evaluations into decision making begins with the questions to be answered and the goals to be reached. The mass flux/discharge calculation must directly address these questions and the remedial objectives. Data use during a decision-making process should be defined. To help managers optimize mass flux or mass discharge data collection, Table 1-1 lists remedial objectives (as identified in Figure 1-1), decision points, and the relative data density needed to achieve each. The data density column is intended only to provide a relative frame of reference and to make the point that different objectives require different data, not to specifically recommend the quantity of data to be gathered. For instance, estimating residual source strength may require relatively fewer data points if the objective is to evaluate source strength reduction during and after treatment. However, if you want to understand heterogeneity in contaminant mass flux across the vertical transect to design a more efficient treatment or you want to estimate the natural attenuation capacity of a plume using multiple transects, then data density requirements increase. Additional detail on each application is found in later sections of this document as referenced in the fourth column.

**Table 1-1. Summary of mass flux data and decision points for contaminant plume remediation and management**

<b>Remedial applications</b>	<b>Mass flux data use</b>	<b>Flux-informed decision points</b>	<b>Relevant document section</b>	<b>Relative data density of mass flux or mass discharge</b>
1. Determine whether you need to treat contamination to achieve remedial goals or MNA is appropriate	Estimate source strength	Is the mass discharge from the source area sufficiently high (for instance, greater than the natural attenuation capacity in the plume) to necessitate active treatment?	3.1	Low
	Estimate contaminant plume stability	Is the trend in contaminant mass flux or discharge throughout the plume indicative of an expanding or contracting plume?	3.1.1	High if using multiple plume transects
	Estimate the balance between the mobile contaminant mass and the natural attenuation capacity of a plume	Is the natural attenuation capacity (estimated from the reduction in contaminant mass discharge measured at a series of transects oriented perpendicular to the plume axis) sufficiently high to achieve remedial action objectives? Or is active treatment required in the source area and/or plume?	3.1.1	Medium to high if using multiple plume transects
2. Evaluate risk to groundwater receptor(s)	Estimate risks and exposures to groundwater receptors over time at various points of potential exposure	Does mass discharge to a receptor location necessitate active treatment of the source area or dissolved-phase plume?	3.2	Low to medium
3. Evaluate remedial alternatives: select appropriate technology or suite of technologies to achieve remedial goals	Determine remedial action objectives to achieve remedial goals	What is the reduction in mass discharge from a source area or across a plume transect needed to achieve remedial goals?	3.3.1	Low to high depending on system design and treatment volume(s)
	Determine appropriate remedial technology or technologies for source and/or plume treatment	What technologies are capable of achieving the required reduction in mass flux or discharge from a source area or across a plume transect?	3.3.2	
Develop and optimize remedial design	Evaluate heterogeneities in source zone architecture	What is the minimum treatment volume or mass required to achieve remedial action objectives?	3.3.3	High
	Estimate source strength reductions necessary to transition technologies (i.e., to in situ bioremediation or MNA)	Has source strength (i.e., discharge) been reduced sufficiently to transition to less-aggressive treatment?	3.3.3	Low
	Estimate distribution of contaminants relative to transmissive zones	What is the optimal treatment configuration to achieve remedial action objectives?	3.3.3	High

<b>Remedial applications</b>	<b>Mass flux data use</b>	<b>Flux-informed decision points</b>	<b>Relevant document section</b>	<b>Relative data density of mass flux or mass discharge</b>
4. Evaluate remedial performance	Determine whether treatment efficiencies are sufficient to achieve remedial goals <ul style="list-style-type: none"> <li>• Compare mass removal for a remediation system to mass discharge estimate</li> <li>• Compare total electron acceptor demand to mass discharge of electron acceptors</li> </ul>	Is treatment achieving mass flux or discharge remedial action objectives and ultimately remedial goals?	3.4	Low to high depending on system design and treatment volume(s)
5. Evaluate compliance and long-term monitoring	Determine contaminant mass discharge or flux limits to achieve remedial goals	Is the remedial system achieving the desired mass flux and/or discharge objectives deemed acceptable for achieving remedial goals?	3.5	Low to medium
6. Site prioritization	Determine mass loading from the source or to a receptor	Measure mass discharge along a transect perpendicular to flow <ul style="list-style-type: none"> <li>• At the downgradient edge of the source zone</li> <li>• Just upgradient of a potential receptor</li> </ul> Compare source strength and potential impacts to receptors among sites to assess resource allocation	3.6	Low to medium

In summary, this technology overview describes the concepts and practice of mass flux and mass discharge to foster the appropriate uses of these tools. Section 2 describes the basic principles of mass flux and mass discharge measurement. Section 3 describes current and potential applications. Section 4 describes methods of estimating mass flux and mass discharge in groundwater, specific models and tool kits, and factors that can affect distributions and estimates. Finally, Sections 5 and 6 summarize specific barriers or challenges associated with mass flux and mass discharge approaches and corresponding research needs.

## 2. CONCEPT AND THEORY OF MASS FLUX AND MASS DISCHARGE

Mass flux ( $J$ ) is the mass of a chemical (e.g., contaminants, amendments, tracers and other chemical additives) that passes through a defined cross-sectional area over a period of time. Simply put, mass flux combines two key features of a contaminant plume: how much contaminant is in the groundwater and how fast the water is moving through a defined cross-sectional area (i.e., the contaminant concentration and the groundwater flux). Mass flux is a vector quantity, and as mentioned earlier, it is expressed as mass/time/area (e.g., g/d/m<sup>2</sup>). Mass discharge ( $M_d$ ) is related to mass flux but is not limited to a defined area. Instead, it represents the total mass of a solute (such a contaminant) moving in the groundwater from a given source. So it is a scalar quantity, expressed as simply mass/time (e.g., g/d).

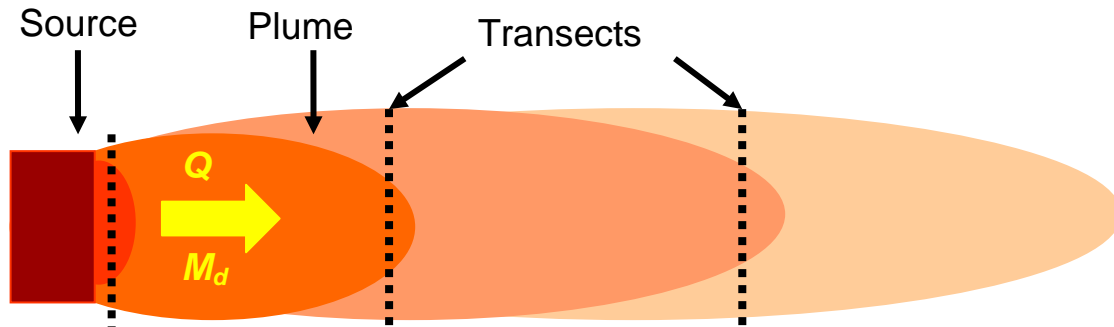
Mass flux and mass discharge estimates are valuable to understanding and managing contaminant plumes, and in fact, these concepts are the basis for existing groundwater fate and transport models and transport phenomena more generally (e.g., Bird, Stewart, and Lightfoot 2007; Hemond and Fechner-Levy 2000). However, mass flux and discharge estimates are not often used in site management decision making, partly because regulations generally focus on the concentrations of contaminants in the groundwater. Also, there has been a lack of appreciation for the value of this metric in decision making despite its use in the models used for natural attenuation evaluations and risk assessments.

This section describes the background information needed to understand mass flux and mass discharge estimates. The first section (Section 2.1) provides definitions and basic concepts. Section 2.2 provides an introduction to mathematical calculations of mass flux and mass discharge. Section 2.3 summarizes mass flux and mass discharge measurement methods. Section 2.4 briefly discusses factors that affect mass flux and discharge. Finally, Section 2.5 discusses the uncertainties and sources of error involved in developing mass flux and mass discharge estimates and methods for minimizing those uncertainties.

### 2.1 Basic Concepts

“Flux” is broadly defined as flow through a medium. In the physical sciences, flux is a rate measurement defined as the flow across a defined area during a defined time. The term “flux” may be applied to the flow of heat, electrons, or other substances, through a wide range of media. Measurements of flux are made across planes or surfaces that perpendicularly intersect the flow. Notably, flux estimates include both the magnitude and the direction of flow. Hence, flux is also a vector quantity (Bird, Stewart, and Lightfoot 2007).

By definition, mass flux is specific to a defined area, but when used for contaminant plumes, the area that is sampled to determine mass flux is usually small compared to the overall dimensions of the plumes. Moreover, for many purposes, the critical issue is not the mass flux across some particular area of the groundwater, but the total mass conveyed by the plume to some point along its length. Hence, a common objective is to measure the mass discharge (i.e., the “total mass flux” across an entire plume). The contaminant mass discharge can be estimated by measuring contaminant concentrations and groundwater fluxes along a transect perpendicular to groundwater flow. Figure 2-1 depicts the total groundwater discharge ( $Q$ ) and total contaminant mass discharge ( $M_d$ ) at three transects across a plume.



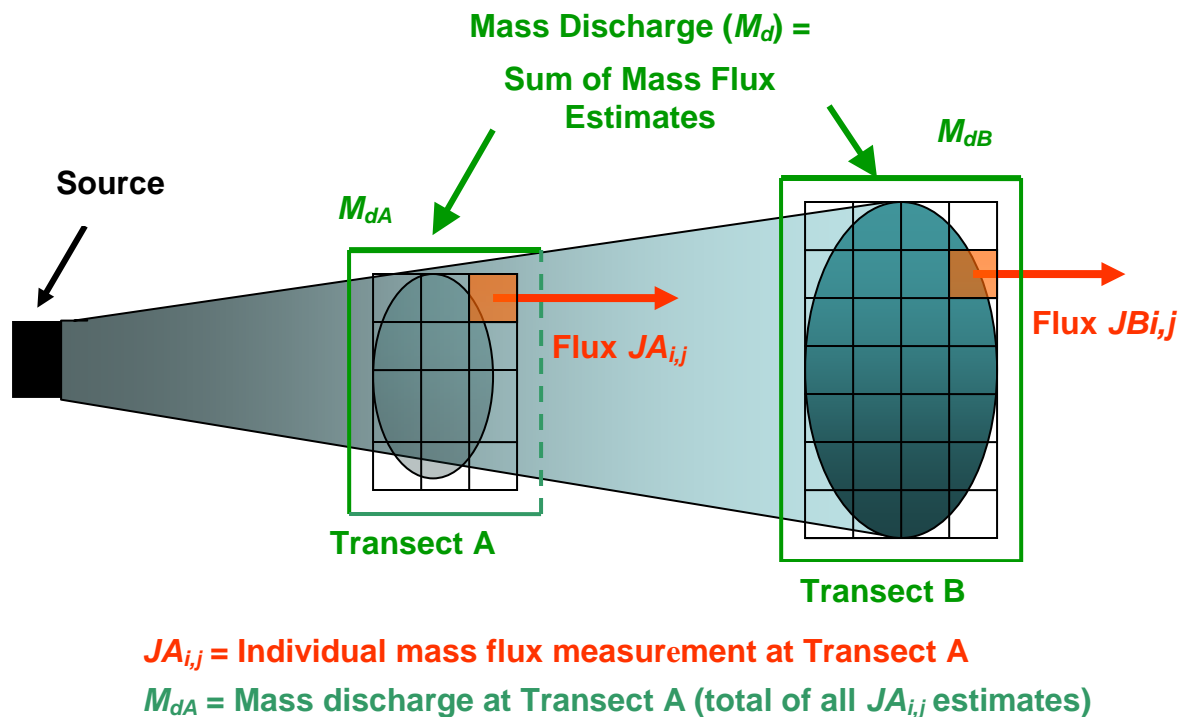
**Across any transect, a contaminant plume conveys:**

- Groundwater discharge,  $Q = L^3/t$  (e.g., volume/d)
- Contaminant mass discharge,  $M_d = \text{mass/time}$  (e.g., g/d)

**Figure 2-1. Contaminant mass discharge in plan view.** Mass discharge ( $M_d$ , the total contaminant mass moving through a transect per unit time) is conceptually similar to groundwater discharge ( $Q$ , the total volume of groundwater moving through a transect per unit time). Mass discharge is the product of groundwater discharge multiplied by the average contaminant concentration. (Graphic courtesy HydroGeoLogic, Inc.)

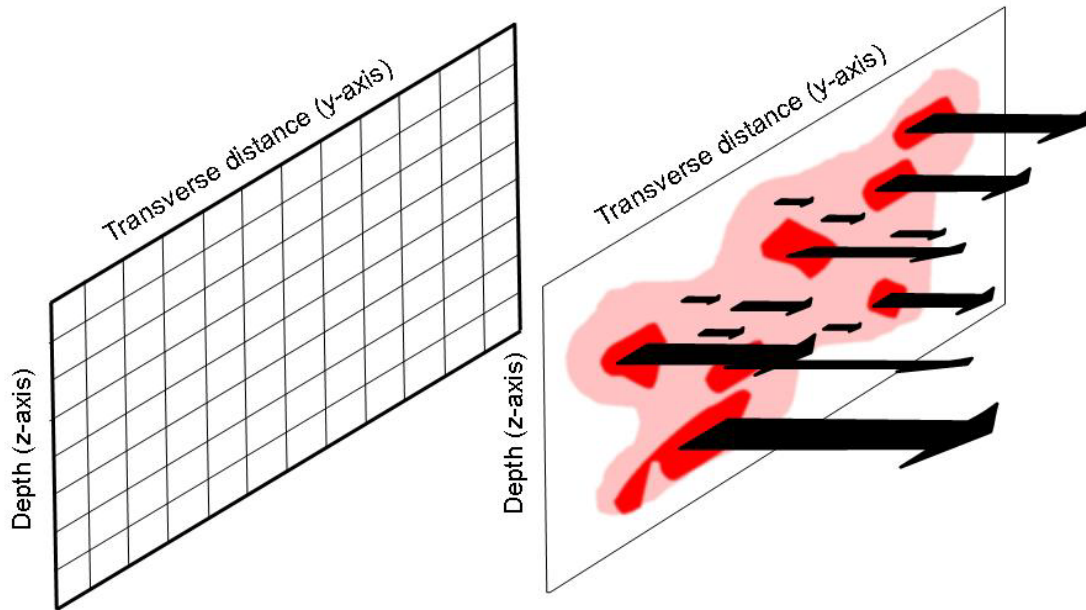
Importantly, flux is a vector, i.e., it is a point measurement with both velocity and concentration varying over all dimensions. On the other hand, discharge is an integrated variable and is a scalar quantity, as long as the location of the boundary is defined. Contaminant mass discharge is therefore the proper term to define the rate of release of contaminants from a source where the control plane is near the source and at which the attenuation properties and processes of the aquifer have had minimal impact. Contaminant mass discharge also can define the total mass crossing a “control plane” or transect at a property boundary or contaminant loading into a body of water adjacent to the plume.

In reality, the contaminant mass moving through the subsurface transect exhibits spatial variability, so several individual mass flux measurements are generally needed unless one is capturing the entire contaminant plume as a single sample. Figure 2-2 provides a conceptual depiction of  $M_d$  and  $J$  values across two transects.



**Figure 2-2. Concepts of mass flux ( $J$ ) and mass discharge ( $M_d$ ).** Flux is the mass moving past a plane of given area per unit time (e.g., g/d/m<sup>2</sup>). Each square in the transect represents the mass flux for that unit area (cell  $i,j$ ) of the transect. Mass discharge is the total mass flux integrated across the entire area of a transect (e.g., g/d). It is therefore the sum of the cells in the transect. There would be two mass discharge values for this example ( $M_{dA}$  and  $M_{dB}$ ) at different distances downgradient from a source. These mass discharge values can be compared to evaluate conditions at the site (e.g., the natural attenuation rate). (Graphic courtesy HydroGeoLogic, Inc.)

Figures 2-3 and 2-4 depict one transect and the variations in flux resulting from variations in both concentrations and transmissivity across a plume. It is important to realize that both groundwater velocities and contaminant concentrations vary significantly across the intersecting plane in most aquifers. The typical spatial variability in both parameters makes measurement of contaminant mass flux challenging. On the other hand, it may be the case that an estimate that provides only an upper limit to the mass discharge may be less costly and just as useful. However, such upper limits can be very useful and are commonly used in risk assessment and transport modeling as a means of dealing with variability.



**Key questions:** 1) What is the minimum size feature that we must be able to detect? 2) What is the appropriate sampling grid spacing to detect a feature of that size?

**Figure 2-3. Variations in mass flux across a transect.** Simultaneous measurements of groundwater flow and contaminant concentrations are made at representative grid points. Mass flux is calculated using those estimates in eq. 2-1. Summing the segments of all mass flux values across the entire plume cross section yields the contaminant mass discharge. (Graphic courtesy ARCADIS.)

## 2.2 Calculating Mass Flux and Mass Discharge

Mathematically, contaminant mass flux is the product of the *contaminant concentration* in groundwater and the *groundwater flux*. Thus, contaminant mass flux ( $J$ ) can be calculated as follows:

$$J = q_0 \cdot C = -K \cdot i \cdot C \quad (2-1)$$

where

- $q_0$  = groundwater flux,  $L^3/L^2/t$  (e.g., volume/area/d)
- $K$  = saturated hydraulic conductivity,  $L/t$ , (e.g., m/d)
- $i$  = hydraulic gradient, dimensionless (e.g., m/m)
- $C$  = contaminant concentration,  $M/L^3$  (e.g., mg/volume)

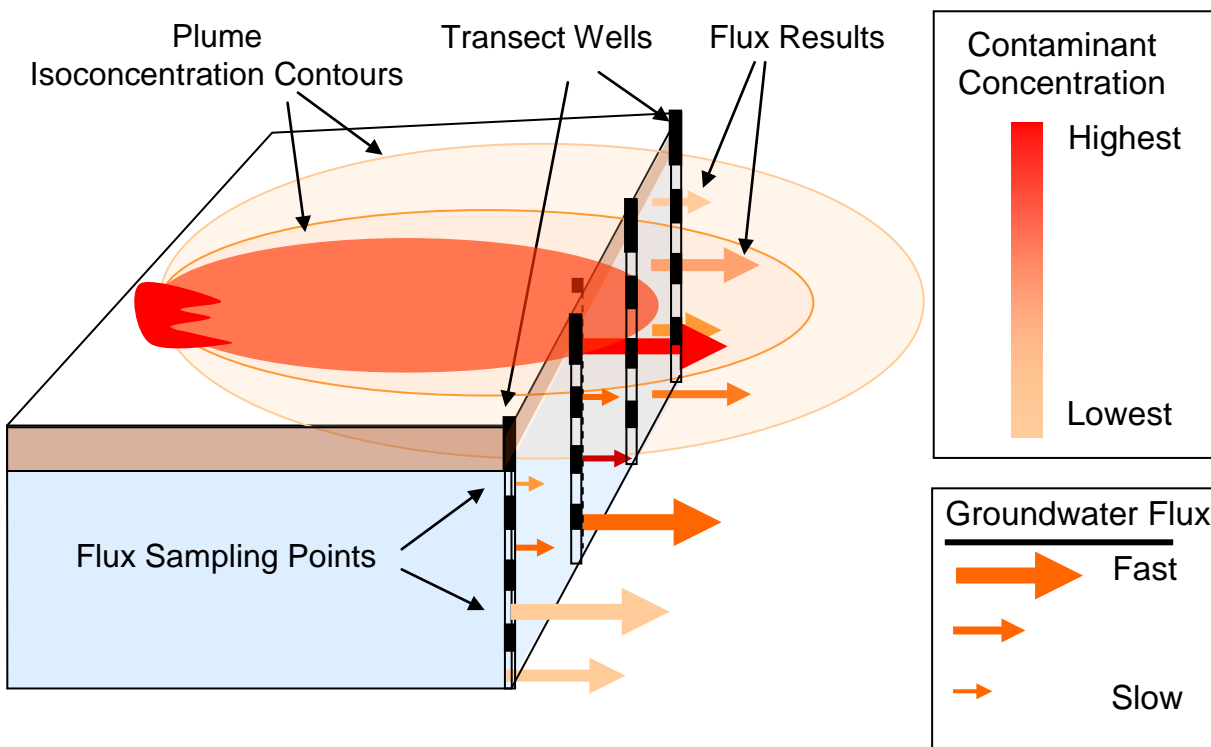
Contaminant mass discharge is the integration of the contaminant mass fluxes across a selected transect:

$$M_d = \int_A J dA \quad (2-2)$$

where

- $A$  = area of the control plane,  $L^2$  (e.g.,  $m^2$ )
- $J$  = spatially variable contaminant flux, as defined in eq. 2.1





**Figure 2-4. Measuring mass flux using wells along a transect.** Results illustrate spatial variations in mass flux across a contaminant plume. (Graphic courtesy HydroGeoLogic, Inc.)

Other equations for calculating the mass discharge for different measurement methods are provided in Section 4.

Note that mass flux ( $J$ ) varies both spatially and temporally across the control plane, and this variation may be significant. Spatial and temporal variations in mass flux are caused by variations in both contaminant concentrations and groundwater flow magnitude and direction, which typically vary widely for most dissolved plumes (Guilbeault, Parker, and Cherry 2005). In contrast, mass discharge ( $M_d$ ) can vary only over time at the control plane since there is only a single value for the entire control plane.

### 2.3 Approaches to Mass Flux Estimation

This document discusses three methods to directly measure mass flux and/or mass discharge:

- **transect methods**, in which concentration and flow data are measured at individual monitoring points
- **well capture/pump test methods**, in which groundwater is extracted and the total flow and mass discharge from the well(s) are measured (Bockelmann, Ptak, and Teutsch 2001)
- **passive flux meters**, in which recently developed devices are placed in wells for a period of time (Hatfield et al. 2004)

Two indirect methods to calculate mass discharge from existing data are as follows:

- calculate and multiply flow rates and contaminant concentrations along **transects based on isocontours** (or along transects of existing monitoring wells, if possible)
- use **solute transport models** that require flow and concentration data as input parameters

It is important to understand the relative strengths and limitations of direct measurements relative to the two indirect approaches (Table 2-1).

**Table 2-1. Advantages and limitations of mass flux and mass discharge estimates**

<b>Method</b>	<b>Advantages</b>	<b>Limitations</b>
All mass flux methods	<ul style="list-style-type: none"> <li>• Improves source strength characterization</li> <li>• Improves potential to understand where high-contaminant-strength areas are and to focus remediation accordingly</li> <li>• Improves assessment of natural and enhanced attenuation</li> <li>• Direct measurement of contaminant loading to receptors</li> <li>• Potential basis for relevant and measurable performance requirements</li> </ul>	<ul style="list-style-type: none"> <li>• Potential increase in characterization and/or monitoring costs</li> <li>• Uncertainties related to subsurface heterogeneities</li> <li>• May require long times for fluxes to reach equilibrium after treatment</li> </ul>
Point and transect sampling	<ul style="list-style-type: none"> <li>• Greater spatial information on flux and variations</li> <li>• Less purge water disposal needed</li> <li>• No change in natural flow regime</li> </ul>	<ul style="list-style-type: none"> <li>• Increased cost for sample points and analyses</li> <li>• Higher risk of error in mass discharge estimates due to missed high-flux zones</li> <li>• Need for high-resolution characterization, especially hydraulic conductivity</li> <li>• Greater risk of interpolation errors</li> </ul>
Well capture or integral pump test	<ul style="list-style-type: none"> <li>• Reduced interpolation error</li> <li>• Greater certainty of capturing all of the mass at a given location</li> <li>• Low potential for missing high-flux zones</li> </ul>	<ul style="list-style-type: none"> <li>• Increased cost for wells and analyses</li> <li>• Increased costs for water treatment and disposal</li> <li>• Potential for error due to under- or over-capture of plume</li> <li>• Loss of spatial information</li> <li>• Potential capture of water that may not migrate under natural flow regimes</li> </ul>

Transects rely on point measurements across a plume, whether using point sampling methods or passive flux meters (PFMs). Integral pump tests (IPTs) actively extract water from one or more points. Both methods rely on data generated specifically for their determination. Transect methods (TMs) will always be limited in their ability to quantify reality because typically only a relatively small volume of the total plume is measured, though in some cases it may be necessary

to take a large number of samples to reduce the overall estimate of uncertainty to acceptable levels. Mass flux estimates based on relatively few measurements of concentrations and groundwater velocity are possible and may be of value, depending on the use of the mass flux and mass discharge values. However, low-density data are less likely to detect extreme contaminant concentration and groundwater velocity values or to produce true median and mean values for either.

An IPT samples the entire plume, and spatial variability is of less concern. However, an IPT measures mass discharge under stressed conditions and requires pumping well(s) and water treatment or disposal. Unfortunately, an IPT does not provide positional information useful in placement of treatment wells or other remedial structures.

PFMs integrate contaminant concentration and groundwater flow rate over time, reducing the variability of the estimates; however, the devices may be best suited to permeable, unconsolidated formation, and multiple deployments may be needed to determine both field time and the effect of any treatment occurring during their deployment.

The two indirect, calculation-based methods (using existing data) can provide initial mass flux estimates that are useful during design of future investigations or mass flux/discharge collection plans. However, the data used are derived from information previously collected and interpreted (second-generation) processes, which may have already introduced uncertainty.

In fact, each method can be useful for different purposes, and different methods may be used at a single site at different times. For example, detailed sampling along transects may be used to characterize a site and design some remediation systems, but a relatively few PFMs may be preferable for long-term monitoring. Conversely, IPTs may provide more accurate estimates of mass discharge, since all of the contaminant mass is captured, which allows better reagent dose calculations.

More detail is provided in Section 4 for those wishing a more comprehensive review of these methods.

## **2.4 Factors that Affect Mass Flux**

The mass flux observed at any location along a contaminant plume represents the integrated effects of transport, storage, and degradation along the flow path. Clearly mass flux estimates are impacted by the factors controlling groundwater velocity (hydraulic conductivity and gradient); thus, changes affecting these parameters (e.g., groundwater extraction rates, groundwater elevation changes, saturated thickness, recharge, plugging of pores, and seasonal variations in velocity or even flow directions) will affect mass flux. Similarly, variations in the contaminant concentrations can be affected by changes in oxidation-reduction potential due to infiltrating precipitation or seasonal water level or groundwater temperature shifts. Variations in contaminant concentration can also be caused by sorption and precipitation of inorganic contaminants.

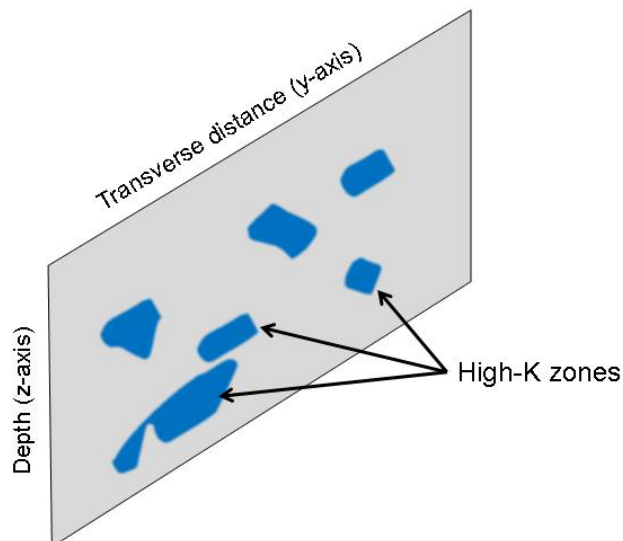
When choosing mass flux measurement points and interpreting mass flux results, it is important to consider the effects of temporal and spatial variations. Because hydraulic conductivity,

contaminant concentrations, groundwater gradients, and degradation mechanisms can vary in space, and in some cases vary in time as well, concurrent measurement of these parameters at equivalent scales is needed to reduce overall error. The following sections discuss the effects of time, the evolution and eventual structure or architecture of the dynamic plume (and spatial variability), and the heterogeneity of the subsurface that can result in enormous variations in concentrations and groundwater velocities over short distances.

#### 2.4.1 Plume Structure and Evolution

Groundwater flow tends to be concentrated in high-conductivity (high- $K$ ) zones that occupy a relatively small portion of the aquifer cross section (see Figure 2-5). Additionally, a series of mass flux measurements along a contaminant plume would show that mass flux varies considerably from the source zone to the leading edge. This information can be useful during plume characterization and selection and design of remedial actions.

For example, Figure 2-6 panel A shows a hypothetical contaminant source, with a developing plume. A series of transverse cross sections is shown. At the leading edge, contaminant arrival is observed only in the highest-velocity (high-conductivity) zones. In

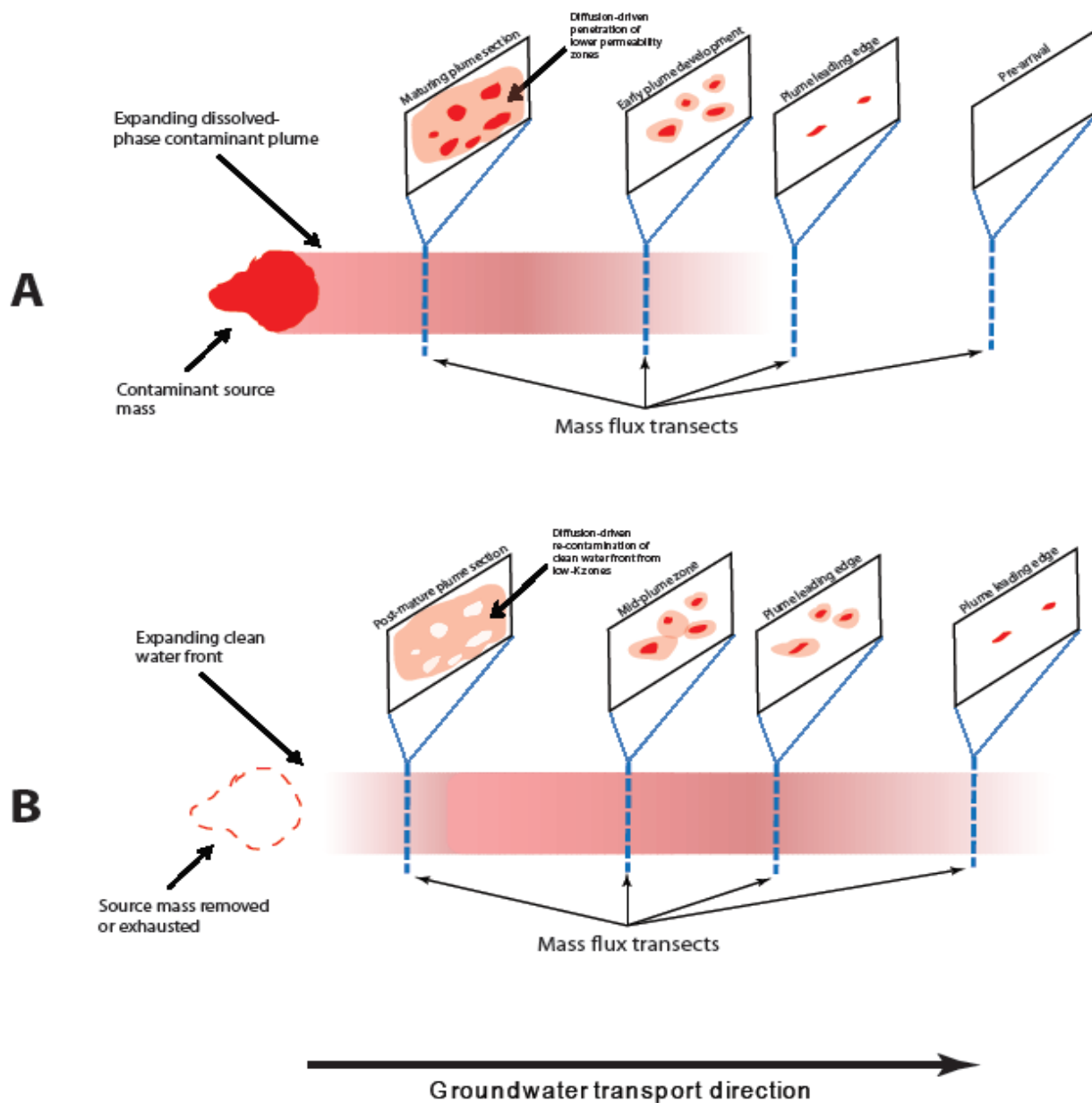


**Figure 2-5. Illustration of hydraulic conductivity ( $K$ ) distribution.**

(Graphic courtesy ARCADIS.)

transsects closer to the source, where the contaminant front arrived earlier, diffusion from the more transmissive zones has caused contaminant mass accumulation in the low-permeability (low- $K$ ) zones, e.g., fine silts and clays, adjacent to the high-flow aquifer channels. This mass storage in less-transmissive zones is characteristic of near-source areas and other areas of a plume that have been in contact with contaminants for an extended time. In contrast, at the leading edge of a plume, where there has been little time for the slow diffusion of contaminant mass into less-transmissive areas, most of the mass will be in the most-transmissive zones.

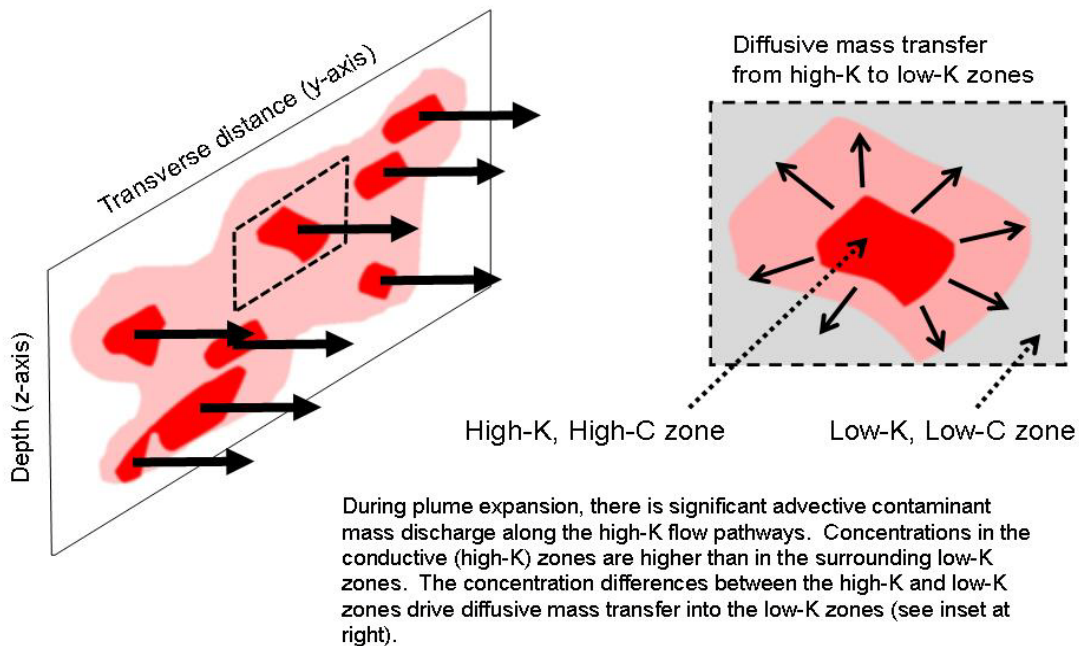
Figure 2-6 panel B shows a plume soon after source removal or exhaustion—the clean water front is beginning to propagate from the upgradient end of the plume. The high- $K$  zones are running at lower concentration than the low- $K$  zones; the low- $K$  zones became contaminated over time by diffusion from the previously contaminated high- $K$  zones. The low- $K$  zones now release residual mass from this second-generation source to recontaminate groundwater flowing primarily through the high- $K$  zones. The clean water front propagates through the high- $K$  zones; therefore, they are colored very lightly (slightly contaminated due to back-diffusion) in the leftmost mass flux transect in panel B. The panel is produced at a time when the treated groundwater has not yet arrived at the second mass flux transect downgradient from the former source area. The treated groundwater cannot travel faster than the groundwater flow rate through the high- $K$  zones, and even then is impacted by continued recontamination from stored mass in the low- $K$  zones. This effect is referred to as “back-diffusion” (Young and Ball 1998).



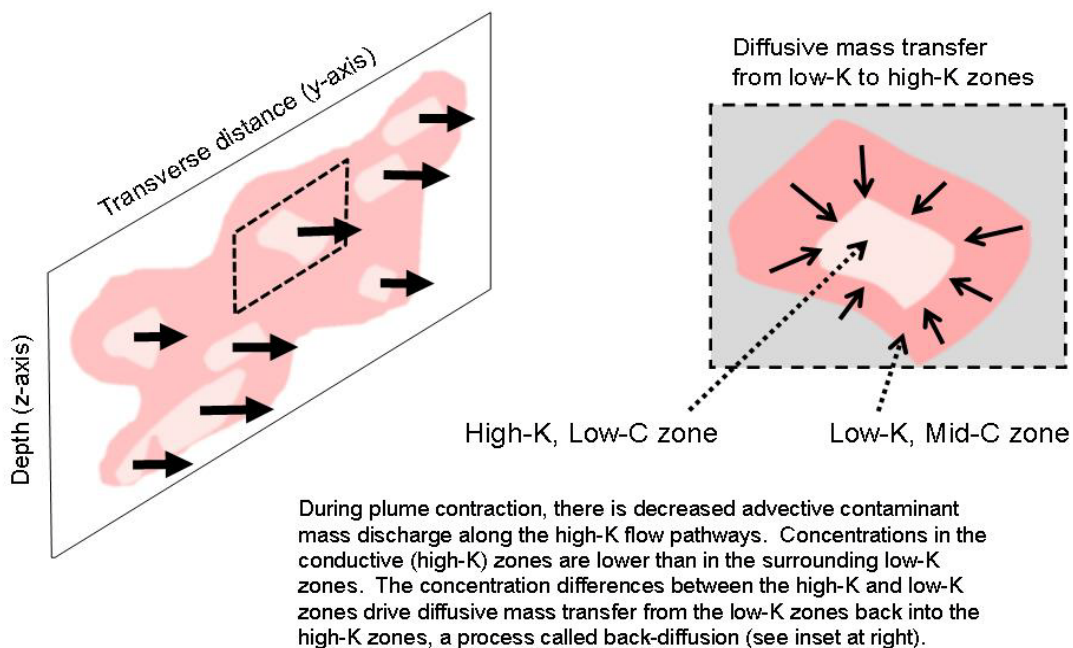
**Figure 2-6. Plume structure and mass flux distribution in a hypothetical contaminant plume developing from a DNAPL source zone.** A series of transects is shown, with the leading edge of contaminant arrival on the right. Note the changes in the mass storage in less transmissive zones with distance from the source. (Figure courtesy ARCADIS.)

As Figure 2-7 conceptually displays, contaminant concentrations in high-conductivity (high- $K$ ) zones in an expanding plume will often exceed those in lower- $K$  zones, but once the plume begins to contract, the reverse will appear. High- $K$  zones, which have had their formerly high contaminant concentration pore water forced out by lower-concentration water emanating from the depleted former source zone, will now have a lower concentration than the adjacent low- $K$  zones.

## Dissolved-phase plume expansion

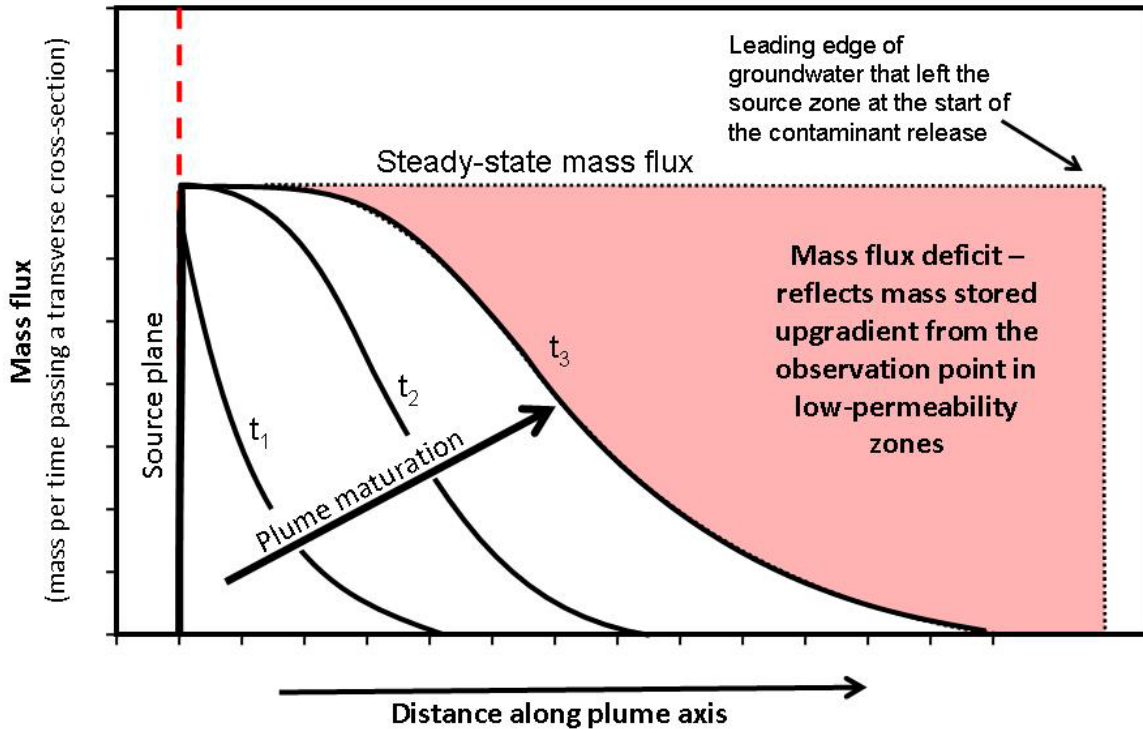


## Dissolved-phase plume contraction



**Figure 2-7. Changes in mass flux distribution over time: plume expansion and contraction through transverse cross-sectional mass flux analysis.** Length of arrow is proportional to the flux. (Graphic courtesy ARCADIS.)

If the measurements were repeated periodically to form a time sequence, the mass flux would be expected to change with time; as storage sites (sorption in both high- and low- $K$  zones and dissolved phase in low- $K$  zones) are filled, the mass flux increases in the downgradient direction. Figure 2-8 depicts this concept and shows that there are two reasons for mass discharge to be less downgradient than through the source plane mass flux: (a) contaminant degradation and (b) mass storage on sorption sites and in low-permeability zones along the groundwater flow paths.



**Figure 2-8. Changes in mass flux distribution in an expanding plume over time.** The mass flux at any location along a plume represents the combined effects of contaminant transport, destructive attenuation (if any), and storage processes (sorption and diffusion into low- $K$  zones). Losses of contaminant mass temporarily lower mass flux relative to the flux that is later observed at plume maturity. (Graphic courtesy ARCADIS.)

In addition, it should be recognized that variations in source strength over time are probably common with non-steady-state source terms. Increases in downgradient mass discharge could be due to an increase in the source strength, which can result from hydrogeologic changes (increased flushing or changes in groundwater flow direction or changes in groundwater levels) or continuing migration of residual nonaqueous-phase liquid (NAPL) to more or less accessible regions of the source zone. It is important to realize that the mass discharge can vary over time for many reasons and to consider all possible explanations for observed changes.

#### 2.4.2 Subsurface Heterogeneity

A key factor affecting mass flux estimates is the high degree of heterogeneity and anisotropy in most aquifer matrices. A high degree of heterogeneity mandates a more intensive sampling effort to obtain a usable representation of mass flux for cross sections transecting the groundwater flow path. Intensive sampling may also be needed to characterize the variations in concentrations

across a control plane as well. Figure 2-9 shows an exposed embankment near Healy, Alaska, illustrating the extreme variations in hydraulic conductivity that can occur in many high-energy depositional environments. Even in sand dune environments, there is a high degree of depositional structure, as shown in Figure 2-10.



**Figure 2-9. Example of a heterogeneous and anisotropic subsurface environment.** In aquifer matrices developed in high-energy depositional environments (braided channels and alluvial fans, for example), the range of hydraulic conductivities over short vertical distances (and groundwater velocities) can exceed 1,000,000-fold. Exposure located near Healy, Alaska, at 63°55'47.87"N, 149°05'55.26"W. (Photo courtesy ARCADIS.)



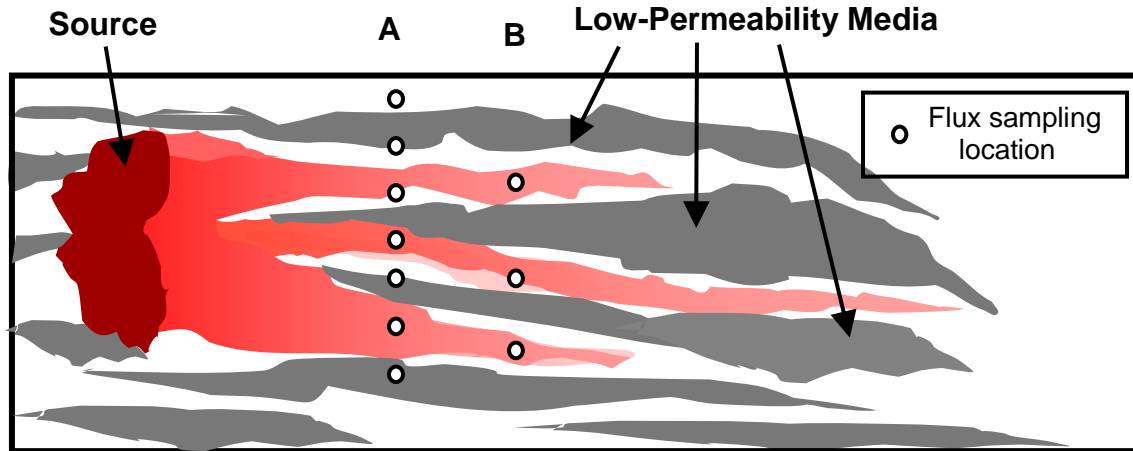
**Figure 2-10. Heterogeneity in apparently homogeneous materials.** Exposure of a sand dune, showing its heterogeneous, anisotropic structure. (Photo courtesy University of Chicago.)

Figure 2-11 illustrates some implications of subsurface heterogeneity for the design and interpretation of mass flux analyses. Any mass flux sampling program should carefully consider the locations of monitoring points to maximize the value of the resulting data. The ability to locate monitoring points optimally for mass flux measurements requires an adequate understanding of subsurface conditions. Uncertainty in a mass discharge estimate will be reflected in the uncertainty of the CSM. That being said, considering that the state of the science uses point estimates of concentrations from monitoring wells within the current regulatory framework, the addition of mass flux, even with limited datasets, can provide more insight into the CSM and improve decision making.

As with all currently used environmental techniques, even methods of measuring mass flux that rely on



capturing the entire plume (such as the IPT), will be affected by heterogeneities in the subsurface. A pump test may not capture the entire plume, or it may capture water that is outside the plume. It will definitely draw water from high- $K$  zones more easily, increasing the measured contaminant concentration of an expanding plume and decreasing that of a contracting plume. Finally, there is always some uncertainty regarding the extrapolation of pump test results under induced flow regimes to the natural flow conditions.



**Figure 2-11. Plan view illustrating the potential impacts of geological heterogeneities on flux estimates and plume architecture.** Transect A employs a regularly spaced series of monitoring points but misses much of the flux and produces a large amount of biased-low (or low-concentration) data. From information in Transect A, locate Transect B considering knowledge of the paleoenvironment and thereby using fewer monitoring points and producing a better estimate of mass discharge for lower cost.

(Graphic courtesy Doug Mackay, Stanford University.)

## 2.5 Managing Uncertainties

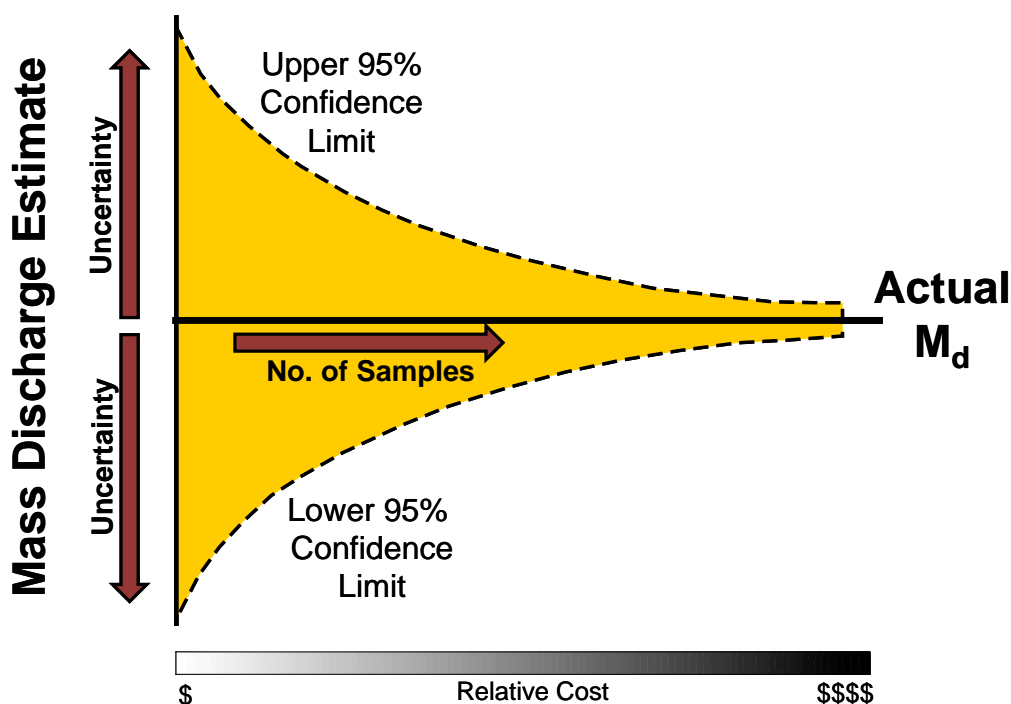
Uncertainties or sources of error associated with determining mass flux are inherent to measurement-based or calculation-based methods. The effect of all sources of error is cumulative and impacts the resulting mass flux estimate.

Inherent uncertainties include spatial and temporal variability in the aquifer. Transect sampling can measure only a small fraction of the groundwater passing through a given transect. An appropriate sampling density will therefore improve the accuracy of a mass flux estimate but only to a certain limit (Kübert and Finkel 2005). Alternatively, characterizing the uncertainty may be part of the data quality objectives, thereby allowing an estimate of the upper limit on certain critical parameters. Sampling densities from points along a transect are commonly less than 1% of the total flow through the transect; thus, it is always possible to miss some fraction of the total discharge, to say the least. Even well-designed studies with high data densities have missed portions of a plume and therefore underestimated discharge (Einarson and Mackay 2001).

One implication of this assessment of uncertainty is that it will always be challenging to obtain enough samples to have high confidence in the accuracy of the mass discharge through any transect (Figure 2-12). Therefore, the accuracy needed for the purposes of any given mass flux

estimate should be defined. For example, the relative comparison of the change in mass flux or discharge over time at a location, as a result of remediation, requires a different level of characterization than the measurement of mass discharge for compliance monitoring. In many cases, accuracy to within an order of magnitude may be sufficient, such as for the following:

- **Evaluating the effects of remediation.** Sale, Zimbron, and Dandy (2008) report that well-implemented source zone remediation projects are likely to reduce source zone groundwater concentrations by about one to possibly two orders of magnitude (90%–99% reduction) from pretreatment levels, so that a measurement resolution of one order of magnitude range would likely be able to show that there was a reduction in mass flux from a site.
- **Prioritizing multiple sites.** Mass discharge estimates at actual sites range over orders of magnitude (Appendix A shows a range of 0.00078–160,000 g/d). Mass flux estimates within an order of magnitude would provide useful information for prioritization across the universe of sites based on mass discharge estimates.



**Figure 2-12. Variance of mass discharge estimates.** The variance of mass discharge estimates is high because they are calculated by multiplying point estimates of two high-variance parameters (groundwater flux and contaminant concentrations), then summing the point estimates across the plane of the transect. (Graphic courtesy Porewater Solutions.)

Section 4.8 provides additional information about managing uncertainty from mass discharge/mass flux estimates.

Sampling most real-world contaminant plumes, even at close spacing and multiple depth intervals, samples only a small fraction of the total discharge. For example, passively sampling all of the water entering a number of 2-inch wells at 5-ft spacing would allow sampling of

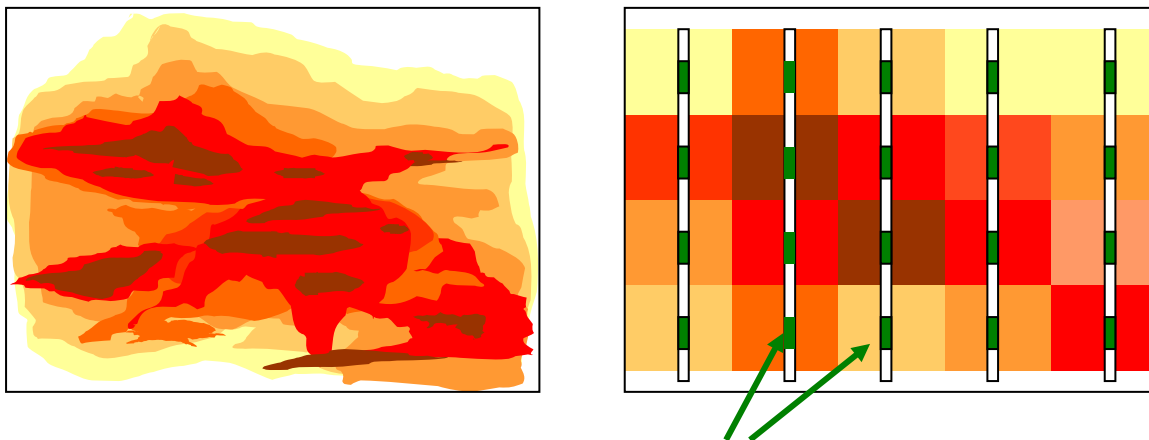
roughly 3% of the total water crossing the transect (i.e., 2 out of every 60 inches, if there is no convergence into or divergence of flow around the sampling wells). For example, Li, Goovaerts, and Abriola (2007) estimated that 6%–7% of the groundwater should be sampled to accurately measure the effect of source zone treatments on mass discharge. They concluded that “most field applications to date may not have been based upon a sample size sufficient to accurately quantify the uncertainty of mass discharge, and the estimated mass discharge may have large errors.”

The greatest sources of error and uncertainty in mass flux or mass discharge estimates include estimates of hydraulic conductivity ( $K$ ) and contaminant concentrations. For example,  $K$  values can vary dramatically over small distances, and they are difficult to measure accurately, an example of measurement-based uncertainty. As a result,  $K$  estimates are often in error by a factor of 10 or more and may represent the greatest source of error in most mass flux estimates based on sampling from a transect of wells. Inaccurate  $K$  estimates affect the accuracy of most mass flux estimates, including IPT results (see Section 4.2.6). Of course, from a practical perspective, this is an “averaging” problem that is addressed by defining a sufficiently representative environmental volume. For example, careful analyses of the relatively homogeneous Borden aquifer clearly shows that  $K$  values can vary by up to three orders of magnitude over relatively short vertical distances. However, researchers have been able to make many useful predictions and calculations about fate and transport by averaging these values appropriately.

Concentration variations can be critical as well. For example, Li (2009 personal communication) and Guilbeault, Parker, and Cherry (2005) have found that for mildly heterogeneous aquifers (in which  $K$  varies by only one order of magnitude or less), most of the uncertainty will be related to the heterogeneity of the concentration field. Guilbeault, Parker, and Cherry (2005) found that concentrations could vary by more than three orders of magnitude over vertical intervals as small as 30 cm in an aquifer with a decades-old source where the remaining dense, nonaqueous-phase liquid (DNAPL) zones were concentrated in thin horizontal layers.

Calculation-based uncertainty includes the effects of interpolation and the potential loss of information from averaging over relatively large areas from a series of multilevel sampling points, as illustrated in Figure 2-13. It is important to consider carefully the methods used to calculate the flux between points and the degree of certainty in the resulting flux and discharge estimates.

Recent publications describe processes that can reduce uncertainty in mass discharge estimates. For example, Guilbeault, Parker, and Cherry (2005) described mass flux estimates at three sites with DNAPL source zones, including a detailed discussion of the influence that vertical and horizontal sampling intervals can have on the accuracy of mass flux estimates. Figure 2-14 shows the concentration (perchloroethene [PCE]) mapping from one of those sites. The cross section spanned 26 m. Two hundred and fifty-seven samples were collected from a total of 12 boring locations and analyzed for contaminant concentrations. Fifteen mass flux hot spots were identified in the cross section. Li and Abriola (2009) developed a spatial sampling design (i.e., locations and depths) algorithm which can automatically guide concentration field characterization to focus on hot-spot areas through which most contaminant mass is transported. Tests of this algorithm using numerically generated three-dimensional plume data suggest that a sample number reduction of up to 50% can be achieved, yielding the same level of characterization accuracy.

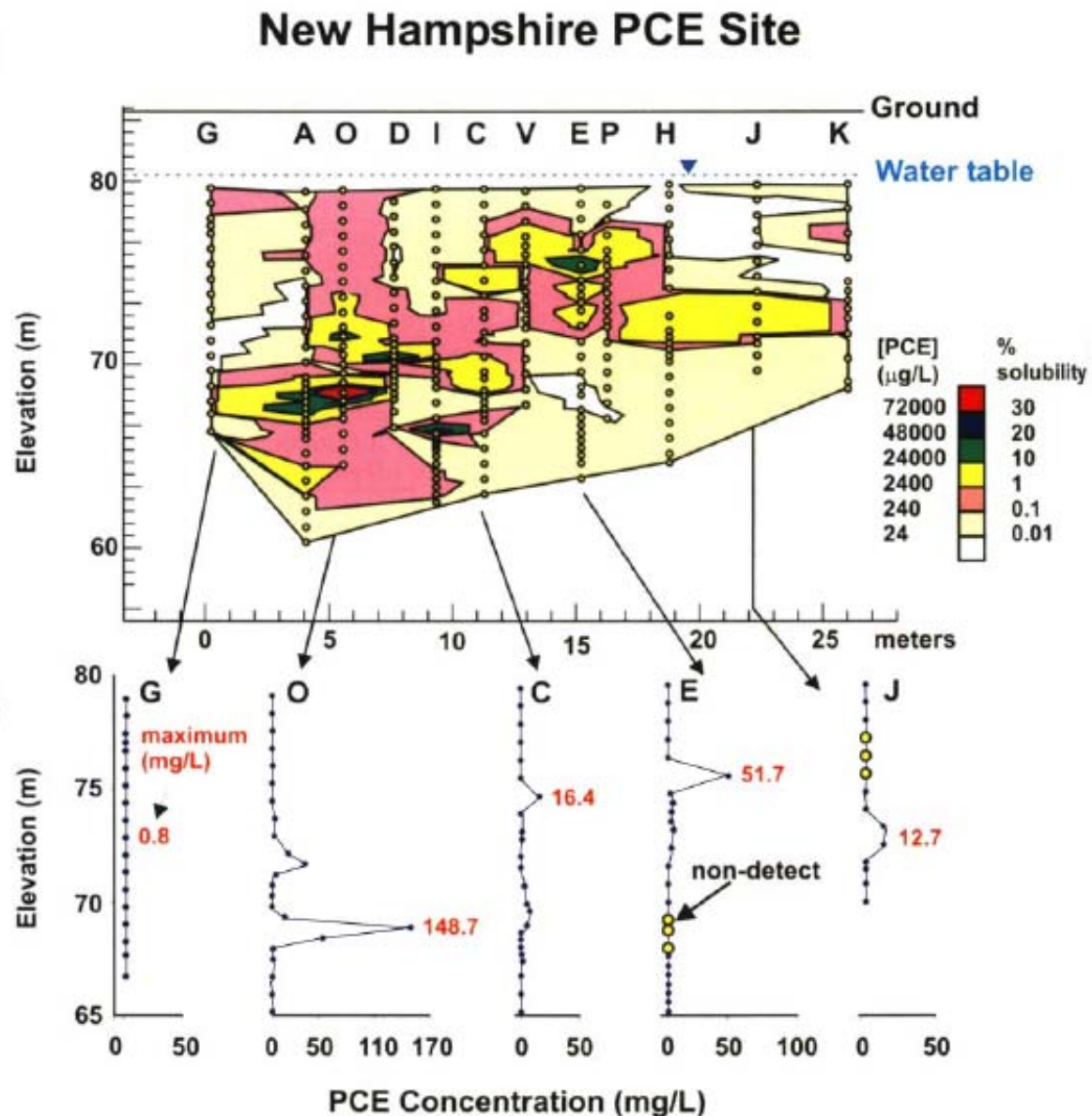


### Multilevel Wells with Flux Sampling Points

**Figure 2-13. Flux interpolations from multilevel in-well sampler data.** Actual flux distribution (left) and interpolated flux distribution (right) illustrate difficulties involved in estimating flux from dispersed sampling points. Notice that the potential for errors increases inversely to the scale of the heterogeneous features and directly with the distance between sampling locations. (Figure courtesy HydroGeoLogic, Inc.)

Based on the work presented by Guilbeault, Parker, and Cherry (2005), factors to consider when designing spacing intervals for a field program may include the following:

- Precharacterization can reduce sampling costs and improve accuracy. Screening technologies such as cone penetrometer testing–membrane interface probe (CPT-MIP, see Section 4.1.6) or Geoprobe® or collection of head-space analyses in vertical soil cores can focus the sampling effort on the areas with relatively high mass fluxes.
- Thin vertical sampling intervals may be needed to accurately estimate the mass discharge at sites with thin DNAPL layers. For example, 30 cm intervals were sampled by Guilbeault, Parker, and Cherry (2005) because the site had a mild degree of heterogeneity and decades-old DNAPL sources. Thicker intervals may be sufficient at sites with fresh DNAPL sources and/or less heterogeneity.
- The vertical spacing also depends on the sampling method. Closer spacing may be needed for passive monitoring wells than for sites where active pumping is used to characterize mass discharge.
- Horizontal spacing can be significantly larger than vertical spacing intervals when characterizing mass flux at sites where DNAPL is distributed predominantly in horizontal layers.
- If multiple transects are used and no intrinsic degradation is believed to be occurring, it may be possible to validate the mass flux distribution through the source plane transect by comparing this estimate to the mass discharge measured at transects farther downgradient. In this case, the use of multiple transects at a site may influence the selection of sample spacing and/or the corresponding uncertainty associated with mass flux and mass discharge estimates.



**Figure 2-14. Example of a mass flux transect sampling program in a heterogeneous subsurface.** Design and representative concentrations from a cross section consisting of 257 samples taken from 12 borings across a 26 m transect. Each small circle represents the location of a paired observation of groundwater flow and contaminant concentration. Results were used to calculate the mass discharge and to map the mass flux distribution. (Reproduced from Guilbeault, Parker, and Cherry 2005.)

### 3. APPLICATIONS FOR MASS FLUX AND MASS DISCHARGE

This section summarizes how mass flux and mass discharge estimates can be applied at sites to address characterization, remediation, and receptor mitigation objectives. Uses of mass flux and mass discharge are grouped in the following categories (see Figure 1-1):

- site characterization and CSM development
- potential impacts and exposure evaluation
- remedy selection and design
- performance monitoring, evaluation, and optimization
- compliance monitoring
- site prioritization

Sections 3.1–3.6 and Table 3-1 describe each use and present case study examples. Additional case example information, including references and web links, is provided in Appendices A and B. Section 3.7 uses a conceptual example to illustrate how mass flux and mass discharge information can be applied. Section 3.8 discusses important regulatory considerations associated with the application of mass flux or mass discharge measurements.

### 3.1 Site Characterization and Conceptual Site Model

Mass flux and mass discharge estimates have several applications relating to site characterization. In most cases mass flux/discharge estimates can also be used to evaluate potential impacts to receptors and to assess performance of a future remedy. Following is a list of site characterization uses for mass flux and mass discharge estimates. Additional detail about these and other applications is provided in Table 3-1.

- Establish baseline mass discharge from a source zone to a plume (i.e., source strength) at a given point in time.
- Identify source zone hot spots and evaluate mass flux distribution of contaminant mass (i.e., those locations where the source is contributing the highest mass discharge to the plume). See example in box at right.
- Determine mass attenuation rates between transects along a common flow path.
- Evaluate whether contaminant mass is primarily contained within high- or low-conductivity (transmissive) zones (high or low  $K$ ).
- Compare the mass discharge distribution of electron donors and acceptors across a transect to the contaminant mass discharge distribution to determine whether specific locations need enhancement as part of the remedy.
- Compare source zone mass discharge (i.e., source strength) to the estimated plume attenuation rate to determine whether multiple sources may be contributing to a plume.

#### Australia Site

Basu et al. (2009) used a flux-based site management approach at a DNAPL-impacted site in Australia to develop an improved CSM and to provide information for more effective and efficient site management. The approach incorporated historical site data with flux measurements to provide insight into the distribution of contaminant mass within the source zone and between the source and plume. Using this approach, they concluded that (a) residual trichloroethene (TCE) in the source zone was small and primarily in low-permeability zones, (b) the plume was disconnecting from the source, (c) biodegradation in the plume was minimal, and (d) residual TCE in the vadose zone was a source of TCE mass moving into the plume during infiltration events. These observations provide the basis for making decisions regarding remedial selection and design.

**Table 3-1. Summary of mass flux and mass discharge applications**

Use/application	Purpose	How applied		Case study example
		Mass flux (g/year/m <sup>2</sup> )	Mass discharge (g/year)	
1. Site characterization and conceptual site model	(a) Establish baseline source strength	--	Measure mass discharge across a transect at downgradient edge of the source zone; use to prioritize site based on source strength; use to select and design remedy; compare baseline with post-remedy mass discharge measurements to assess performance (Soga, Page, and Illangasekare 2004).	Fort Lewis Military Reservation, Wash.: Used a 10-well transect with passive flux meters and a variation of the integral pumping test to establish baseline source zone flux distribution and mass discharge for comparison to post-remediation measurements to assess remediation performance and effectiveness (Brooks et al. 2008).
	(b) Identify source zone hot spots and mass flux distribution	Measure baseline mass flux distribution across transect at downgradient edge of source zone; use to select and target remedy based on where the highest mass flux occurs; compare to post-remedy mass flux distribution to assess performance (Soga, Page, and Illangasekare 2004).	--	DNAPL-impacted site in Australia incorporated historical site data with flux measurements to better assess the distribution of contaminant mass in the source zone and between the source and plume (Basu et al. 2009).
	(c) Evaluate mass attenuation rates within specific areas of the plume	--	Measure mass discharge across two or more transects along a common flow path; the difference between mass discharge measurements is the attenuation rate over the portion of the plume between transects (assuming system equilibrium); use changes in localized attenuation rates to assess remedy performance and effectiveness.	Kao and Wang (2001) and Landmeyer et al. (2001) used transects of multilevel monitoring wells to calculate mass discharge and attenuation rates between transects.

**Table 3-1 (continued)**

Use/application	Purpose	How applied		Case study example
		Mass flux (g/year/m <sup>2</sup> )	Mass flux (g/year/m <sup>2</sup> )	
1. Site characterization and conceptual site model (continued)	(d) Determine whether contaminant mass is mainly within high- or low-transmissive zones	Measure mass flux distribution along transect near the source zone and compare with the groundwater flux distribution and lithology.	--	Basu et al. (2006) conducted depth-discrete flux monitoring indicating that the zone of higher permeability and lower concentrations needs to be considered as a target zone for remediation because it represents a relatively large portion of the source strength, which shows that focusing remediation only in the zone of high concentrations may be “suboptimal.” Basu et al. (2009) used mass flux and specific discharge measurements to demonstrate that residual DNAPL mass was present in low-permeability zones and that source treatment was unwarranted.
	(e) Evaluate aqueous electron donor/acceptor supply and localized availability	Measure the mass flux distribution of electron acceptors and donors across one or more transects and compare to the contaminant mass flux distribution to target enhancements if needed. Use information to refine characterization of biodegradation reactions (i.e., terminal electron-accepting processes) responsible for contaminant attenuation.	--	Former manufacturing plant, Stuttgart, Germany—Evaluated natural attenuation between two transects downgradient of the source zone. Mass discharge at each transect used to estimate first-order biodegradation rates. Changes in mass discharge of electron acceptors and metabolic by-products between transects was also evaluated to provide additional lines of evidence for biodegradation (Bockelmann, Ptak, and Teutsch 2001).
	(f) Determine whether multiple sources may be contributing to a plume	--	If plume attenuation rate exceeds the mass discharge from a known source zone, then there are additional source(s).	Methyl tertiary-butyl ether (MtBE) site, Calistoga, Calif.—Mass discharge estimates suggest that a release from one site is probably responsible for supply well impacts (Einarson et al. 2005).



Table 3-1 (continued)

Use/ application	Purpose	How applied		Case study example
		Mass flux (g/year/m <sup>2</sup> )	Mass flux (g/year/m <sup>2</sup> )	
2. Potential impact and exposure assessment	Estimate the actual and allowable mass discharge to potential receptors	--	Measure the mass discharge contributing to downgradient receptor exposure; compare to allowable mass discharge based on acceptable exposure point concentration and mixing zone assumptions (see Section 3.2).	Service station, Tahoe City, Calif.—Used mass discharge estimate from a transect of wells to estimate the maximum concentration to an adjacent river (Buscheck, Nijhawan, and O’Reilly 2003). Fuel release site, Morro Bay, Calif.—Used mass discharge framework to evaluate potential threat of MtBE plume to nearby water supply wells (Beckett, Stanley, and Walsh 2005). Industrial site, Conn.—Evaluated decreasing mass discharge across three transects situated between the DNAPL source zone and a river. Used to characterize natural attenuation processes for TCE and by-products along groundwater flow path and support mass balance assessment (Chapman et al. 2007).
3. Remediation selection and design	(a) Establish/develop appropriate remedial action objectives (RAOs)	Use baseline mass flux estimates to establish appropriate reduction targets as potential RAOs. Use mass flux/mass discharge reductions to evaluate RAOs and revise if necessary.	Use baseline mass discharge estimates to establish appropriate reduction targets as potential RAOs. Use mass flux/mass discharge reductions to evaluate RAOs and revise if necessary.	
	(b) Select and design remediation systems	Determine the permeability of mass flux hot spots and geologic units to assist with technology selection (e.g., some technologies do not effectively treat mass in low-permeability units); use knowledge of contaminant mass flux relative to lithology to design well placement, injection parameters, etc. (e.g., targeted remediation of hot-spot areas, permeable reactive barrier design based on maximum mass flux zones).	Use the target reduction in mass discharge (e.g., 90%, 99%, 99.9%, etc.) to screen for applicable technologies.	Fuel terminal, San Jose, Calif.—Conducted a demonstration project using mass flux measurements from a transect of oxygen delivery wells and transects of upgradient and downgradient monitoring wells to compare dissolved oxygen delivery and demand. Results used to evaluate the scale and location of a treatment system (Buscheck, Nijhawan, and O’Reilly 2003).

**Table 3-1 (continued)**

Use/application	Purpose	How applied		Case study example
		Mass flux (g/year/m <sup>2</sup> )	Mass flux (g/year/m <sup>2</sup> )	
4. Remediation performance monitoring and optimization	(a) Assess remediation performance	Measure changes in source zone mass flux to determine whether treatment system is performing as planned.	Measure changes in source zone mass discharge to determine whether treatment system is performing as planned.	DNAPL sources, Hill Air Force Base, Utah and Fort Lewis Military Reservation, Wash.—Used a 10-well transect at each site, with passive flux meters and a variation of the IPT, to establish baseline source zone flux distribution and mass discharge. Used changes in source zone mass flux and discharge to assess remediation performance (Brooks et al. 2008). Well 12A Superfund site, Tacoma, Wash.—Mass discharge was used to assess source zone remediation performance and establish compliance targets. The goal was to reduce source zone mass discharge by 90% as both the source and plume were treated (USEPA 2009).
	(b) Evaluate remediation efficiency	Compare baseline to current mass flux distribution to evaluate whether targeted hot-spot areas are being addressed, the rate of mass flux decline (if sufficient data available), the benefit of additional remediation, and the distribution of injected reagent.	Compare baseline to current mass discharge to evaluate the effectiveness of treatment to date and the rate of decline in mass discharge; use to extrapolate remediation time frame if sufficient data available (need longer-term performance data to reduce uncertainty).	Former gas station site, Ontario—Used three transects to evaluate benzene, toluene, ethylbenzene, and xylenes (BTEX) mass flux reduction downgradient of oxygen-releasing compound treatment zone. Mass discharge used to evaluate degree to which natural attenuation was occurring (Chapman et al. 1997).
	(c) Optimize remediation system operations and monitoring	If performance monitoring indicates that remedy is not practicable, can use current mass flux distribution to evaluate alternative technologies or remedial configurations. Use mass flux distribution across transect to identify data gaps in monitoring network.	If performance monitoring indicates that remedy is not effective, use current mass discharge to evaluate alternative technologies.	Well 12A Superfund site, Tacoma, Wash.—Mass discharge was used to assess source zone remediation performance and establish compliance targets. Set 90% mass discharge reduction goal as trigger for transition to alternative remedy (MNA) (USEPA 2009). Service station, Strathroy, Ontario—Mass flux and discharge data used to optimize delivery of dissolved oxygen to permeable reactive barrier (Chapman et al. 1997).

**Table 3-1 (continued)**

Use/application	Purpose	How applied		Case study example
		Mass flux (g/year/m <sup>2</sup> )	Mass flux (g/year/m <sup>2</sup> )	
5. Compliance monitoring	Monitor compliance with regulatory objectives	Measure mass flux at appropriate locations and compare to acceptable compliance targets for mass flux reduction.	Measure mass discharge at appropriate locations and compare to acceptable compliance targets for mass discharge reduction.	Well 12A Superfund site, Tacoma, Wash.—Mass discharge was used to assess source zone remediation performance and establish compliance targets. The goal was to reduce source zone mass discharge by 90% while both the source and plume were being treated (USEPA 2009).
6. Site prioritization	Prioritize sites based on mass discharge from the source (i.e., source strength) or to a potential receptor	--	Measure mass discharge across a transect perpendicular to flow (a) at the downgradient edge of the source zone and/or (b) just upgradient of a potential receptor. Evaluate source strength and potential impacts to receptors (see Section 3.2). Compare among sites to prioritize resource allocation and cleanup time frames.	Multiple California sites—Compared mass flux and/or discharge estimates to maximum concentrations from monitoring wells. Showed that sites with the highest concentrations are not necessarily the sites with the highest mass discharge (Buscheck, Nijhawan, and O'Reilly 2003). Chlorinated solvent site, Austria—Used IPT method to evaluate mass discharge at three transects to quantify relative strengths of different source zones contributing to a plume, to determine which source zones to target for further characterization and remediation (Bauer et al. 2004).

### 3.1.1 Mass Balance Assessments Using Mass Discharge

ITRC's *Enhanced Attenuation: Chlorinated Organics* (ITRC 2008a) defines a mass balance assessment as including a quantitative estimation of the source strength (i.e., source zone mass discharge) into a dissolved phase plume, which is then compared to the plume attenuation rate. If the mass discharge from the source is greater than the plume attenuation rate, then the dissolved plume will expand in length. If the mass discharge and plume attenuation rates are similar in magnitude, then the plume will be stable. And if the mass discharge is less than the plume attenuation rate, then the mass delivered by the plume will decrease.

In general, the plume attenuation rate can be evaluated using models and/or historical concentration data and standard lines of evidence, such as contaminant concentration vs. time and/or distance plots along the plume centerline, molar fraction plots, and the distribution of geochemical indicator parameters (e.g., electron acceptors and donors, dissolved oxygen, nitrate, Fe(II), sulfate, methane, redox potential, pH, etc.). There are several excellent references on this topic including Chapelle et al. (2003) and Wiedemeier et al. (1998, 1999, 2004). However, as shown previously in Figure 2-7, the plume attenuation rate can be misinterpreted if “losses” due to sorption or diffusion into low-permeability zones (i.e., changes in mass storage) and dispersion are not considered in the case of expanding or shrinking plumes.

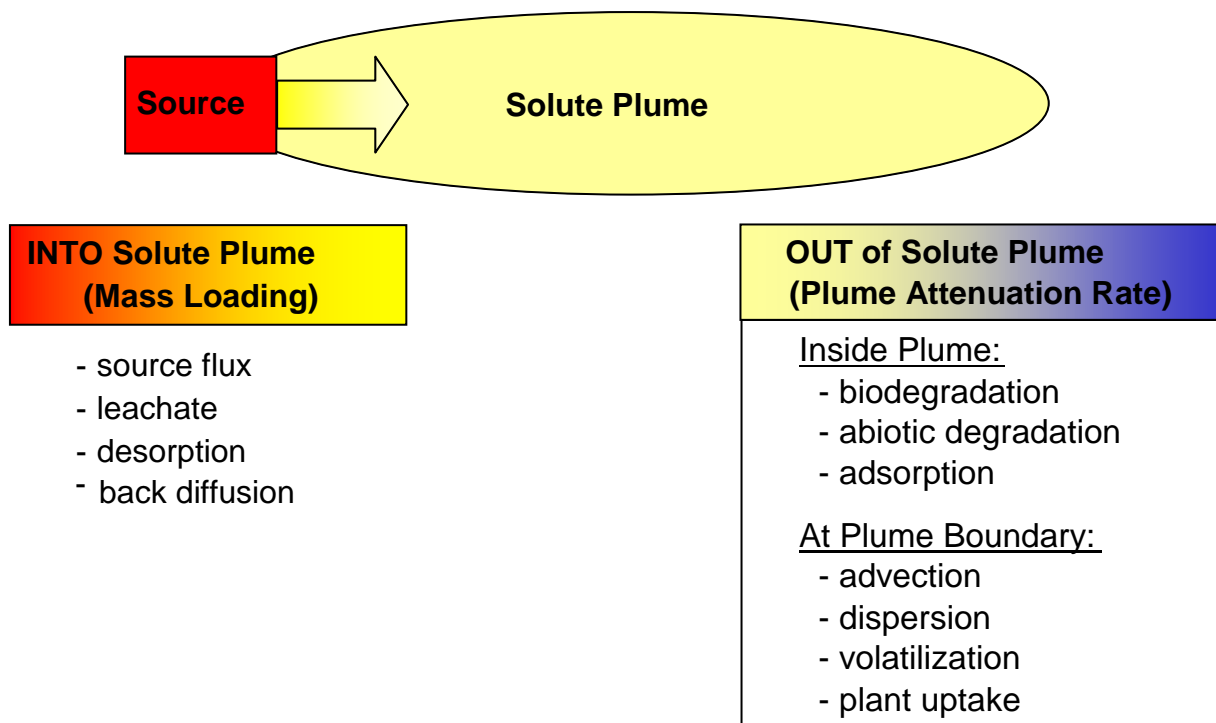
Figure 3-1 lists the components of a mass balance assessment. Benefits of performing a mass balance assessment can include the following:

- refining the CSM with respect to the quantitative significance of processes affecting source strength and plume attenuation
- identifying data gaps that require further characterization
- providing an additional line of evidence that validates a plume stability evaluation
- facilitating the prediction of changes to plume extent caused by the reduction in mass discharge during source zone treatment

Mass discharge estimates at a site can be used to support a mass balance assessment in the following manner:

- For stable plumes, mass discharge can be used to facilitate the estimation or validation of the plume attenuation rate.
- For expanding plumes, the mass discharge from the source zone can be used to predict the future stable extent of the plume.
- Measuring the reduction in mass discharge during or after source zone treatment can be used to predict the corresponding change in aqueous plume extent downgradient of the source zone.

Components of a mass balance assessment are described by Borden et al. (1997), Chapelle et al. (2003, 2004), Imbrigiotta et al. (1997), Looney et al. (2006), and Wiedemeier et al. (1998, 1999, 2004).



**Figure 3-1. Example of mass balance for a dissolved plume.** (Modified from ITRC 2008a.)

Mass discharge estimates between two transects across a plume along a common flow path can estimate the mass attenuation rate in the portion of the plume between the transects, which can then be used with similar plume segment rates to assess the plume attenuation rate. Estimating attenuation rates between transects must consider the contaminant travel time between the transects. For example, if mass discharge is changing at the upgradient transect in response to source zone treatment, then the attenuation rate calculation must account for the time it takes for that effect to reach the downgradient transect. Otherwise, the mass attenuation rate will be too low or, conceivably, negative.

An emerging “mass balance” use for mass discharge estimates is to determine whether multiple sources may be contributing to a single plume or comingled plumes. Because mass discharge is a good indicator of source strength, it may help determine whether a given source has the ability to generate/sustain a given plume or whether another source must be present. Comparing the mass discharge from a known source to the estimated plume attenuation rate can indicate whether an additional source is present, particularly if the plume attenuation rate is comparable to the known source mass discharge and the plume is still increasing. Using mass discharge estimates in this way can also lead to improved allocation of remedial resources and of responsibilities and liability among multiple responsible parties.

### 3.2 Potential Impact and Exposure Evaluation

There is a growing recognition that mass flux data can supplement concentration data to provide a more complete measure of the potential impact to a receptor posed by a contaminant plume. Point concentrations alone do not provide sufficient information to calculate downgradient impacts. For example, two plumes with the same contaminant concentrations may affect

receptors differently because one plume may be moving faster and therefore discharging greater contaminant mass over time. Additionally, one plume may attenuate rapidly, while another is sustained for many years, yielding dramatically different potential exposure time frames.

Mass discharge can be particularly important if the contaminant discharge from the plume mixes with clean water at or before an exposure point such as a supply well or surface water body. In such cases, mass discharge to the mixing zone is more important to estimate accurately than the point concentration. However, site characterizations generally focus more on concentration data than on the hydraulic conductivity and/or groundwater fluxes, so risk assessments often have to rely on uncertain groundwater flow estimates and cannot account for spatial differences in flow rates.

Einarson and Mackay (2001) proposed a framework for using mass discharge to prioritize site cleanups by considering the interaction of a contaminant plume with a downgradient water supply well. The framework uses mass discharge to estimate the resulting exposure concentration in water produced from the well. To make this calculation, the following equation was presented:

$$C_{sw} = M_d \div Q_{sw} \quad (3-1)$$

where

$C_{sw}$  = contaminant concentration in water extracted from the supply well,  $M/L^3$  (e.g., mg/L)

$M_d$  = mass discharge of plume located near edge of water supply well capture zone,  $M/t$  (e.g., g/d)

$Q_{sw}$  = pumping rate of supply well,  $L^3/t$  (e.g., L/d)

Consider the following example. A plume with a mass discharge of 1,000 mg/d TCE (as measured across a transect at the junction of the edges of the plume and the well capture zone) is captured by a domestic well with a pumping rate of 1,000 L/d. The resulting concentration in the domestic water supply would be 1.0 mg/L (1,000 mg/d  $\div$  1,000 L/d). However, if the same plume were captured by a large public water supply well pumping 1,000,000 L/d (about 200 gallons per minute [gpm]), then the resulting concentration in water extracted by the water supply well would only be 0.001 mg/L, which is below the maximum contaminant level (MCL) for TCE. While cleanup goals should not rely on blending in a supply well, this example reflects the importance of mass discharge in assessing potential impacts to a receptor, remedial strategies, and prioritizing site cleanups.

This same approach can be applied to groundwater plumes that discharge or threaten to discharge to a surface water body. For example, Burton et al. (2002) discuss an approach at a Maryland site where managers calculated the contaminant mass discharge to a river using point concentrations and groundwater discharge estimates and then proposed the use of a mixing zone to estimate potential exceedances of surface water quality criteria. The Mass Flux Toolkit (Farhat, Newell, and Nickols 2006) has calculation modules for both water supply well and surface water discharge scenarios.

### **3.3 Remedy Selection and Design**

Mass flux and mass discharge data can be particularly valuable during the remediation planning process, including the development of remedial action objectives (RAOs), technology selection, and remedial design. Specific applications of mass flux or mass discharge data for each of these stages of remediation planning are described in more detail below. Additional applications involving mass flux or discharge for performance monitoring and optimization are discussed in Section 3.4.

#### 3.3.1 Remedial Action Objectives

Complete source remediation within a reasonable time frame can be a difficult goal to accomplish due to technical and economical limitations. Regardless, it may be desirable to establish interim goals or RAOs based on partial source remediation and mass discharge reduction. An example of this application might be to reduce source zone mass discharge to a level that can accommodate implementation of a long-term MNA remedy for the dissolved-phase plume or to facilitate a risk-based RAO. In such cases, the mass flux or mass discharge targets can be used as RAOs, in addition to or in place of concentration-based RAOs, to provide a more meaningful trigger for transitioning to the MNA or risk-based remedy.

#### 3.3.2 Remedy Selection

Remedial technologies vary in their ability to treat contaminants within low-permeability zones. For example, remedies that rely on groundwater capture or emplacement of chemical/biological agents typically address contaminants mainly in the transmissive zones, while remedies such as excavation, in situ mixing, physical containment, and in situ heating can reasonably address both the low-permeability and transmissive zones. Therefore, understanding the contaminant mass distribution, whether contaminant mass is predominantly in low-permeability or transmissive zones, will lead to better remedy selection and design. Measuring mass flux can provide this information.

Similarly, measuring mass flux across transects within the plume can improve estimates of plume attenuation rates and mass loss over time. Understanding the distribution as well as the seasonal and long-term stability of attenuation rates within the plume can lead to better remedy selection and remedy targeting in areas that need additional treatment and enhanced attenuation. At some point, it may be useful to reevaluate technology selection and pursue an alternate remedy. Sequenced technologies may even be part of the formal remedial strategy. Mass flux can be the metric triggering reevaluation.

#### 3.3.3 Remedial Design

Prior ITRC documents (ITRC 2004, 2008a) have concluded that mass flux estimates can improve remediation decisions historically based on only concentration estimates because mass flux estimates can help locate areas contributing the most and the least contaminant mass to a plume.

Remediation technologies vary in their ability to treat mass in high- and low- $K$  zones (Sale et al. 2008). Understanding the distribution of mass flux across transects and how it relates to the lithology and/or the distribution of groundwater flux across the transects can provide valuable information for placement of pumping wells, injection points, and monitoring wells.

An example of how mass flux can influence remedial design is the use of a permeable reactive barrier, such as a zero-valent iron wall or biobarrier. Such barriers must be designed to provide sufficient reactive capacity and retention time to treat the incoming contaminant mass. Thus, both groundwater velocity and contaminant mass are important design parameters. Mass flux estimates provide the necessary data inputs and indicate contaminant distribution across the treatment plane. In conjunction with other data, mass flux can indicate where the barrier thickness or reactive capacity needs to be increased to adequately treat the incoming contaminant mass. Designing the barrier based on average groundwater velocity alone could underestimate the treatment capacity and/or retention time needed and predispose the permeable reactive barrier to premature exhaustion and failure.

### **3.4 Performance Monitoring and Optimization**

Mass flux/discharge estimates can be used to evaluate changes within the source zone or plume, remedy performance, and system optimization. For example, if a cleanup is not reaching milestones when anticipated, mass flux/discharge can be used to more precisely quantify the changes that are occurring and to identify physical and operational problems.

The combination of mass flux/discharge estimates and point concentration estimates facilitates the determination of contamination trends and analysis of remedial system operations better than either alone. Mass flux/discharge estimates can provide valuable information to determine whether or how soon remedial goals will be met, to decide when and where to transition between technologies, and to optimize remediation technology performance (USEPA 2003). Following are some ways that mass flux/discharge information can benefit remediation performance monitoring and optimization:

- Mass flux and mass discharge measurements can better assess the effects of source zone treatment, particularly if remediation is likely to disproportionately affect higher- and lower- $K$  zones because the mass flux distribution identifies source zone hot spots where the greatest mass is being discharged, which allows for better treatment targeting. Mass flux reductions in the targeted hot-spot zones better demonstrate the effects of treatment than point concentration data alone in systems where flows change due to natural or artificial conditions because concentration and flow are integrated into a single metric.
- Post-remediation mass flux mapping can be used to evaluate remediation effectiveness and estimate the potential benefits of additional remediation efforts and/or the efficacy of MNA. For example, in cases where concentrations are depleted in high- $K$  zones but not in low- $K$  zones, a change in remediation approach may be required if mass reductions in low- $K$  zones are needed to achieve site closure. Alternatively, mass flux data from more transmissive zones may reveal that treatment of these areas alone may achieve the desired effects and goals as quickly as treatment of the entire area.



- Contaminant mass discharge estimates quantify the benefits of concentration reductions, whether through engineered remediation systems or MNA. For example, calculation of mass flux in each well along a transect, and for the well group as a whole, is the first step in treatment impact analysis (see boxes at right and on next page). However, additional data management will increase understanding further. Qualifying well data that show little or no contaminant flux reduction (for example, due to poor reagent distribution or other operational problems resulting in ineffective treatment) will provide a clearer picture of past treatment impact and show the potential value of specific efforts to improve treatment in those areas.
- Mass flux analyses can reveal treatment impacts on subsurface hydrodynamics. For example, portions of the subsurface may become clogged due to precipitation of inorganic by-products or biomass growth. Mass flux estimates over time can indicate how the mass flux distribution has changed in response to such impacts.

#### Hill Air Force Base, Utah

The effectiveness of a surfactant flood to treat a DNAPL source at the Hill Air Force Base Operable Unit 2 was evaluated by monitoring changes in contaminant mass discharge downgradient of the source. While a substantial (>90%) reduction in TCE mass discharge was noted, dichloroethene (DCE) mass discharge increased as a result of source treatment. These results suggest the surfactant used for in situ flushing enhanced reductive dechlorination of TCE. Even with this increase, the total molar discharge of TCE and DCE declined almost 90% as a result of partial DNAPL mass removal from the source zone (Brooks et al. 2008).

Figure 2-7 illustrates an important point to consider when using mass flux estimates in assessing remediation performance and changes over time. The mass flux at any location along a plume represents the combined effects of contaminant transport, destructive attenuation (if any), and storage processes (sorption and diffusion into low-*K* zones). Losses of contaminant mass to storage create a mass flux deficit relative to the flux that is later observed at plume maturity. It is therefore important to recognize that, in a transient plume, storage losses can be inadvertently interpreted as degradation.

### 3.5 Compliance Monitoring

The change in mass flux or mass discharge at the source zone quantifies source remediation performance, while in the dissolved-phase plume it documents the response of the plume to source or plume remediation. The key metric in evaluating remediation performance is the change in mass flux or mass discharge from baseline estimates.

Similarly, mass flux and mass discharge can be used for regulatory compliance monitoring to augment concentration-based data. For example, concentration data may indicate an exceedence of the regulatory standard at the compliance point. However, mass flux data may indicate there is little flow or discharge occurring. Conversely, where concentration data are low, mass flux data could indicate much higher than expected mass discharge is occurring due to higher groundwater flow despite the lower contaminant concentration. In both cases, compliance metrics could be based on the maintenance of or reduction to a low or zero mass flux to prevent impacts to downgradient receptors.

An example of the proposed use of mass flux and mass discharge as compliance monitoring parameters is contained in the preferred remedy in the proposed plan for the Well 12A Superfund site located in Tacoma, Washington (USAPA 2009, see box at right). Mass flux data for the site would be used for two purposes:

- Mass flux data obtained at monitoring wells closer to the active groundwater treatment areas may be used to optimize the treatment system and to focus treatment in areas that are exhibiting higher mass flux.
- The mass discharge across a plane of transect monitoring wells would be monitored over time. This plane of measurement wells will be situated along the downgradient boundary of the active treatment zone. Mass discharge estimates across this plane of monitoring wells will determine when the remedial goal of 90% reduction has been achieved. Once this goal has been achieved, and concentrations of contaminants of concern (COCs) are below applicable MCLs at compliance monitoring wells, the groundwater extraction and treatment system will be shut down.

#### Using Mass Flux for Compliance Monitoring

Upon detecting volatile organic compounds (VOCs), mainly TCE, in Well 12A in 1981, USEPA conducted an investigation, and the Time Oil building was identified as the primary source area. The Time Oil building is located approximately 2000 feet northeast of well 12A and has a long history of paint and lacquer manufacturing and waste-oil recycling that dates back to approximately 1923. As USEPA became involved with the site, several remedial actions were implemented, including a groundwater extraction system which continues to operate but is ineffective in reducing contaminant mass or maintaining hydraulic control of dissolved-phase groundwater contamination.

As remediation efforts continued, USEPA and the Washington State Department of Ecology have developed a proposed plan combining thermal remediation with the existing groundwater extraction system to reduce source zone contamination. An RAO listed in the proposed plan requires the reduction of mass flux by 90% at the source zone flux plane, identified as the 300 ppb TCE isopleth, and meeting the 5 ppb TCE MCL criteria in fringe-area compliance wells. Passive treatment is expected to occur in the zone between the 300 and 5 ppb TCE isopleths (USEPA 2001b).

### 3.6 Site Prioritization

Because mass discharge provides a quantitative estimate of source strength and an estimate of the potential impacts to downgradient receptors, it can help regulators and responsible parties prioritize among different sites. For example, two sites that have relatively similar concentrations could have significantly different potentials for affecting resources or impacting receptors. But this distinction may not be evident based on concentration data alone. By improving assessment of source strength, plume attenuation rate, and potential impacts to a receptor, mass discharge at the source zone or within the plume can be used as an additional tool to help regulatory agencies or responsible parties prioritize cleanup resources and time frames within a site or among multiple sites. In this way, mass discharge information provides additional context for evaluating point concentration data and the potential threat to receptors and beneficial uses at the site.

Using mass discharge to prioritize site cleanup and manage environmental liabilities is increasingly being performed by industry—sometimes outside the regulatory framework. Examples of where mass discharge estimates have been used by Chevron to prioritize site cleanups are described by Buscheck, Nijhawan, and O'Reilly (2003). Also, there are large

industrial companies that are voluntarily measuring mass discharge downgradient from their contaminated properties to better define their environmental liabilities (M. D. Einarson, personal communication, 2009). Finally, at sites where mass discharge analyses show potentially significant risks to downgradient receptors, remediation can be performed to mitigate the risk of future impacts to those receptors.

### 3.7 Conceptual Examples for Using Mass Flux and Mass Discharge

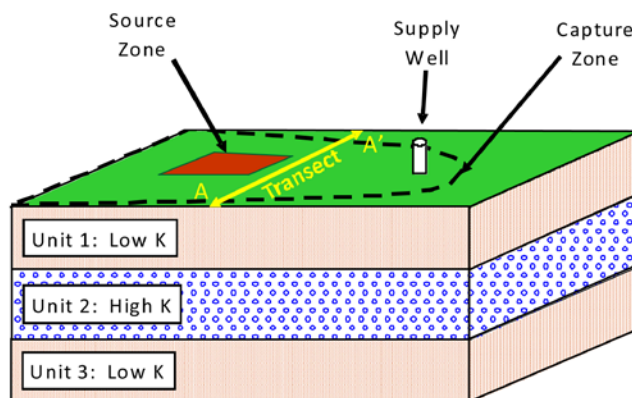
This section presents a conceptual site example of how mass flux/discharge estimates discussed in the previous sections can be applied. The example is based on a hypothetical site with simplified geologic conditions.

#### 3.7.1 Site Setting

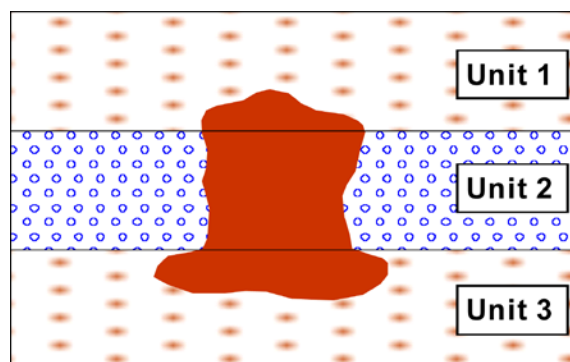
In this example, a DNAPL source zone is situated at the site, and there is one COC that exceeds cleanup criteria in groundwater. The source area is underlain by three hydrostratigraphic units, which have been impacted by DNAPL migration below the release area (see Figure 3-2):

- Unit 1: fine-grained, silty sand with low permeability
- Unit 2: coarse-grained sand with high permeability
- Unit 3: fine-grained, silty sand with low permeability

A water supply well is situated downgradient of the source zone and is screened through all three hydrostratigraphic units. The majority of water pumped by the supply well is transmitted through Unit 2 because this unit is highly transmissive relative to Units 1 and 3. Figure 3-3 illustrates the cross section (transect A-A') of the capture zone for the supply well, which extends beyond the boundary of the source zone.



**Figure 3-2. Site setting.**  
(Graphic courtesy Porewater Solutions, Inc.)



**Figure 3-3. Source zone along transect A-A'.** (Graphic courtesy Porewater Solutions, Inc.)

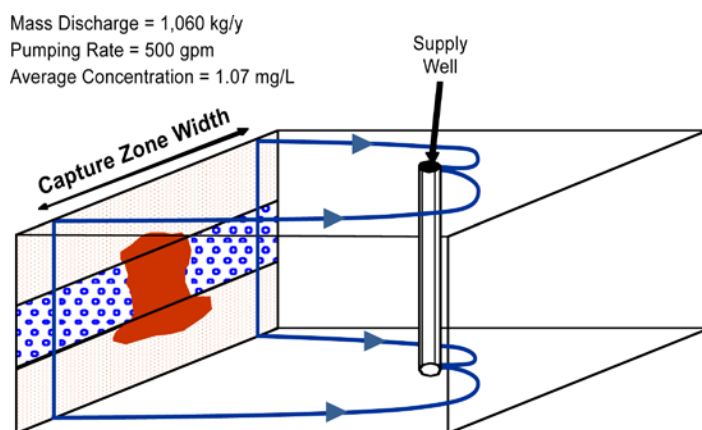
#### 3.7.2 Use of Mass Flux for Site Characterization and CSM Development

As part of the remedial investigation (RI) for the site, the mass flux and mass discharge were estimated along the transect A-A' corresponding to the cross-section location shown in Figure 3-2 downgradient of the DNAPL source zone. Figure 3-3 presents a transect through the three hydrostratigraphic units, including the extent of the source zone in each of the three units. The mass discharge from the source zone in Units 1, 2, and 3 was estimated to be 10, 1000, and 50 kg/year, respectively, for a total mass discharge of 1060 kg/year. This estimate of mass

discharge represents a baseline measurement prior to remedial activities at the site. For the conceptual model, the mass discharge data provide an important characterization of the source architecture relative to sediment geology. In this case, the greatest mass discharge occurs in the most transmissive unit, which is an important consideration for remedial planning as discussed below. The aquifer attenuation capacity was calculated to be approximately 500 kg/year in the dissolved-phase plume downgradient of the source zone. Because the mass discharge from the source zone is larger than the aquifer attenuation capacity, the dissolved-phase plume will expand over time. Additional monitoring should be conducted to confirm this analysis. Optional modeling can be conducted using the source strength (i.e., mass discharge from the source) as an input, as well as user-defined attenuation properties, to evaluate the future steady-state length of the plume.

### 3.7.3 Potential Impact and Exposure Evaluation

With the supply well pumping 500 gpm, the supply well capture zone was determined to extend beyond the DNAPL source zone (Figure 3-4) so that the supply well captures the full source zone mass discharge in addition to clean water beyond it. The average COC concentration in water extracted from the supply well is determined using the eq. 3-1 presented in Section 3.2. Based on the pumping rate and total mass discharge over all three hydrostratigraphic units, the average concentration at the supply well was estimated to be approximately 1 mg/L. Assuming that the regulatory concentration limit for the COC at the supply well is 0.2 mg/L, the mass discharge from the source zone must be reduced by at least 860 kg/year to ensure that the groundwater concentration is below the 0.2 mg/L regulatory limit. For this example, the effects of aquifer attenuation are ignored. If considered, they would justify a higher mass discharge target from the source zone. This example demonstrates the benefit of relying on mass discharge data, which more closely correlate to the remedial objectives for protection of a supply well or surface water body, rather than relying on one or a series of point-specific concentration estimates.



**Figure 3-4. Mass discharge to a supply well.**

(Graphic courtesy Porewater Solutions, Inc.)

The potential impacts of a plume of groundwater contamination on usage of groundwater or on receiving water bodies are proportional to the strength of the mass discharge of the plume. Clearly a large mass discharge would present more of a potential problem to large-scale consumption of water than a small mass discharge, and the same would be true of receiving water bodies, as illustrated by Leu and Hadley (1987). This current ITRC document has focused on approaches and techniques for measuring mass discharge. With more quantitative correlations between mass discharge and actual water usage and base flow or assimilative capacity of surface waters, perhaps a more useful and quantitative classification could be developed to be able to categorize plumes by mass discharge. This type of plume magnitude classification system would

provide a way of matching remediation and management strategies for plumes in proportion to their potential impacts. This idea is identified as a research need in Section 6.

#### 3.7.4 Remediation Selection and Design

In this example, based on the target reduction from 1060 to 200 kg/year for mass discharge and assuming that mass removal from the low-permeability units (1 and 3) will be negligible, a reduction in mass discharge of at least 81% from Unit 2 is required (Figure 3-3). This level of mass discharge reduction may be difficult to achieve, and thus it may be necessary to implement a long-term plume management strategy to ensure additional attenuation of the plume is achieved downgradient of the source zone or that the plume is hydraulically contained until the mass discharge reduction is achieved.

A technology that includes the injection of soluble substrates (e.g., enhanced bioremediation or in situ chemical oxidation) into Unit 2 was considered for this example site. Although such a technology may not achieve efficient distribution of the soluble substrate into the less-permeable Units 1 and 3, these units have such a small component of mass discharge relative to Unit 2 that remediation may still be effective. Therefore, while desorption from Units 1 and 3 will increase in response to concentration gradient increases caused by remediation of Unit 2, the release of contaminants adsorbed to the soil may not be rapid or large enough to require remediation of the low- $K$  zones.

#### 3.7.5 Performance Monitoring

In this example, prior to full-scale implementation, a pilot test was conducted to evaluate the feasibility of treatment using a soluble substrate injection technology. The pilot test was conducted over a relatively long period of time, and the mass discharge was estimated across the transect shown in Figure 3-3 at several time intervals during and at the end of the pilot test. Comparison of the pilot test data to the baseline mass discharge estimate supports estimation of the time required to achieve the RAOs provided that the pilot test duration was sufficiently long for its maximum impact to be observed.

The mass flux distribution was also evaluated at the end of the pilot test and compared to the baseline mass flux distribution. This comparison provided a comprehensive assessment of the portion of the source zone that was most effectively remediated and the portion where remediation was limited during the pilot test. These data were used to confirm that a specific remedial technology was or was not feasible and, if necessary, to adjust the remedial design prior to full-scale implementation to improve the remedial efficiency and impact.

After six months of operating the full-scale system, a similar mass flux distribution assessment provided valuable information on the longer-term performance of the remedy. This assessment was used to confirm the remediation time frame estimate and to adjust the remedial implementation.

### **3.8 Regulatory Considerations**

#### **3.8.1 Remedies That Temporarily Increase Mass Flux**

As noted earlier, some remedies, such as source zone bioremediation, may increase mass flux across the DNAPL/groundwater interface (ITRC 2008b). Thus, bioremediation of DNAPL source zones may cause a temporary increase in mass flux away from the source area that could, in turn, cause a temporary expansion of the plume, particularly with respect to contaminant breakdown products (notably vinyl chloride when TCE is present). Recent research has suggested that this temporary increase in breakdown product distribution could be beneficial as the volume of the plume increases, which increases the rate of biodegradation of the breakdown products (ITRC 2008b). While these are desirable attributes and practices for bioremediation, they contradict conventional thinking and regulatory agency preferences for approaches that limit contaminant spreading. Understanding and effectively monitoring the effects of enhanced dissolution or degradation remedies will enable project managers to determine whether the system is working as planned and to be confident that the effects of treatment can be controlled with the proper engineering.

#### **3.8.2 Mass Flux to Complement/Support Concentration-Based Decision Making**

Regulations and regulatory policies typically focus on groundwater concentrations in the decision-making process without consideration of mass flux. This focus is understandable since risk assessments generally use exposure point concentrations as input to assess the risk to a given receptor. However, as discussed in Section 3.2, mass flux/discharge information provides an additional line of evidence to assess potential impacts to receptors. Thus, a more practical procedure is to use mass flux/discharge information in conjunction with point concentration data. For example, although concentration data may exceed risk-based standards for a nearby receptor, there may be little flow or contaminant movement, except within small zones. Mass flux/discharge measurements can be used to refine the risk assessment by determining the total contaminant mass likely to reach the receptor. If measurements indicate minimal mass flux or mass discharge, the potential risk may be acceptable. Using mass flux data with point concentration data from wells allows an more informed decision based on a more complete picture of contaminant magnitude, distribution, mobility, and, ultimately, actual threat to receptors.

Mass flux can also be helpful in establishing remediation performance requirements. For example, complete source removal may not be feasible within a reasonable time frame at all DNAPL source zones, so it may be useful to establish interim RAOs for DNAPL source zones that recognize the limitations to complete source removal (Sale et al. 2008). In such cases, it can be helpful to establish interim remedial goals and performance metrics based on partial source treatment demonstrated by reductions of mass flux and mass discharge from the source area. For example, source goals could include mass flux/discharge reductions to achieve plume stability and protect downgradient receptors or to reduce the mass flux/discharge to the point that the remaining concentration and risks can be controlled more cost-effectively by some other active treatment technology. Goals based on both contaminant concentration and mass flux/discharge information ideally are more achievable and feasible.

### 3.8.3 Summary

The review of case studies showed that mass flux/discharge estimates have been useful for several site management objectives and that evaluating mass flux/discharge can improve CSMs and lead to more efficient remediation. Specific findings from the case study review include the following:

- **Mass information has improved decision making.** For example, it has been used as an interim remediation goal and trigger for transition between technologies.
- **Mass information has reduced remediation costs.** For example, mass flux estimates have been used to identify high-priority target treatment layers in stratified aquifers, leading to more cost-effective cleanup.
- **Mass information has been used to prioritize sites.** For example, responsible parties have used mass discharge estimates to identify sites that must be remediated first and to schedule remediation in regional flow systems with multiple sources.
- **Mass information has been used to predict and evaluate remediation performance.** Mass discharge, high-resolution mapping, and available analytical tools have provided the basis to estimate natural attenuation rates, plume responses to source treatment, and remediation time frames.
- **Transect data have proven to be particularly valuable.** Well transects have provided more credible estimates of natural attenuation rates than the more typical practice of relying on a line of wells along a flow path because transect data are less susceptible to temporal and spatial variations in flow direction and strength.

## 4. MEASURING MASS FLUX AND MASS DISCHARGE

There are five basic methods used to calculate mass flux and/or mass discharge:

- transect methods: use individual monitoring points to integrate concentration and flow data (flow data are most commonly derived from aquifer tests but can be obtained from tracer tests)
- well capture/pump test methods: extract groundwater and measure the flow and mass discharge from the wells
- passive flux meters: estimate mass flux directly in wells
- transects based on isocontours
- solute transport models

Mass flux and/or mass discharge estimates are used to develop better CSMs (see Section 3.1), evaluate contaminant impact on downgradient receptors such as water supply wells or surface water (see Section 3.2), select and design remedies (see Section 3.3), determine the effectiveness of remediation projects (see Section 3.4), monitor compliance (see Section 3.5), and prioritize

sites (see Section 3.6). Understanding the methods available for measuring and estimating mass flux and their relative strengths and limitations is important to making the best use of the information.

The following sections provide descriptions of these methods, a general comparison, and a discussion of the accuracy requirements for mass flux or mass discharge calculations. The technical backgrounds, strengths, and limitations of methods to calculate estimates of mass flux or mass discharge from the measured data and model simulations, and sources of uncertainty in the estimates are also presented.

#### **4.1 Transect Methods**

TM, the oldest and most common method, uses estimates of groundwater contaminant concentration and groundwater velocity at a series of monitoring points across a plume (Figure 4-1). TM has several variations with regard to the data collected and the methods used. TM is described by Nichols and Roth (2004) as follows:

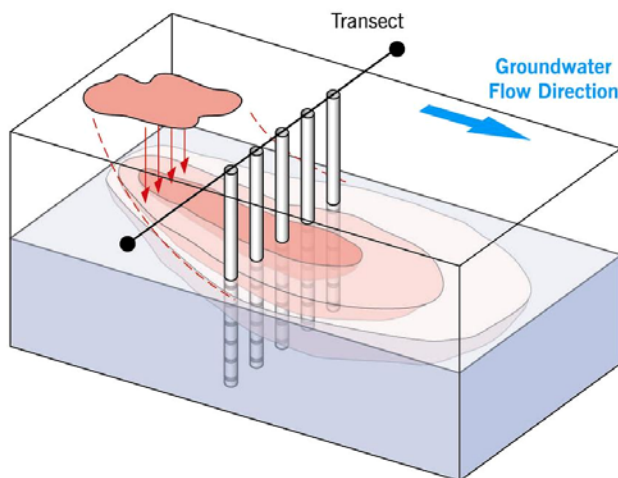
[The transect method] relies on groundwater samples from single- or multi-level monitoring well data interpolated along a transect across the plume, perpendicular to groundwater flow. A vertical cross-section across the transect is divided into any number of sub-areas, each representing a discrete area of uniform concentration and groundwater flow discharge. The total mass flux is simply the sum of the fluxes from each of these subareas.

It should be noted the authors use the term “total mass flux” instead of “mass discharge.”

The transect is a control plane across the plume, perpendicular to the groundwater flow direction. Monitoring points (either temporary or permanent) within the control plane are sampled for contaminant concentration. Specific discharge of groundwater (also called Darcy velocity) through the control plane is also measured to provide flow data.

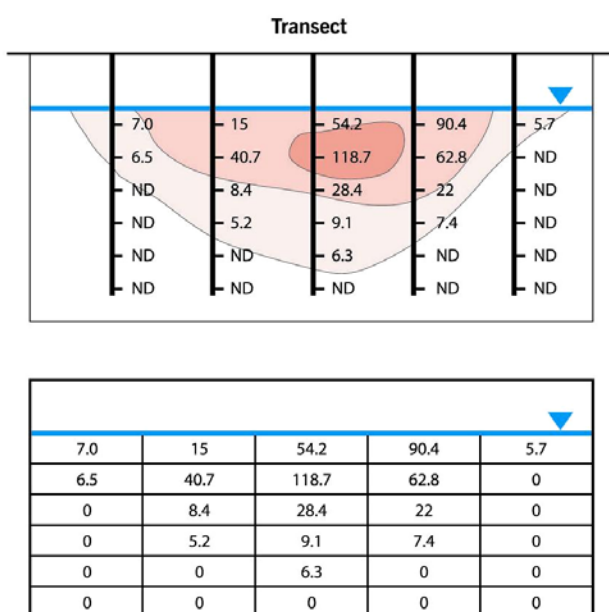
Theoretically the transect should be perpendicular to the actual flow vector so that at sites with vertical flow the transect would be not exactly vertical, but at an angle. At most sites, however, the horizontal flow component is significantly larger than the vertical flow component, and the error introduced by having an exactly vertical transect is likely to be small. Before installing a vertical transect, the vertical flow component should be estimated and compared to the horizontal flow component, and if there is a significant vertical flow, the transect may need to be redesigned or the flow calculation needs to account for only horizontal flow.





Some key insights on the type of monitoring well network were presented by Einarson and Mackay (2001):

- Single-screened wells may be useful if the vertical extent of the plume is limited or if the aquifer media (and groundwater flow) is relatively homogeneous.
- It is preferable to use transects of multilevel monitoring wells.
- If possible, the transect should be perpendicular to groundwater flow lines. If the flow lines are not parallel, the transect would (ideally) be curvilinear.
- To ensure all the mass discharge is captured, sampling points should extend a sufficient distance (both horizontally and vertically) so that the entire plume is bounded by nondetect points.



**Figure 4-1. Multilevel monitor well (three-dimensional) transect mass flux.**  
(Concentrations in units of  $\mu\text{g/L}$ .)

#### 4.1.1 Steps to Apply the Transect Method

The following steps are typically used for estimating mass flux when using TM (Farhat, Newell, and Nichols 2006; Einarson and Mackay 2001):

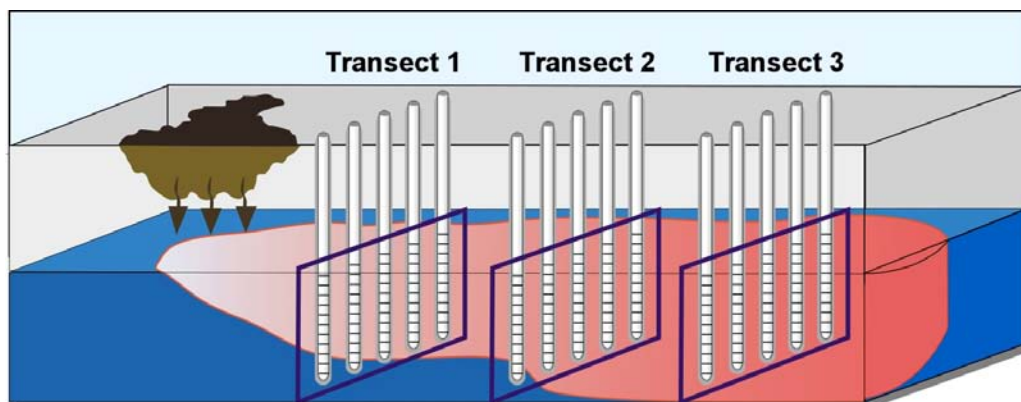
**Step 1. Characterize plume concentrations.** For each selected plume transect, sufficient groundwater sampling points are needed to define the following:

- The full width and thickness of the plume (unless just a subsection of the plume is to be evaluated).
- The distribution of contaminant concentrations within the plume. Either single-level (typically wells that are fully screened across the plume) or multilevel groundwater monitoring points may be used for this purpose. Multilevel monitoring points provide a more

detailed two-dimensional characterization of contaminant concentrations in groundwater. Nonetheless, single-level groundwater monitoring networks, while not providing a detailed picture of the vertical distribution of mass flux, are still used extensively to generate mass discharge estimates. For transects where single-level wells are not fully screened across the plume, users can either note that the calculated mass discharge is less than the actual mass discharge or do Step 4 (below) with a transect that includes extrapolated concentrations that extend to the estimated edge of the plumes. For example of this second option, if there is a transect with single-level wells that do not extend fully to an aquitard a short distance below the screened interval, one can extend the transect all the way to the aquitard if there is some basis for assuming the plume is located in this interval. Software tools such as the Mass Flux Toolkit (Farhat, Newell, Nichols 2006 and described below) can help users with this type of extrapolation.

**Step 2. Characterize groundwater flow.** To characterize the specific discharge or Darcy velocity ( $q$ ) across each plume transect, representative measurements are required for both the hydraulic flow gradient ( $i$ ) and the hydraulic conductivity ( $K$ ) of the flow system (where  $q = K \cdot i$ ). Please note that heterogeneous conditions make collection of representative data more difficult (see Section 2.4.2). The groundwater flow direction and hydraulic gradient for each segment of a transect line can be determined from a potentiometric surface contour map based on static water level measurements at available sampling points. Representative measurements of the hydraulic conductivity of the groundwater-bearing unit should be obtained at one or more locations, using an appropriate method (e.g., pumping tests, slug tests, PFMs, borehole dilution (BHD) tests, tracer tests, or other techniques).

**Step 3. Select plume transects.** Transects should be located to define the distribution and concentrations of contaminants and specific discharge, as defined in Steps 1 and 2 above. Whether using multilevel or single-screen monitoring wells, the transect is a plane extending across the full width and depth of the plume, perpendicular to the direction of groundwater flow (Figure 4-2).

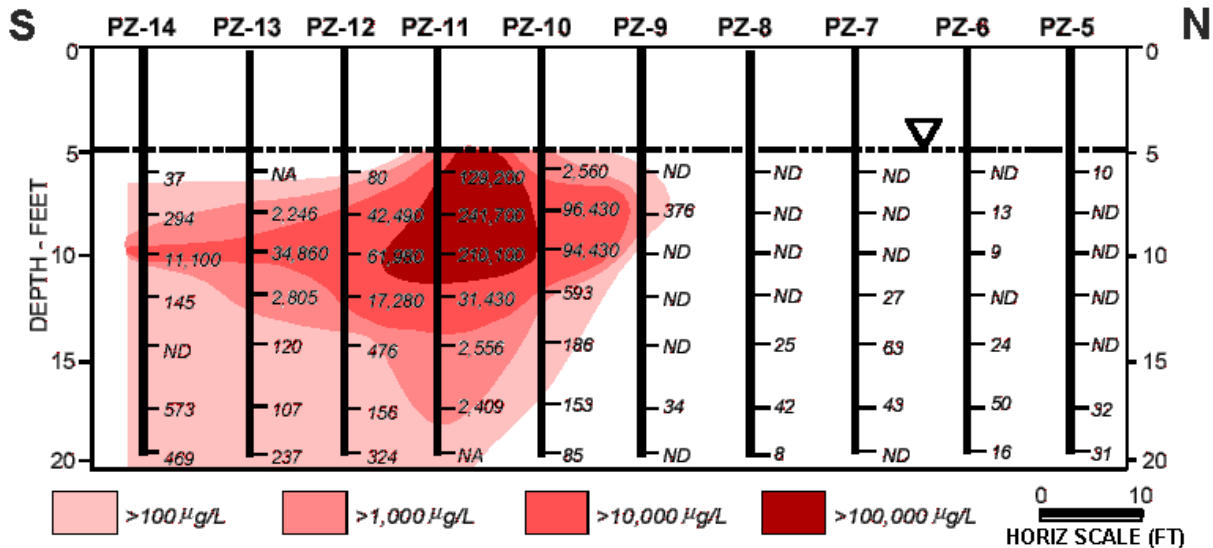


**Figure 4-2. Example of multiple transects intercepting an MtBE plume.**

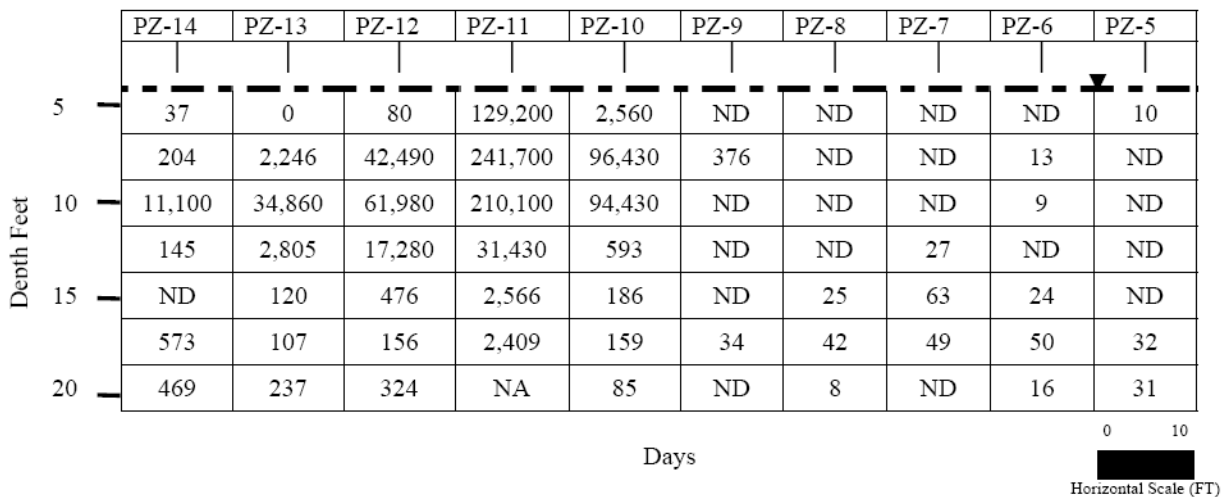
(Adapted from Einarson and Mackay 2001.)

**Step 4. Apply interpolation method.** At some sites, there will be a high-density array of concentration and groundwater flow data to support the mass flux calculations. At sites with less data, interpolation can fill gaps or smooth available concentration and/or flow data. There are several methods that can be used, including kriging, nearest neighbor, and Thiessen polygons.

For the Thiessen polygon method, one of the most commonly used techniques, each transect is divided into subareas (rectangles or polygons). Using the transect method, monitoring points are located directly on the transect to construct transect polygons. The dividing line between subareas is typically halfway between measurement points. For ease of calculation, the polygons should be reduced to rectangles if the monitoring points are uniformly spaced vertically; if the monitoring points are not uniformly spaced, then polygons are required (Figures 4-2 through 4-4 are examples of multiple vertical transects).



**Figure 4-3. MtBE concentration profile for Transect 1, shown in Figure 4-2 intercepting an MtBE plume in groundwater.** (Adapted from Einarson and Mackay 2001.)



**Figure 4-4 Transect 1 from Figures 4-2 and 4-3, which has been divided into polygons (rectangles).** The polygons were created by drawing horizontal lines halfway between sampling points along each piezometer and the vertical lines halfway between each piezometer. The MtBE concentration ( $\mu\text{g/L}$ ) is listed in the center of each polygon. (Einarson and Mackay 2001).

There are no accepted rules of thumb or general guidelines on what constitutes an appropriate sample density. Sections 2.5, 4.1.3, and 4.8 present research results and current knowledge related to the design of a mass flux/discharge system and the potential uncertainty associated with the results.

Kriging typically involves using a computer program to interpolate between data points (e.g., Isaaks and Srivastava 1989, Kitanidis and Shen 1996). The SURFER and Groundwater Modeling Software (GMS) software programs both include kriging algorithms. The nearest-neighbor algorithm is a simple interpolation technique where one simply selects the value of the nearest point, and does not consider the values of other neighboring points relative to that unknown point, yielding a piecewise-constant interpolation.

**Step 5. Calculate mass discharge through the transect.** The total contaminant mass discharge through the transect is calculated by summing the contributions from each of  $n$  polygons (rectangles in this case) as follows (as modified from Farhat, Newell, and Nichols 2006; see Table 4.1):

$$M_d = \sum_{j=1}^n M_{dj} = \sum_{j=1}^n C_j \cdot q_j \cdot A_j \quad (4-1)$$

where

$M_d$  = mass discharge,  $M/t$  (e.g., g/d)

$M_{dj}$  = portion of total transect mass discharge through polygon  $j$ ,  $M/t$  (e.g., g/d)

$C_j$  = concentration of constituent at polygon  $j$  in transect,  $M/L^3$  (e.g., mg/L or g/m<sup>3</sup>)

$q_j$  = specific discharge (also called Darcy velocity) through polygon  $j$ ,  $L/t$  (e.g., m/d)

$A_j$  = flow area through polygon  $j$ ,  $L^2$  (e.g., length<sup>2</sup> or m<sup>2</sup>)

$q_j$  can be calculated using eq. 4-2:

$$q_j = -K_j \cdot i_j \quad (4-2)$$

where

$K_j$  = hydraulic conductivity at polygon  $j$ ,  $L/t$  (e.g., cm/sec)

$i_j$  = hydraulic gradient at polygon  $j$ ,  $L/L$  (e.g., cm/cm)

For example, in Figure 4.4, the portion of the total mass discharge from one of the polygons in the example above (in this case the polygon associated with the top reading for the PZ-11 piezometer), the calculation would be as follows (from Einarson and Mackay 2001):

$C_j$  = 129,200 µg/L (129.2 mg/L) cis-DCE

$A_j$  = 1.67 ft × 10 ft = 16.7 ft<sup>2</sup> (0.52 m × 3.04 m = 1.55 m<sup>2</sup>) (the first 5 ft are divided into three rectangles so that the vertical distance for the top polygon is 1.67 ft)

$q_j = -K_j \cdot i_j = 6.5 \times 10^{-3}$  cm/sec • -0.0029 ft/ft =  $1.88 \times 10^{-5}$  cm/sec =  $1.62 \times 10^{-2}$  m/d

( $K$  was the average of several hydraulic conductivity measurements across this particular transect, and  $i$  was a measured hydraulic gradient through the transect)

(example of Variation 1, see Section 4.1.3) (Einarson and Mackay 2001)

$$M_{dj} = C_j q_j A_j$$

$$M_{dj} = 3.27 \text{ g/d (this is the mass flux from polygon [PZ-11, 5–6.67 ft] (Note: 1000 L per m}^3\text{))}$$

To calculate the mass discharge through the entire transect, this calculation is repeated for each polygon, and the results summed. The final units are in terms of mass per time, most commonly milligrams or grams per day or kilograms per year. In the example shown above, the mass discharge from all polygons is 31.0 g/d.

**Table 4-1. Transect method summary** (Adapted from Newell, Connor, and Rowan 2003.)

Flux term	Groundwater mass discharge—transect method
Equation	$M_d = \sum_{j=1}^n M_{dj} = \sum_{j=1}^n C_j \cdot q_j \cdot A_j \quad (4-1)$
Input data	<p><math>C_j</math> = concentration of constituent at an individual measurement point in transect, <math>\mu\text{g/L}</math></p> <p><math>q_j</math> = specific discharge (also called Darcy velocity) through polygon associated with an individual measurement (cm/sec). <math>q_j</math> can be calculated using the following equation:</p> $q_j = -K_j \cdot i_j$ <p>where</p> <p><math>K_j</math> = hydraulic conductivity at individual point, cm/sec</p> <p><math>i_j</math> = hydraulic gradient through transect, cm/cm</p> <p><math>A_j</math> = area associated with an individual measurement, <math>\text{m}^2</math></p>

The Groundwater Remediation Strategies Tool (Newell, Connor, and Rowan 2003) and the Mass Flux Toolkit (Farhat, Newell, and Nichols 2006) are useful for completing mass discharge estimates.

#### 4.1.2 Key Points Regarding the Transect Method

Some of the key considerations related to application of the transect method are summarized below.

- Sufficient data density is important.** Contaminant plumes and groundwater flow fields are heterogeneous, where concentrations and specific discharge can vary by an order of magnitude (or more) over a few meters or less transverse to groundwater flow. Mass flux or mass discharge projects that sample more of the area of the transect (either by a large number of points or long screens that average concentrations) will be more likely to capture the high mass flux zones. When applying the transect method, practitioners must balance the need for accuracy with sampling density. For example, evaluation of the hydraulic conductivity of each polygon will improve the mass flux and discharge estimates concurrently with the collection of more discrete groundwater samples. Sections 2.5, 4.1.3, and 4.8 present research results and current knowledge related to the design of a mass flux/discharge system and the potential uncertainty associated with the results.

- **Porosity is not used for mass flux/mass discharge calculations using the standard TM.** Mass flux is determined by multiplying the specific discharge of a polygon (also called the Darcy velocity, in units of length divided by time) by the area of the polygon and the concentration in the polygon. Porosity is used for calculating seepage velocity (or average linear velocity), which represents the average rate at which the water moves between two points and is not applicable to mass flux or mass discharge calculations using the standard TM.
- **Retardation (via the use of a retardation factor) is not a term in the equation to calculate mass flux.** While important for solute transport and PFM calculations, retardation is not relevant to mass flux/discharge calculations because mass discharge/flux are based on the specific discharge that contains a contaminant. The geochemical system in each polygon is assumed to already be at steady state with respect to adsorptive processes.
- **Mass flux can be calculated for any dissolved constituent.** Metals, chlorinated organics, MtBE, inorganic ions—all can be evaluated using the mass flux methodology as long as the concentration data represent dissolved constituents migrating in flowing groundwater. The key concept is that contaminants are migrating in flowing groundwater and there is a measurement system (e.g., transect point, well capture, etc.) that samples the flowing groundwater.

However, if a large fraction of the contaminant mass is sorbed to suspended solids in the groundwater samples, then the mass flux calculations may be incorrect. For example, if unfiltered samples from an undeveloped well in a fine-grained unit are collected and if these samples have high concentrations of suspended solids with metals or organics sorbed to their surfaces, then the transport of these metals or organics will be overestimated (unless the groundwater is actually transporting the suspended solids). This problem can be avoided or minimized with properly developed wells, low-flow sampling techniques, passive sampling methods, or filtering samples. In most cases, however, properly collected groundwater samples are not highly turbid and therefore can be used for mass flux calculations. Cases where filtering might result in inaccurate results are cases where facilitated transport via colloids (e.g., plutonium) is an important transport process. (Note: The issue of filtering groundwater samples is complex and controversial. For more information see Matanoski and Murarka 1997, Luftig 2003, and Indiana DEM 2005).

#### 4.1.3 Sampling Methods

Mass flux measurements can be performed using monitoring wells or temporary monitoring points installed with direct-push devices. Monitoring wells typically have longer screens (1.5 m or longer) that provide a flow-weighted concentration for that screened interval (if pumped at a high enough rate). Direct-push data will have shorter screened intervals (a few centimeters) but more sample points vertically. Various types of direct-push sampling devices (e.g., the BAT Sampler, ConeSipper, etc.) afford users very controlled and spatially distinct sampling and characterization opportunities. These devices can be deployed with many types of rigs. Furthermore, it is possible to collect complementary data and samples for the calculation of mass flux estimates during a single mobilization.

Mass discharge represents the overall mass passing through the control plane over a given period of time. The mass flux literature indicates that very dense vertical sampling (i.e., the short screen

case) is needed if the goal is to detect concentration hot spots (e.g., Guilbeault, Parker, and Cherry 2005) or to know how mass flux (mass per area per time) is distributed across the control plane to optimize a remediation project targeting hot zones. If calculating mass discharge is the goal (for example, to quantify impact to a well or stream), either many points with short screens or a few wells with longer screens can be used. There are conflicting views about the use of long ( $\geq 10$  ft) well screens for mass discharge estimates. In theory, a long well screen (if pumped hard enough) will provide a flow-weighted average concentration from that location and can be a cost-effective method to sample a large part of the aquifer. On the other hand, some researchers and practitioners feel that long well screens are not preferred for mass discharge monitoring without detailed site characterization (dense vertical aquifer sampling) that has demonstrated that the data from long-screened wells are representative of the vertical distribution of contaminants. The groundwater community is currently evaluating these complex issues.

At most sites, existing monitoring well networks are not designed to fully capture the mass flux through a particular transect. Instead, wells in such networks were designed to delineate plume boundaries, establish centerline plume concentrations, and provide estimates of source concentrations. (There are indirect methods that use conventional monitoring well network data to estimate mass flux, as described in Section 4-4.)

At some sites, the flow field is evaluated at a different resolution than the concentration field. For example, transects typically have multiple concentration measurement points (e.g., 70 monitoring points in the example shown in Figure 4-4). However, the number of aquifer testing points is more variable. At some sites, individual aquifer tests may be performed at each polygon, so the calculation of the polygon mass flux (Step 5 from Section 4.1.1) will have an individual concentration term ( $C_i$ ) and individual hydraulic conductivity term ( $K_i$ ). However, it is rare to have individual hydraulic gradient terms for each point, so a site-wide gradient is often used. Table 4-2 presents the most common variations of the transect method based on data density.

**Table 4-2. Common variations of the transect method**

Variation	Concentration values	Hydraulic conductivity values	Hydraulic gradient values
1	One per polygon	One per polygon	One for entire transect
2	One per polygon	Several for transect	One for entire transect
3	One per polygon	One for entire transect	One for entire transect

At the current time, most examples of Variation 1 are from research sites; most examples of mass flux/mass discharge applications for site management purposes are based on Variations 2 and 3, though there is some disagreement among groundwater professionals who use the transect method regarding the accuracy of these methods. For example, Guilbeault, Parker, and Cherry (2005) state, “This assumption of homogenous hydraulic conductivity in sand aquifers is commonly used in calculations of plume mass-discharge (Semprini et al. 1995, Wilson et al. 2000).” In addition, several key research papers (e.g., Guilbeault Parker, and Cherry 2005; Nichols and Roth 2004; Einarson and McKay 2001) used Variation 3 to calculate mass discharge. Brooks et al. (2008) used Variation 3 of the TM to compute mass discharge values at two sites and compared these results against the PFM and a pumping test method (see Sections 4.2.5 and 4.3.2). In this case, hydraulic conductivity values from groundwater models were used

to estimate a transect-wide hydraulic conductivity value. The authors commented on the use of transect-wide estimates of hydraulic properties as follows:

As employed here, TM results may have been impacted by uncertainty associated with homogeneity assumptions in order to use (a transect-wide)  $K$  and (a transect-wide)  $i$  to calculate (a transect-wide)  $q$ . The appropriateness of using (a transect-wide)  $K$  and (a transect-wide)  $i$  estimates to complete the TM approach given the spatial variability of PFM results may be questioned; however, hydraulic conductivity values based on pumping tests or slug tests completed at one or a few locations across a site and site-wide estimates of hydraulic gradient are routinely used in typical site characterization approaches.

Li and Abriola (2009) evaluated different sampling strategies for estimating mass discharge and concluded, “for highly heterogeneous permeability fields, the uncertainty from the permeability field may contribute significantly to the uncertainty of mass discharge; therefore, characterization of the permeability field may be important and statistics from the permeability field may need to be incorporated in the sampling algorithm.” Basu et al. (2006) used both Variations 1 and 3 to estimate mass discharge at a TCE site in the Midwest. PFMs were used to estimate concentrations and specific discharge at multiple points across a transect. These values were then used to estimate a mass discharge of the 365 g/d using Variation 1 and 414 g/d using Variation 3 (13% difference in mass discharge). The authors commented that Variation 1 “yielded a better estimate” of the source strength than Variation 3.

Kübert and Finkel (2005) compared several methods, including Variations 1 and 3, by constructing a hypothetical plume and applying Monte Carlo techniques to evaluate error. Comparing Variation 3 (their Method D) with Variation 1 (their method C) revealed that both methods show the same performance for low- to moderate-conductivity variances (aquifer heterogeneity) with “no significant difference” in the error of the two variations. For larger variances in hydraulic conductivity in the hypothetical plume, the result of the comparison depends on the sampling grid resolution: while Variation 3 “performs better for coarse resolutions (horizontally and/or vertically),” Variation 1 “yields a higher accuracy if sampling wells or levels are close.” However, if the sampling grid is inappropriately designed, Variation 1 may lead to a severe misinterpretation due to inaccurate well-specific hydraulic conductivity values. Kübert and Finkel (2005) also concluded that the use of well-specific hydraulic gradient values did not show any significant reduction in estimation errors.

In summary, Variation 1 is likely to provide more accurate mass flux or mass discharge estimates than Variation 2, and Variation 2 will likely be more accurate than Variation 3. However, many (or perhaps most) of the mass flux or mass discharge calculations performed using the transect method now (i.e., in the 2010 time frame) are probably calculated using Variation 3. It is difficult to determine the accuracy of different mass flux/discharge calculation methods. Section 4.8 provides a discussion of uncertainty issues related to mass flux/discharge in general.

#### 4.1.4 Data Analysis Methods

When calculating mass flux/discharge from data-rich transects, the user likely will determine the subarea or polygon boundaries as follows:



- drawing rectangles or polygons around the concentration monitoring points (The polygons are formed by connecting lines at the halfway point between each sampling point on the transect.)
- truncating the subareas in areas where the plume is no longer present (This could be where nondetect values are measured or the edge of the plume is anticipated to be.)
- accounting for hydrogeologic boundaries such as the top of the water table, a confining unit at the top, and/or an aquitard at the bottom of the water-bearing unit
- accounting for cases where there are different sampling densities of concentration, hydraulic conductivity, and hydraulic gradient data (for example, a transect with 30 concentration estimates, 5 hydraulic conductivity estimates, and a uniform hydraulic gradient estimate across the transect)

The first method to determine mass flux/mass discharge is to set up the array of subareas or polygons. There are several computation techniques, with the most common described below. The first method is to compute the mass discharge for each polygon separately. The calculations can be quite labor-intensive as one progresses across the aquifer.

A second approach is to put the data into a spreadsheets, with one array showing the concentration data, another array showing hydraulic conductivity data, and a third array showing hydraulic gradient data. Cells in each array represent subareas, and the data for each subarea on each of the three arrays are used to calculate the subarea mass flux in a fourth array (after making the appropriate conversions).

A third approach is to interpolate the distribution of the contaminant in the vertical plane using software contouring or kriging packages. The pros and cons of using computer software to contour groundwater data are well known to groundwater professionals. While computer contouring methods do provide considerable labor-saving advantages, particularly for large datasets, one researcher (Siegel 2008) has stated that hydrogeologists should “contour using your head, not your computer,” and has listed this rule as one of the 10 “fundamental principles” of hydrogeology. If computer contouring is used, it should be carefully checked to make certain that boundary conditions and internal points are honored and that the final output is a reasonable representation of the contaminant distribution.

A fourth approach is calculate mass flux using specialized software, such as the Mass Flux Toolkit program (Farhat, Newell, and Nichols 2006), a free downloadable software tool developed as part of the Department of Defense Environmental Security Technology Certification Program (ESTCP) research program. With this tool, users enter concentration data in terms of coordinates and type of monitoring point (single point or screened interval from monitoring wells). Next hydraulic conductivity data are entered or imported from electronic datasets (either as multiple points or a single site-wide estimate), followed by hydraulic gradient data. Figure 4-5 shows the input screen for the Mass Flux Toolkit. Users can then select the type and resolution of the subarea grid. Many times the available data do not fill an entire grid of subareas, so users select one of several ways to interpolate the “in-between” data, including nearest neighbor, linear interpolation, or log interpolation (recommended by some practitioners as the best method) or enter their own estimated values. Figure 4-6 shows the results screen for a transect calculation involving MtBE.

**Input Data and Grid**

File Location and ID: **Transect**  
 Description: **MTDE**

4. CHOOSE TRANSECT: **Transect1**      6. CHOOSE TIME PERIOD: **1**

6. ENTER TRANSECT DATA

6.1 Distance of Transect From Source: **100** (ft)

6.2  Data Velocity     Hydraulic Conductivity    6.5  Sampling Interval     Mid Point of Sampling Interval

6.3 Hydraulic Conductivity Units: **cm/sec**

6.4 Uniform Hydraulic Conductivity?: **yes** → Hydraulic Conductivity: **3.00E-02** (cm/sec)

6.5 Uniform Hydraulic Gradient?: **yes** → Hydraulic Gradient: **3.00E-02** (cm/ft)

Monitoring Point	Distance of Monitoring Point from Start of Transect (ft)	Sampling Interval (ft)		Plume Top (ft)	Plume Bottom (ft)	Concentration (mg/L)	
		Top	Bottom			Concentration A	Concentration B
Start of Transect	0					1	0
End of Transect	90					1	0
TR-1	10	5	10	5	5	2.3	
TR-2	20	10	15	5	15	0.42	
TR-3	30	5	10	5	20	5.7	
TR-4	37.5	10	15	5	25	7.5	
TR-5	45	5	10	5	20	0.9	
TR-6	45	10	15	5	20	20.0	
TR-7	45	15	20	5	20	9.5	
TR-8	52.5	5	10	5	20	54.1	
TR-9	52.5	10	15	5	20	7.3	
TR-10	62.5	5	10	5	20	0.07	
TR-11	60	5	10	5	15	4.5	
TR-12	60	10	15	5	15	5.6	

7. CHOOSE GRID (OPTIONAL): **Current Grid**      Pathwidth by: **1**      Retrowidth: **10**

8. SELECT CONSTITUENT FOR CALCULATIONS: **MTDE**      n: **Constituent B**

Number of rows: **10**      Number of columns: **7**

Next Step: **Continue Data Input**

Buttons: **Back to Transect Calculator Screen**, **Input All Data**, **Export All Data**, **See Constituent Grids**, **Clear Screen**, **Print Example**, **Restore Table Formatting**, **Print**, **HELP**

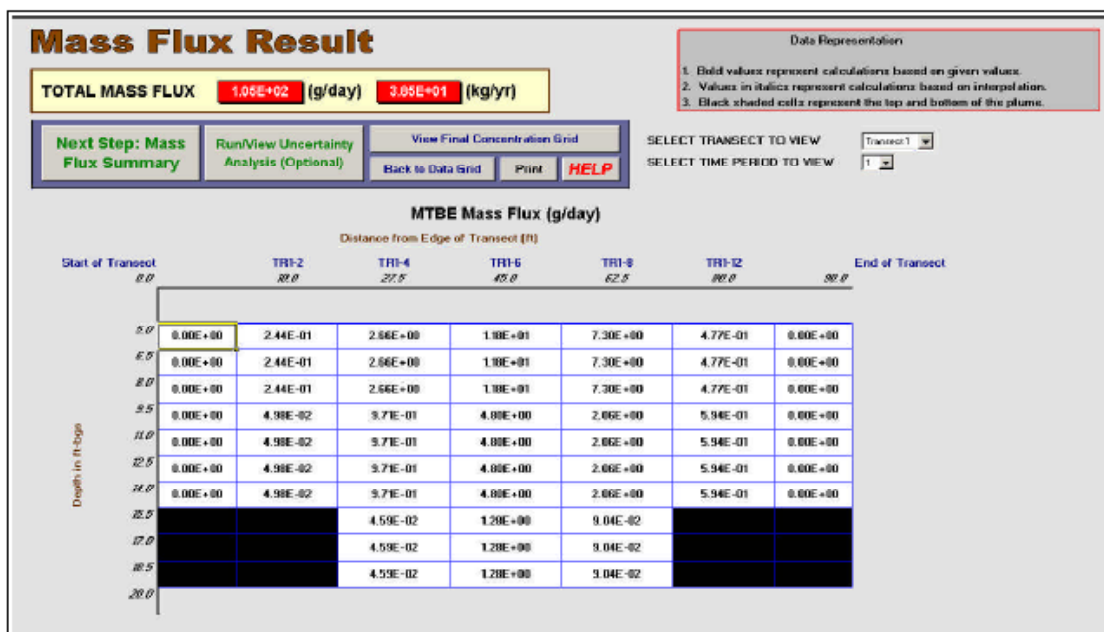
Figure 4-5. Input screen for Mass Flux Toolkit. (Farhat, Newell, and Nichols 2006)

More than one transect can be calculated to show how mass flux changes as one moves farther downgradient from the source zone, and transect data over time can be entered to evaluate temporal changes in mass flux. A detailed case study is provided as Example 1 in the Mass Flux Toolkit User's Manual.

#### 4.1.5 Uncertainty Associated with the Transect Method

Mass discharge estimates are based on integrating flow and concentration data, both of which have uncertainty; therefore, the overall mass discharge value itself will have some uncertainty. Nichols and Roth (2004) summarized the uncertainty in transect-based mass flux estimates as follows:

Although the transect method allows for an improved understanding of the concentration distribution across a plume and is easy to calculate, the underlying assumptions (e.g., that the monitoring well transect adequately describes the plume) and data required may impart an unknown degree of uncertainty in the resulting mass-flux estimate. Reducing uncertainty with this method may require that many samples be taken in space and over time, with potentially higher analytical costs.



**Figure 4-6. Results screen for Mass Flux Toolkit.** (Farhat, Newell, and Nichols 2006)

Einarson and Mackay (2001) concluded as follows:

There are, of course, uncertainties associated with the calculation of contaminant  $M_d$  (mass discharge) using data collected from sampling transects. Uncertainties are associated with the density of the sampling grid, methods used to integrate the mass traversing the transect (techniques for integrating the contaminant mass typically include numerical kriging routines and Thiessen polygons), and estimation of the groundwater specific discharge within each hydrostratigraphic unit. It should be noted that the accuracy of the  $M_d$  estimate is, in general, likely to improve with the number of monitoring points in the sampling transect.

(Note: Einarson and Mackay use and describe the calculation of mass discharge [units of mass per time flowing through a vertical transect] but interpret  $M_d$  as mass flux, which is actually units of mass per area per time.)

The Mass Flux Toolkit provides quantitative examples of uncertainty. For example, Fraser, McLaren, and Barker (2005) evaluated mass flux vs. sampling density for a naphthalene plume at the Borden research aquifer:

When the sampling grid density was reduced from 1.7 points per meter squared to 0.7 points per meter squared, the range (as a standard deviation) in mass discharge increased to more than 50%. Guilbeault et al. (2005) showed that 75% of the mass flux occurred within 5% to 10% of the transect cross section area for three plumes in Ontario, New Hampshire and Florida, and that a spacing no larger than 15 to 30 cm was needed at some locations to identify high concentration zones. However, mass flux calculations using a relatively sparse sampling network (<10 sampling points) for two transects showed similar total mass flux estimates (Nichols et al. 2005).

The Mass Flux Toolkit identified three main sources of uncertainty associated with the transect method:

- **Type 1.** Uncertainty in the actual concentration, hydraulic conductivity, and gradient measurements. Uncertainty in the water quality data (concentration) is due to variability over time and space. Temporal uncertainty can be estimated by evaluating temporal trends over time and evaluating the amount of “time-independent” data variability (basically the scatter observed above and below a trend line). Therefore, a mass flux/discharge estimate derived using point concentrations from a single sample event will have uncertainty due to time-independent variability (for more information on time-independent variability in point concentration measurements, see McHugh, Liu, and Newell 2010). Spatial uncertainty relates to whether the measurement grid was able to capture the variability in groundwater concentrations in the transect. Groundwater practitioners can estimate the accuracy of the hydrologic measurements (hydraulic conductivity and hydraulic gradient) that are being used for the mass flux calculation. At most sites, the use of a single value for hydraulic conductivity and hydraulic gradient will produce uncertainty. *Remediation Hydraulics* (Payne, Quinnan, and Potter 2008) provides a detailed evaluation of the variation in hydraulic conductivity at the plume-level scale.
- **Type 2.** Uncertainty in the interpolation scheme. Different interpolation schemes will result in different mass flux estimates. Some interpolation schemes, such as kriging, provide local estimates of uncertainty.
- **Type 3.** Uncertainty associated with unmeasured values. The uncertainty associated with areas of high mass flux that may be missed by the monitoring scheme is difficult to assess.

To help users understand and manage this uncertainty, the Mass Flux Toolkit includes an uncertainty module that uses a Monte Carlo approach (a class of computational algorithms that rely on repeated random sampling to compute their results) to analyze the Type 1 uncertainty in the actual concentration, hydraulic conductivity, and gradient measurements. With this tool, groundwater practitioners can estimate the accuracy of the hydrologic measurements used for the mass flux calculation. Instead of a single value, users input a probability distributions of all of the key input variables, such as contaminant concentration, hydraulic conductivity, and gradient. The Monte Carlo algorithm calculates thousands or tens of thousands of “realizations” and performs statistics to describe the potential for different output results. While a relatively simple statistical method, this approach requires that the users know or estimate the probability distributions of the key input variables. In addition, it is not calibrated to actual measurements and assumes independency among input variables, which may cause overestimation of the mass flux uncertainty.

Another uncertainty option is a geostatistical approach that quantifies mass discharge and the associated uncertainty using geostatistical stochastic simulation (Li, Goovaerts, and Abriola 2007). This approach evaluates the Type 2 and Type 3 uncertainty and provides a range of possible mass discharge values with the probability of occurrence. This approach essentially generates many equally probable mass flux realizations for the transect, which are all

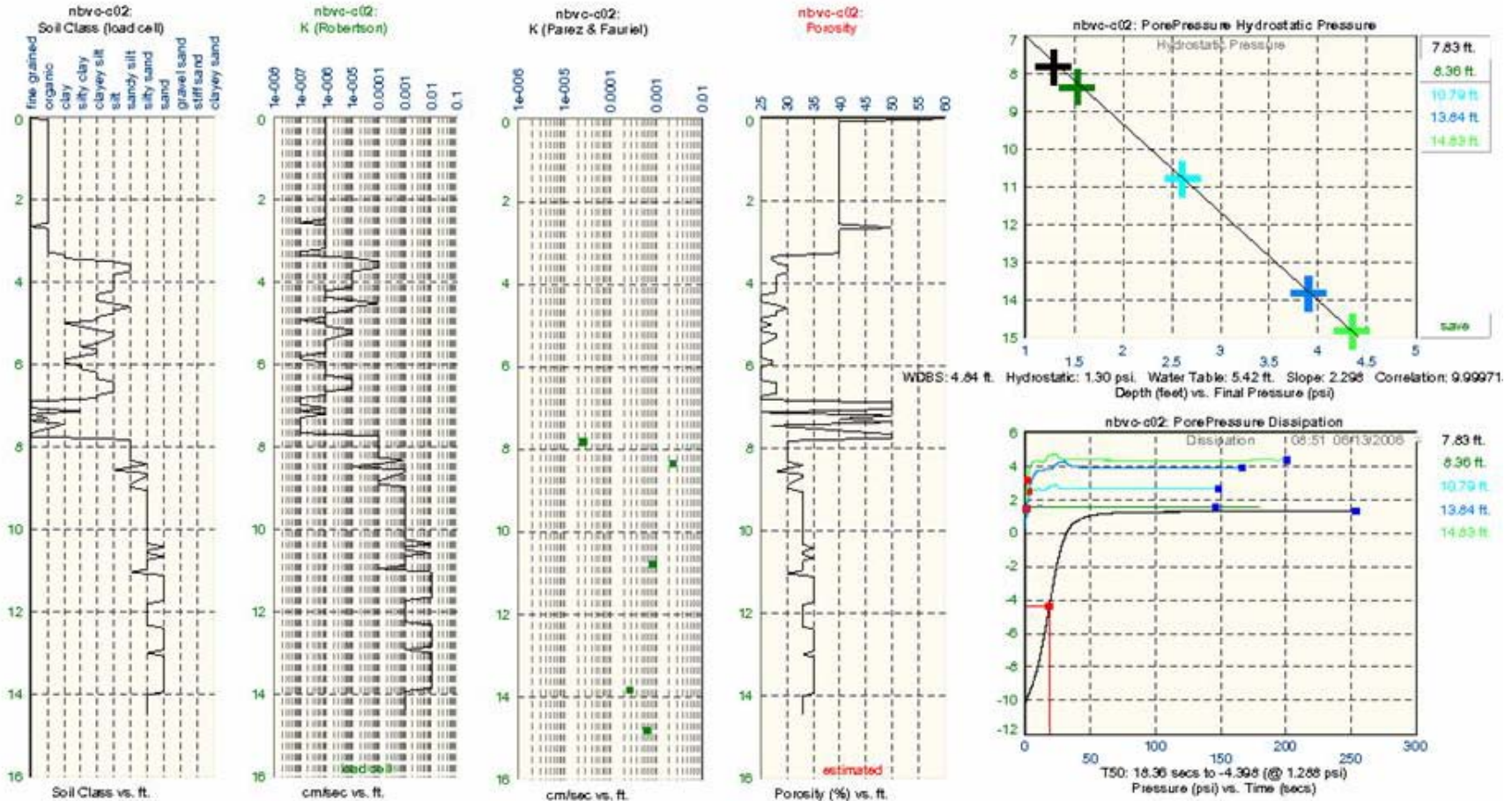
representative of the sample data. The possible mass discharge values are then calculated from these mass flux realizations. This approach is similar to the Monte Carlo approach, but it does not require prior information about input variables; it is conditional to the data and considers the correlation between input variables.

#### 4.1.6 Transect Method Using Advanced Piezocone/Membrane Interface Probe/Confirmation Method

A modification of the transect method developed by Kram et al. (2008) employs the high-resolution piezocone (HRP), a MIP, and confirmation analyses to estimate plume characteristics, including mass flux distribution estimates in two and three dimensions (transects in any orientation: vertical, horizontal, or at an angle). Key procedural elements and technologies are briefly discussed below.

A piezocone (American Society of Testing and Materials [ASTM] D5778 and D6067) is a sensor probe consisting of a porous element connected to a customized transducer that converts pore water pressure to water level. A high-resolution piezocone (U.S. Patents 6,208,940 and 6,236,941) is a push sensor probe capable of generating highly resolved hydraulic head values ( $\pm 1$  inch of water level) while simultaneously collecting critical soil type information. The porous element is filled with viscous oil that is in contact with the transducer, which is located inside the probe housing. As the probe is advanced through the soil, water pressures are transferred through the oil-filled porous element directly to the transducer. The signal is recorded and converted to hydraulic head estimations through correlations between recorded signal and hydrostatic pressure. Since the environment is disturbed when the probe is advanced, dissipation of the pressure while the probe is held in place yields critical information related to hydraulic conductivity. The piezocone is also capable of generating soil type estimates based on measurements of vertical resistance to force and sleeve friction or on pore pressure and vertical resistance to force.

Figure 4-7 displays one available WinOCPT version of the HRP output for a single push with five dissipation tests. From the left are columns representing soil type classification, hydraulic conductivity (based on a Robertson and Campanella [1989] lookup chart), hydraulic conductivity at specific depths (based on Parez and Fauriel [1988] pressure dissipation relationships), and effective porosity estimates (based on soil type lookup chart). Depths are listed along the y axes. The dissipation curves for specific depths where tests were conducted are displayed along the lower right portion of the graphic. Final pressures and hydraulic conductivity values are derived from this dissipation test summary. The hydraulic pressure profile is presented in the upper-right graph, along with calculated water depth below surface and corrected water table depth (relative to sea level). All hydraulic data becomes available for additional processing via the GMS platform.



**Figure 4-7. High-resolution piezocone output example for a single push.** Moving left to right, panels of data show soil type versus depth, hydraulic conductivity versus depth (based on the Robertson and Campanella [1989] soil type conversion), hydraulic conductivity versus depth (based on the Parez and Fauriel [1988] relationships), effective porosity, pressure dissipation tests for specific depths, and head versus depth. Dissipation tests are used to determine *K* and head values for specific test depths. (Kram et al. 2008)

The MIP is a semiquantitative tool for the characterization of contaminant concentrations. It incorporates a thin polymer film supported by a stainless screen. The film is a permeable membrane through which volatile contaminants and aquifer constituents migrate. It is placed in a heated block attached to the probe and heated to approximately 100–120°C. A carrier gas sweeps the zone where volatile constituents that have passed through the film have collected and brings them to the surface for rapid analysis via gas chromatography or ion trap mass spectrometry. A new heated trunkline MIP system has recently been commercialized to increase the accuracy of this screening tool. However, confirmation samples are always recommended and, in the opinion of some, necessary for mass flux/discharge calculation.

In addition, the MIP samples the entire matrix, including NAPL, dissolved phase, and sorbed phase. Therefore, using MIP data for mass discharge calculation may bias the results as mass flux/discharge are defined as aqueous-phase concentrations only. Nevertheless, other concentration measurement methods can be used with the piezocone technique for mass discharge calculation.

The hydraulic data (from the HRP) can be combined with the contaminant distribution (e.g., from the MIP and confirmation data) using a calculation tool such as the GMS package. The end result is a distribution of mass flux across the transect. For this approach, GMS has been modified to allow practitioners to interpolate key parameters and then calculate both the groundwater velocity and mass flux distributions. Hydraulic conductivity interpolation options include conventional geostatistical approaches and coupled soil type and dissipation value constraints, as well as more complicated approaches such as the Markov Chain transitional probabilities techniques (an interpolation approach that is useful when articulating the geospatial relationship of facies and other similar types of deposits and characteristics).

A key requirement includes conversion of individual head values from the piezocone to a gradient field. This is accomplished using a finite-difference approach to solve for gradient at each grid node. At each node, collocated interpolated  $K$  and effective porosity values are merged with gradient to calculate seepage velocity; then this value is merged with collocated and interpolated concentration values resulting from the chemical concentration estimates. The net result is a three-dimensional flux distribution field. Transects of flux distributions can be generated using the visualization tools in GMS. A mass discharge value can be derived by integrating the flux distribution across the transect. This surface can represent a source control plane or any other transect (e.g., plume centerline) of interest.

Mass discharge can be estimated by integrating the mass flux values throughout the plane, which converts the individual flux values (in mass/area/time) to a time-stamped cumulative flux (or discharge value) in units of mass/time. Note that the existing version of the piezocone/MIP/confirmation version uses seepage velocity to calculate mass flux, while the calculation of mass discharge through a transect using the definitions in this document would require the use of specific discharge (also called Darcy groundwater velocity) to calculate mass discharge. Future software iterations in development will enable modelers to use either relationship.

The GMS software package can be used to interpolate between measured transects (either at different places in the plume and/or at different times) to generate interpolated mass flux. Note

that the uncertainty in the interpolated mass flux data is likely to be higher than the uncertainty in mass flux data generated from piezocone/MIP/confirmation measurements at actual transects. In practice, uncertainty can be reduced by collecting data from locations reflecting the highest levels of uncertainty (e.g., within and around the plume between transects intended to be used for long-term monitoring). An appropriate field sequence of data collection activities could be as follows: deployment of the semiquantitative MIP for plume delineation, use of a confirmation sample collection tool for dissolved-phase quantification and MIP value normalizations, then deployment of the HRP for detailed hydraulic assessment in discrete locations as a basis for remediation design and to establish long-term monitoring networks for remediation performance evaluation. Once a long-term monitoring network has been deployed, head and concentration values can be measured and processed using GMS to derive time-lapsed flux assessments. Pneumatic slug-testing of the installed monitoring points can be performed and compared to the hydraulic information originally provided by the piezocone.

Key limitations or issues to the method are as follows:

- The interpolation methods may not be robust between transects.
- The use of the MIPs may not accurately capture the mass flux in groundwater due to measurement of sorbed and NAPL phases (if present).

To date, the HRP method has not been directly compared to other more traditional flux and discharge characterization approaches included in this document. Kram et al. (2008) used a control approach composed of 39 customized small screen wells (e.g., 3/4-inch diameter with 6-inch prepacked screens) installed in 13 clusters, each composed of three wells set to three specific depth ranges within the anticipated solute travel pathway of the test domain. The test cell spanned 10 × 25 ft (in map view). Head and hydraulic conductivity measurements were performed in each well, then compared to the HRP readings from identical depths and offset by 1 ft in map view. While slight directional and velocity nuances associated with each data set were observed, the general gradient and head distributions displayed exceptional agreement within the well cluster domain. Hydraulic measurements from each data set (HRP and wells) were incorporated into flux models by simulating solute transport and concentration distributions over time based on the exported velocity fields resulting from each of the measurement data sets. Concentrations were incorporated into GMS flux renderings by combining the simulated concentration fields over time with velocity fields derived for each data set, with very good agreement (e.g., spatial, temporal, and via model efficiency metrics) between the well and HRP-derived iterations.

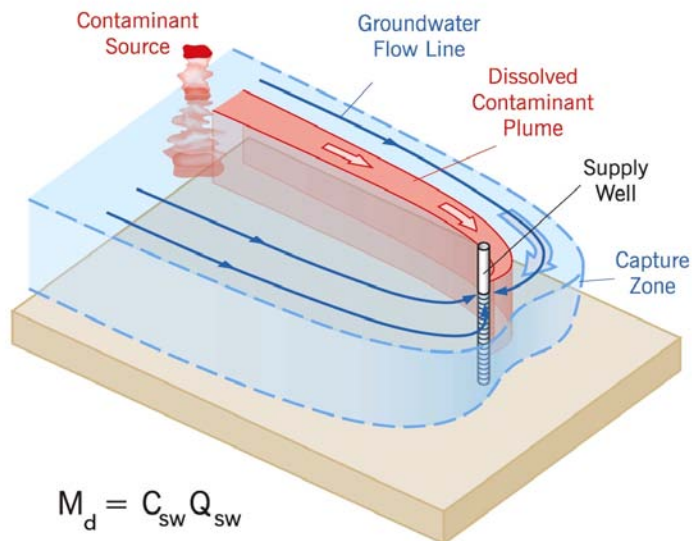
## **4.2 Well Capture/Pumping Test Methods**

### **4.2.1 Well Capture Method**

Nichols and Roth (2004) describe an alternative mass discharge method in which an extraction well fully captures a contaminant plume (Figure 4-8). By measuring the concentration and flow rate of the well, the mass discharge (in units of mass per time) can be calculated. This approach assumes that the well or well system fully captures the horizontal and vertical extent of the contaminant plume and that the well (or wells) is located far enough downgradient of the source that the pumping does not induce high discharge of contaminants from the source due to



increased dissolution of source materials. This distance can be evaluated using the concept of drawdown cones, which can be evaluated using the Theis equation or a groundwater flow model. For permeable aquifers used for water supply, this distance is often relatively small. One advantage of this method is that the well is an effective tool to integrate flow and concentration so that even small concentration hot spots and high-transmissivity zones are captured by the well. The method has relatively few data requirements, but the test must achieve the following conditions: (a) the pumping well should not increase the flow through the source zone (this might increase the dissolution rate and concentrations may or may not change), (b) pumping should be continued long enough so that relatively steady-state conditions can be achieved, and (c) complete or near-complete capture of the high-discharge portions of the plume must be confirmed using groundwater potentiometric surface data or tracers. The need for complete capture is a site-specific decision depending on the level of accuracy needed at a particular site. Performance monitoring data from most hydraulic capture systems will provide mass discharge data once flow rate and concentration data are multiplied using appropriate conversion factors.



**Figure 4-8. Diagram of well capture method to measure mass discharge.**  $M_d$  = mass discharge,  $C_{sw}$  = concentration from the supply well,  $Q_{sw}$  = flow rate of the supply well. (Nichols and Roth 2004)

One of the most easily performed and least expensive estimates of mass discharge can be obtained from existing data from a pump-and-treat system, which inherently uses the well capture method (if the system captures the entire plume). Existing pump-and-treat systems, where both flow and concentration data are collected, are often ideal “monitoring systems” to determine mass discharge. Changes in the concentration over time can make the interpretation of test results more complicated. Unfortunately for some purposes, the spatial distribution of mass flux (in units of mass per time per area) is not revealed using this method unless multiple recovery wells are involved where individual headers can be sampled. This is the key disadvantage to the well capture method in that the site managers only get the single value, mass discharge in units of mass/time. Information about the structure of the plume, the location of high-discharge zones, etc. is not provided by this method.

#### *Calculation Approach*

In its simplest form, the following calculation is used to determine mass discharge from any pumping well that has captured a plume (modified from Nichols and Roth 2004):

$$M_d = Q \cdot C \quad (4-3)$$

where

$M_d$  = mass discharge in units of mass per time,  $M/t$  (e.g., g/d)

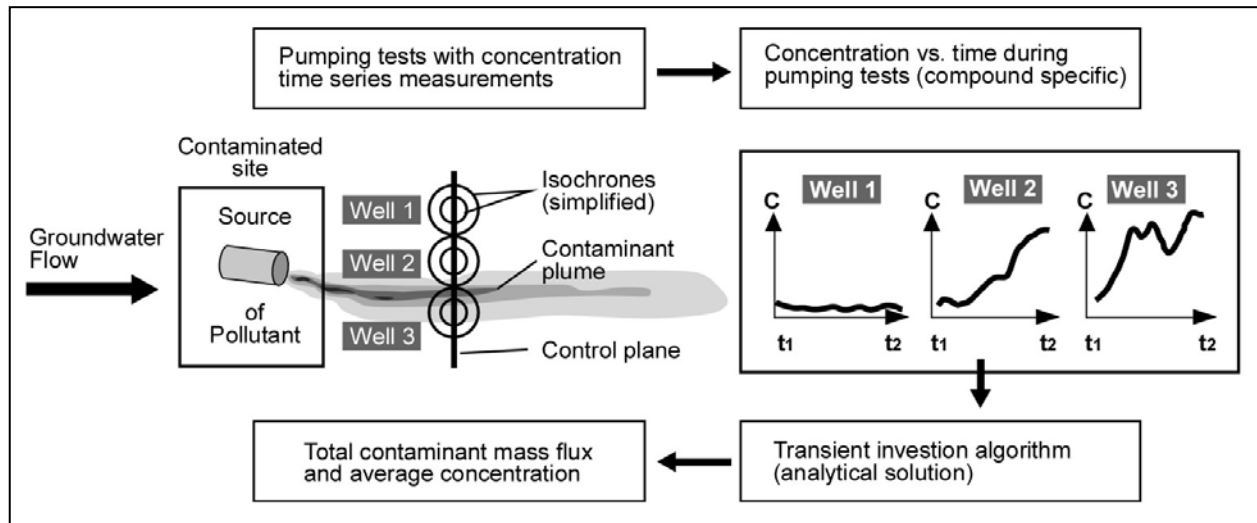
$Q$  = water flow (pumping) from the well,  $L^3/t$  (e.g., volume/d)

$C$  = concentration of contaminant in the extracted well water,  $M/L^3$  (e.g., mg/volume)

If more than one well is used, the values are summed to determine the mass discharge.

#### 4.2.2 Integral Pump Test

A more sophisticated well capture method, the IPT, was developed by researchers at the University of Tübingen in Germany (Holder et al. 1998; Schwarz et al. 1998; Ptak and Teutsch 2000; Teutsch et al. 2000; Bockelmann, Ptak, and Teutsch 2001). Using frequent concentration values measured in the discharge from a pumping well over the duration of a pump test, an analytical solution is then used to back-calculate the mass discharge (see Section 4.2.2.2) that would be required to produce the observed concentration vs. time data. The method assumes (a) steady-state conditions, (b) homogeneous or moderately heterogeneous conditions (i.e., conditions where the scale of local heterogeneities is much smaller than the investigation scale; the analytical solution derived for homogeneous and isotropic formations [Swartz et al. 1998; Bockelmann, Ptak, and Teutsch 2001] may not be accurate for highly heterogeneous aquifers), (c) the equation is practical only for radially symmetrical capture zones, and (d) negligible or linear contaminant concentration gradient within each capture well zone flow path. In more sophisticated analyses, numerical solute transport models are used to reconstruct mass flux patterns in a water-bearing unit at complex sites. Figure 4-9 shows a conceptual depiction of the time series approach.



**Figure 4-9. Process for estimating mass flux using integral pump test series data.**

(Bockelmann, Ptak, and Teutsch 2001)

More recently Bauer et al. (2004) and Bayer-Raich et al. (2006) have refined the IPT method to account for the combined effects of linear instantaneous sorption/retardation and multiple wells.

#### 4.2.2.1 Integral Pump Test Advantages and Limitations

The advantages of the IPT method include the following:

- does not require interpolation of contaminant concentrations between subareas
- requires fewer wells (only pumping well[s] and enough monitoring wells to ensure that the entire plume has been captured)
- samples large quantities of plume water, which results in better flow and concentration data and improves integration results
- can be applied to existing plume containment systems

The limitations of the IPT method include the following:

- can generate large volumes of contaminated water, which must be managed
- pumping can change plume chemistry, such as by introduction of oxygen-rich water from clean zones
- can be difficult to determine whether plume is fully captured by the pumping well(s)
- if the pumping well is in the source zone, the dissolution rate may change compared to conditions prior to pumping
- no information on the spatial distribution of contamination parallel to groundwater flow
- difficulty in obtaining a unique solution

#### Calculation Approach

With the IPT, the concentration vs. time data from the pumping well(s) are combined with solute transport models to derive the upstream concentration field under natural-flow conditions to yield a mass discharge. The developers of the method have used both analytical and numerical solutions to derive a backwards-calculation approach where conditions in the aquifer and plume are reconstructed so that they result in the observed concentrations coming from the pumping well.

In the Bayer-Raich et al. (2006) methodology, the mass discharge along a multiple well IPT control plane is obtained from the following equations:

$$M_{CPg} = \sum_{k=1}^{N_{well}} l_{CPw}^{(k)} b^{(k)} q_o^{(k)} C_{av}^{(k)} \quad (4-4)$$

and

$$C_{av}^{(k)} \approx \frac{1}{\sqrt{t_i}} \sum_{k=1}^i C_w t_k (\sqrt{t_i - t_{k-1}} - \sqrt{t_i - t_k}) \quad (4-5)$$

where

$M_{CPg}$  = mass discharge through the control plane in units of time,  $M/t$  (e.g., g/d)

$N_{well}$  = total number of IPT wells

$l_{CPw}^{(k)}$  = length of control plane associated with well  $k$ ,  $L$

- $b^{(k)}$  = aquifer thickness,  $L$   
 $q_o^{(k)}$  = Darcy velocity,  $L/t$  (e.g., ft/d)  
 $C_{av}^{(k)}$  = average concentration,  $M/L^3$  (e.g., g/volume)  
 $C_w$  = concentration from the well,  $M/L^3$  (e.g., g/volume)  
 $i$  = number of samples  
 $t_i$  = time of taking the  $i^{th}$  sample,  $t$  (typically d)

Note the analytical method is not able to uniquely predict the spatial distribution of concentration in the dimension perpendicular to flow. In other words, there could be several different concentration profiles (plume contours in the vertical transect) that could explain the signal generated by this type of pumping test. Therefore, there is some uncertainty in this method, and in some cases the final answer (average concentration) may not exactly match what is actually present in the field.

#### 4.2.3 Modified Integral Pump Test

The modified integral pump test (MIPT) is a simple field method which can be used to estimate contaminant mass flux averaged over a large subsurface volume. The method is different from IPT in that it is used to measure the Darcy velocity directly (without separate measurements of hydraulic conductivity and hydraulic gradient) and avoids the need for complex data analysis.

The MIPT method assumes that the aquifer is confined, isotropic, and homogenous (i.e., the transmissivity, which is the hydraulic conductivity multiplied by the aquifer saturated thickness, is constant) with a uniform thickness ( $b$ ) under steady-state and uniform flow conditions. Note that these are the same assumptions required to evaluate pump test data with the commonly applied Theis method and other aquifer test analysis methods. The Darcy velocity ( $q_o$ ) can be determined by measuring the head difference between pumping wells and monitoring wells, when the pumping wells are pumped at different flow rates. For an aquifer of thickness  $b$  and a transect perpendicular to groundwater flow, the head difference,  $\Delta h$ , between a pumping well at the origin and a downgradient monitoring well at distance,  $\Delta x$ , can be expressed by the following equation (Brooks et al. 2008, Goltz et al. 2009):

$$\Delta h = -\frac{q_o b}{T} \Delta x + \frac{1}{2\pi T} \sum_{i=0}^N Q_i \ln \frac{r_{o(i)}}{r_{p(i)}} \quad (4-6)$$

where

- $r_{o[i]}$  = distance to the observation well from the  $i^{th}$  pumping well,  $L$   
 $r_{p[i]}$  = distance between the  $i^{th}$  pumping well and the origin,  $L$   
 $T$  = aquifer transmissivity,  $L^2/t$  (e.g., area/time). The transmissivity is the hydraulic conductivity,  $L/t$  (length/time), multiplied by the aquifer saturated thickness,  $L$   
 $Q_i$  = rate of the  $i^{th}$  pumping well,  $L^3/t$  (volume/time)

If the field measurements of  $\Delta h$  are plotted by the following function:

$$\sum_{i=0}^N Q_i \ln \frac{r_{o(i)}}{r_{p(i)}} \quad (4-7)$$

then the graph will be a straight line with slope  $1/2\pi T$  and an intercept of  $-q_o b \Delta x / T$ .

When  $\Delta h = 0$ , the Darcy velocity ( $q_o$ ) can be calculated from eq. 4-8:

$$q_o = \frac{1}{2\pi b \Delta x_i} \sum_{i=0}^N Q_i \ln \frac{r_{o(i)}}{r_{p(i)}} \quad (4-8)$$

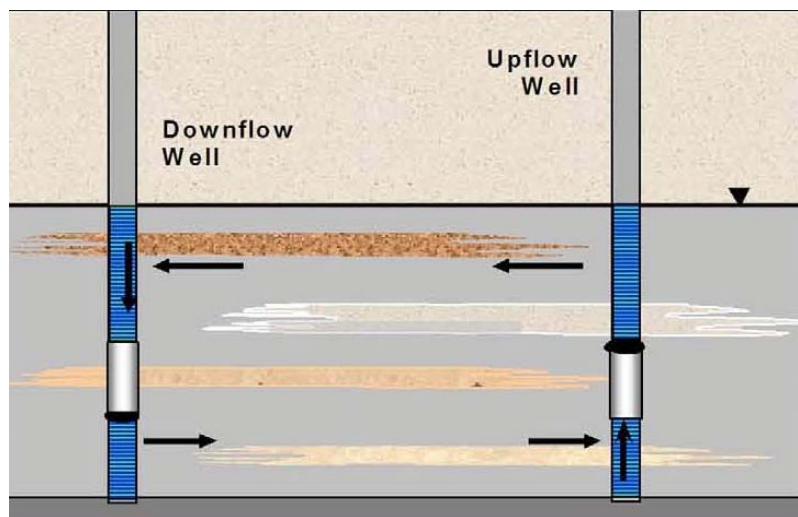
After the Darcy velocity is calculated, the mass flux can be determined by multiplying  $q_o$  by the contaminant concentration. The contaminant concentration estimates are made over time at the pumping well and averaged.

The MIPT can be considered an emerging method to calculate mass flux (Goltz et al. 2009). It has been applied at several field sites, including sites in Utah (Hill Air Force Base [AFB]), Washington (Ft. Lewis, as reported by Brooks et al. [2008]), the Borden Site in Canada, and a site in Jacksonville, Florida.

#### 4.2.4 Tandem Circulating Wells

Another well pumping method to measure mass flux is the use of tandem circulating wells (TCWs), also called tandem recirculating wells (TRWs). This method should be considered as an experimental approach as it has not been applied in the field to calculate mass flux (Goltz et al. 2009). The method uses two dual-screened wells: one extracts water from a lower depth and pumps it upward to inject at a shallow depth; the second operates in the opposite direction. This arrangement results in the water circulating between the two wells without being brought to the surface (Figure 4-10).

For calculating the mass flux, the hydraulic gradient can be determined by measuring the piezometric surface at the two wells (with the pumps turned off) and a third piezometer, located near the pumping well, to form a triangle of wells. Hydraulic conductivity is then measured by pumping the two wells and evaluating the resulting head data from the wells. Contaminant



**Figure 4-10. Cross section showing TCW operation.**  
Natural groundwater flow is perpendicular to page surface.  
(Goltz et al. 2009)

concentration is measured by sampling the contaminated water as it flows through the wells. Mass discharge is then obtained by combining the gradient, hydraulic conductivity, and concentration data. The primary advantage of this method is that no wastewater is produced. One potential difficulty is that some regulatory agencies are hesitant to allow reinjection of contaminated groundwater into an aquifer, even if the aquifer is already contaminated and the groundwater is not pumped above grade (see USEPA 2000).

A modification of the TCW method is the addition of a tracer. This technique determines the fractional flow between the two wells by injecting and monitoring tracers at the two injection screens. The fractional flow is the fraction of water drawn into one well's extraction screen that originated from the other well's injection screen. Possible tracers include bromide, chloride, and nitrate, one injected into the upflow well and one into the downflow well. This method has not been applied at a field site as of mid-2010.

#### 4.2.5 Comparison of Well Capture/Pump Test Methods to Transect Method

The MIPT has been compared to other mass discharge estimate methods at two sites (Brooks et al. 2008):

- Hill AFB
  - pretreatment—MIPT: 76 g/d, TM: 78 g/d
  - post-treatment—MIPT: 3.9 g/d, TM: 7.2 g/d
- Ft. Lewis
  - pretreatment—MIPT: 466 g/d, TM: 599 g/d
  - post-treatment—MIPT: 1.5 g/d, TM: 1.9 g/d

All transect method calculations were performed using Variation 3, where average hydraulic conductivity values are determined during previous characterization efforts. Both the Hill and Ft. Lewis transects comprised 10 wells with 5–21 vertical measurements per well.

The Hill AFB site overlooks the Weber Valley and is located on a terrace in an east-facing slope of an old floodplain formed by the Weber River. The shallow, unconfined, paleo-channel aquifer at the site occurs in heterogeneous alluvium (Brooks et al. 2008). The transect-wide average specific discharge ( $q$ ) determined from PFM deployments was  $2.5 \pm 1.8$  cm/d (spatial mean and standard deviation of all PFM measurements) for pretreatment conditions and  $1.5 \pm 0.7$  cm/d under post-treatment conditions.

The Ft. Lewis site has a surficial, unconfined aquifer 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 the site, 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 (Brooks et al. 2008). Tracer depletion data from PFM deployments yielded a transect-wide average specific discharge ( $q$ ) estimate of  $27 \pm 19$  cm/d for pretreatment conditions and  $16 \pm 12$  cm/d under post-treatment conditions.

The absolute accuracy of either method is not known. The relative differences between the two methods range from –46% to –3%, calculated by the equation (TM measurements – IPT

measurements) ÷ TM measurements. The differences are relatively small considering the variability in groundwater flow and groundwater monitoring data and the overall range in mass discharge estimates, which has a factor of 200 or more.

#### 4.2.6 Sensitivity/Uncertainty

IPTs also have uncertainties associated with flux calculations. Inevitably, one must extrapolate from the induced-flow measurements to the flux under natural flow conditions, and there may be errors inherent in such extrapolations. One source of error is pumping-induced changes in the natural flow regime in the area. Perhaps more importantly, pumping may draw water from less-transmissive zones or “dead-end” fractures or pores that do not normally contribute to the mass flux. Such waters can contain relatively high contaminant concentrations since they transmit little to no flow and therefore may be in equilibrium with near-solubility pore water concentrations in the surrounding matrix. However, regardless of contaminant concentrations, the energy required to draw water from low-transmissivity zones would be substantially greater than that required to draw a greater than nonpumping conditions volume of water from more transmissive zones. Therefore, the impact of contaminants in water from less-transmissive zones on the total mass would not be proportional to their percentage of the aquifer volume.

There are other potential sources of error in pumping tests. There is the potential for missing part of the plume, given the difficulties in finding and fully delineating source zones and in predicting capture zones. In addition, spatial information is sacrificed to some extent in pumping tests as opposed to discrete transect sampling. However, careful measurement of contaminant pulses during pumping can provide some information on the distances between flux pathways and the extraction well (Schwarz et al. 1998). For example, pumping tests conducted during the Vandenberg AFB demonstration project (Appendix A) underestimated flux significantly (roughly 50% of the actual flux), but it was later discovered that the flux estimates were so low because the pumping wells did not entirely capture the plume, which had been predicted from assumed  $K$  values. When more-accurate  $K$  values were used, the pumping tests were in fact both accurate and precise in their measurements of the plume area actually sampled. When important factors such as  $K$  are assumed, a sensitivity analysis should be performed and the results presented as a range.

One can reduce the error in pumping tests by stepping up the pumping rate over time. This technique has been recommended in a review of mass flux measurement methods (Goltz et al. 2007). The authors recommend starting at less than the suspected natural groundwater flow rate and monitoring the results at different steps until reaching a pumping rate that ensures complete capture without “overcapture” of the contaminated plume and potential error due to dilution by uncontaminated water. An abundance of data from well-spaced piezometers is very helpful in determining capture zones.

### **4.3 Passive Flux Meters**

Recently, the PFM has been developed to measure cumulative groundwater and contaminant fluxes in the saturated zone at hazardous waste sites (Hatfield et al. 2002a, 2002b; Annable et al. 2005). The PFM consists of a permeable sorbent infused with soluble tracers packed in a nylon mesh tube. The device is placed in a borehole or monitoring well for a known exposure period,

where it intercepts the groundwater flow, causing dissolved contaminants to sorb to the sorbent and the soluble tracers to leach out. The measurements of the contaminants and the remaining resident tracer can then be used to estimate groundwater and contaminant fluxes. By using several PFMs across a transect, the average mass flux and total mass discharge through the control plane can be estimated.

All sorbents have a limited capacity to trap contaminants when used in a PFM. Using estimates of contaminant concentration and Darcy flux anticipated, the test duration can be selected to avoid loading the sorbent to capacity. In general, this is very unlikely for most organic contaminants on activated carbon. However, low molecular weight compounds should be checked carefully. If the compound mass on the sorbent is near the capacity, then some quantity of contaminant has passed through the device, and the mass flux reported should be noted as a minimum, recognizing that the actual mass flux was greater. For a more accurate value, the PFM should be redeployed for a shorter duration (M. D. Annable, personal communication, 2009).

The following section describes how the mass flux,  $J_c$ , is calculated based on the design and use of the PFM. The following equation from Hatfield et al. (2002b) can be used to determine the mass flux:

$$J_c = q_o \cdot C_F \quad (4-9)$$

where

$J_c$  = time-averaged advective contaminant mass flux,  $M/L^2/t$  (e.g., mass/area/time)

$C_F$  = flux averaged concentration of contaminant in the groundwater,  $M/L^3$  (e.g., mass/volume)

$q_o$  = specific discharge of the aquifer,  $L/t$  (e.g., length/time)

The PFM is designed with a diameter approximately the same as the diameter of the borehole or monitoring well in which it is installed to help ensure groundwater flow is through the PFM instead of around it in open space. The PFM may be separated into different vertical zones isolated by impermeable barriers such as rubber/neoprene washers. These help prevent vertical flow within the PFM (but not the filter pack) and allow the PFM to be used to assess different zones in the aquifer. PFM spacing should be based on the geology and groundwater flow characteristics of the aquifer (Annable et al. 2005).

When constructing the PFM, the sorbent, which can be varied based on the contaminant, is impregnated with a known amount of water-soluble tracers (Hatfield et al. 2004). The unit is then placed in a well or borehole and exposed to the groundwater flow for from a few days to a month. During the PFM deployment, portions of the soluble tracers are released, and contaminants are sorbed. The extent to which tracers are removed from and contaminants are loaded onto the PFM is determined by the groundwater velocity, the affinities of the tracers and contaminants to the PFM sorbent, and the concentrations of contaminants in the groundwater flowing through the PFM. The optimum exposure period would allow one half of the initial tracer mass to be removed from the PFM. When the PFM is removed, the sorbent is extracted to quantify the mass of contaminants intercepted by the groundwater flow and the mass of resident tracer remaining ( $M_R$ ) on the sorbent. If the  $M_R$  value is  $>0.3$ , the following equation may be used



to determine  $q$ , the specific discharge through the PFM assuming reversible, linear, and instantaneous contaminant partitioning between the sorbent and water (Annable et al. 2005):

$$q = \frac{1.67r\theta R_d(1 - M_R)}{t} \quad (4-10)$$

where

$r$  = radius of the PFM cylinder,  $L$  (length)

$\theta$  = dimensionless water content of the PFM which may be determined by gravimetric analysis (only after conversion, must go from g water/g solid to volume of water/volume of soil or volume total)

$R_d$  = retardation factor of the resident tracer on the sorbent (Note: The retardation factor in this equation assumes linear partitioning between the sorbent and the water.)

$t$  = sampling duration

$M_R$  = relative mass of tracer remaining in the PFM sorbent (percentage)

For an equation applicable to  $M_R$  values  $<0.3$ , see Annable et al. (2005). Since the flow is typically unknown in field applications, multiple tracers with differing retardation factors need to be applied to the sorbent. This method allows for flexibility when using different exposure periods for the PFMs.

The retardation factor of the resident tracer on the sorbent ( $R_d$ ) is calculated by eq. 4-11 (Hatfield et al. 2004):

$$R_d = \frac{\theta + \rho_b K_p c_0^{n-1}}{\theta} \quad (4-11)$$

where

$\rho_b$  = bulk density of the sorptive matrix,  $M/L^3$  (mass/volume)

$c_0$  = initial dissolved aqueous resident tracer concentration in the pore fluid,  $M/L^3$  (e.g., mass/volume)

$K_{pE}$  = Freundlich coefficient or the reversible distribution coefficient for the sorbent–aqueous phase partitioning of the resident tracer,  $L^{3n}/M^n$  (volume/mass)

As the groundwater flows through the PFM, which is installed in a borehole or monitoring well, the fluid streamlines within the PFM are assumed to be parallel. This principle was demonstrated for a homogenous, permeable, circular element placed in a homogenous aquifer with a differing permeability (Strack and Haitjema 1981, Annable et al. 2005). Groundwater flow is assumed to be horizontal or near horizontal through the PFM (Hatfield et al. 2004). However, the permeability differences between the aquifer and the PFM may produce aquifer flows that converge or diverge near the PFM. This convergence or divergence ( $\alpha$ ) must be taken into account when determining the undisturbed aquifer flow,  $q_0$ . Since the specific discharge of water flowing through the sorbent in the PFM,  $q$ , is linearly related to the specific discharge of the groundwater ( $q_0$ ), the following equations show this relationship, where  $\alpha$  is function of the difference in hydraulic conductivities between the aquifer and a monitoring well or borehole:

$$q = \alpha q_o \quad (4-12)$$

or

$$\alpha = \frac{q}{q_o} \quad (4-13)$$

Specifically, for a PFM situated in a borehole, eq. 4-14 provides an estimation of  $\alpha$  (Strack and Haitjema 1981):

$$\alpha = \frac{2k}{k + k_o} \quad (4-14)$$

where

$k$  = permeability of the PFM (darcies, or any unit consistent with  $k_o$ )

$k_o$  = permeability in the immediate vicinity of the PFM in the formation (Note: This is needed even though tracers are used to estimate flow.)

For a fully screened monitoring well without a filter pack,  $\alpha$  can be determined from eq. 4-15 (Hatfield et al. 2004):

$$\alpha = \frac{4}{\left(1 + \frac{1}{K_S}\right)\left(1 + \frac{K_S}{K_D}\right) + \left(1 - \frac{1}{K_S}\right)\left(1 - \frac{K_S}{K_D}\right)\left(\frac{1}{R_S}\right)^2} \quad (4-15)$$

where

$K_D$  =  $k_D/k_o$ , the dimensionless ratio of  $k_D$  (the uniform hydraulic conductivity of the PFM sorptive matrix,  $L/t$  [length/time]) to  $k_o$  (the uniform local hydraulic conductivity of the surrounding aquifer,  $L/t$  [length/time])

$K_S$  =  $k_s/k_o$ , the dimensionless ratio of  $k_s$  (the well screen hydraulic conductivity) to  $k_o$  (the uniform local hydraulic conductivity of the surrounding aquifer,  $L/t$  [length/time])

$R_S$  =  $r_o/r$ , the dimensionless ratio  $r_o$  (the outside radius of the well screen,  $L$  [length]) to  $r$  (the PFM radius,  $L$  [length])

Using  $q = \alpha \cdot q_o$ , the specific discharge of the aquifer,  $q_o$ , may be determined. Next, the flux averaged concentration of the contaminant,  $C_F$ , needs to be determined using eq. 4-16 (modified from Hatfield et al. 2004):

$$C_F = \frac{M_C}{\pi r^2 L (1 - M_{RC}) \theta R_{dc}} \quad (4-16)$$

where

$M_C$  = mass of contaminant sorbed

$L$  = length of the sorbent matrix for the vertical thickness of aquifer interval sampled

$M_{RC}$  = the relative mass of a resident tracer retained after time period  $t$

- $r$  = radius of the PFM cylinder  
 $R_{dc}$  = retardation of contaminant on the sorbent  
 $\theta$  = volumetric water content in the PFM

Subsequently, as further defined in Hatfield et al. (2004), the mass flux ( $J_c$ ) may be calculated by multiplying the specific discharge of the aquifer ( $q_0$ ) by the flux averaged concentration ( $C_F$ ):

$$J_c = q_0 C_F \quad (4-17)$$

where

- $J_c$  = time-averaged advective contaminant mass flux,  $M/L^2/t$  (e.g., mass/area/time)  
 $C_F$  = flux averaged concentration of contaminant in the groundwater,  $M/L^3$  (e.g., mass/volume)  
 $q_0$  = specific discharge of the aquifer,  $L/t$  (e.g., length/time)

#### 4.3.1 Simplified Method

This process of determining the mass flux can be simplified. If reversible, linear, and instantaneous contaminant partitioning between the water and sorbent is assumed, the contaminant mass flux ( $J_c$ ) can be determined from eq. 4-18 (modified from Annable et al. 2005):

$$J_c = \frac{qM_c}{\alpha\pi r^2 L(1 - M_{RC})\theta R_{dc}} \quad (4-18)$$

where

- $M_c$  = mass of contaminant sorbed  
 $L$  = length of the sorbent matrix for the vertical thickness of aquifer interval sampled  
 $R_{dc}$  = retardation of contaminant on the sorbent  
 $M_{RC}$  = the relative mass of a resident tracer retained after time period  $t$  where the tracer has the same retardation as  $R_{dc}$   
 $\theta$  = dimensionless water content in the PFM  
 $q$  = specific discharge of water through the PFM  
 $r$  = radius of the PRM cylinder  
 $\alpha$  = convergence or divergence of flow around the PFM

This equation combines a few steps already discussed.

To determine the contaminant flux ( $J_c$ ) for high values of  $R_{dc}$  or a short exposure period, the assumption can be made that all contaminant mass entering the monitoring well is adsorbed by the PFM sorbent. The following simplified equation (Annable et al. 2005) can then be used:

$$J_c = \frac{M_c}{2\alpha r L t} \quad (4-19)$$

where

- $M_c$  = mass of contaminant sorbed

- $L$  = length of the sorbent matrix for the vertical thickness of aquifer interval sampled  
 $r$  = radius of the PFM cylinder  
 $t$  = exposure period of PFM to groundwater  
 $\alpha$  = convergence or divergence of flow around the PFM

A total time-averaged contaminant mass discharge  $M_d$  ( $M/t$ ) may be determined by spatially integrating the incremental measures of contaminant mass flux  $J_c$  ( $M/L^2/t$ ) and specific discharge  $q_0$  ( $L/t$ ) across the control plane of area  $dA$  ( $L^2$ ) (modified from Hatfield et al. 2004).

$$M_d = \int_{A_s} J_c dA = \int_{A_s} q_0 C_F dA \quad (4-20)$$

where

- $C_F$  = flux averaged contaminant concentration in groundwater,  $M/L^3$  (e.g., mass/volume)  
 $A_s$  = source area or the area of the control plane orthogonal to groundwater flow,  $L^2$

Similar to the transect method, the integration in eq. 4-21 can be approximated by summing sectionalized mass flux values across the control plan (Figure 2-3) where the sectionalized values can be obtained by interpolating the actual mass flux measurements from multiple locations. Any interpolation method can be used for this regionalization, and the results are subject to the benefits and limitations of the selected interpolation method. For example, the Thiessen polygon method introduced in Step 4 of Section 4.1.1 can be used and the approximation equation as follows:

$$M_d = \sum_{i=1}^n J_i A_i \quad (4-21)$$

where

- $M_d$  = mass discharge,  $M/t$  (mass/time)  
 $J_i$  = mass flux estimate at location  $i$ ,  $M/L^2/t$  (mass/area/time)  
 $A_i$  = area of polygon  $i$ ,  $L^2$  (length<sup>2</sup>), the area that the mass flux estimate  $J_i$  represents  
 $n$  = number of polygons sectionalizing the control plan

Although there are several technologies available to estimate mass flux, the PFM can directly measure subsurface solute flux at the monitoring locations in the plume, which the transect method alone cannot, and can provide a simultaneous measure of both cumulative groundwater and contaminant fluxes. The PFM is able to show variations in groundwater and contaminant fluxes over the depth of an aquifer, which contributes to better spatial interpretation and subsequently better site characterization.

#### 4.3.2 Sensitivity/Uncertainty

The PFM is a developing technology which provides mass flux data similar to data collected by other sampling methods under specific conditions. For example, the PFM test methods have been compared to other mass discharge measurement methods at two sites (Brooks et al. 2008):

- Hill AFB
  - pretreatment—PFM: 76 g/d, TM: 78 g/d
  - post-treatment—PFM: 6 g/d, TM: 7.2 g/d
- Ft. Lewis
  - pretreatment—PFM: 646 g/d, TM: 599 g/d
  - post-treatment—PFM: 2.3 g/d, TM: 1.9 g/d

Section 4.2.5 has a description of both sites. Variation 3 was used to compute the mass discharge for the transect method. The absolute accuracy of either method is not known. The relative differences between the two methods ranged from –17% to –8% as determined by subtracting the PFM measurements from the TM measurements and dividing by the TM measurements. The differences are relatively small considering the variability in groundwater flow and groundwater monitoring data and the overall range in mass discharge estimates, which has a factor of 200 or more.

However, there are several uncertainties associated with the PFM technology:

- Biostimulation conducted at National Aeronautics and Space Administration (NASA) Launch Complex (LC)-34 site appeared to influence the mass flux calculations (ESTCP 2006b). The integrity of the tracer alcohols appeared to be compromised during biostimulation and bioaugmentation, which subsequently overestimated water flux. This result was demonstrated as initial estimate of groundwater flux estimates made by the PFMs and multilevel samplers (MLSs) were within 20% when using ethanol as a tracer. During biostimulation, the isopropanol tracer provided an estimate within 30%. After bioaugmentation, estimates were within 67%. Also during bioremediation, when comparing the estimates of contaminant fluxes using the PFMs and the transect method, the estimates were significantly different (95%–189%). PFM estimates for vinyl chloride and ethene fluxes were much higher than estimates using the transect method or extraction well data. This suggests that the PFM sorbent trapped volatile compounds or that TCE and DCE degraded while on the sorbent (Baumann 1989, Scamehorn 1979, ESTCP 2006b.)
- At the second site (Port Hueneme, see Appendix B), the authors noted that PFMs installed in pushed wells tended to calculate a lower groundwater and contaminant flux than those installed in drilled wells. This was also observed by Bartlett et al. (2004) and ESTCP (2006c). However, the flux-averaged concentrations ( $C_F$ ) between the drilled and pushed wells did not vary significantly. This observation may be related to convergence or decreased hydraulic conductivity associated with the pushed wells.
- The PFM technique appears better suited to quantify mass discharge in a permeable unconsolidated aquifer. A new type of PFM device for fractured-rock applications is being developed under ESTCP (see [www.estcp.org/Technology/ER-0831-FS.cfm](http://www.estcp.org/Technology/ER-0831-FS.cfm)). Site characterization requires a detailed understanding of the geology to understand how best to construct and place the PFMs.
- The PFM records a point measurement over time and therefore does not account for contaminants in flow paths not intercepted by the flow meter. As with all of these methods,

the PFM assumes horizontal flow, which may not be valid at all sites. The authors' experience is that vertical flow occurs at most sites but is generally small compared to the horizontal flow. However, there are certainly cases where vertical gradients are important or even dominate. In these cases mass flux/discharge measurement techniques should be evaluated carefully to determine whether the vertical flow will cause faulty results.

Hatfield et al. (2004) reported that the use of PFMs in the field poses several challenges. First, multiple wells and PFMs are needed to estimate total contaminant discharge through the transect. The resultant discharge estimate is sure to contain uncertainties, as it is generated from spatially integrating point measures of flux. Second, competitive sorption or rate-limited sorption may limit the ability of the PFM to capture and retain target contaminants. If either is not considered in the interpretation of results, calculations may not reflect true contaminant fluxes. Finally, long-term flux monitoring may be problematic because natural changes in flow direction can invalidate flux measurements. PFMs should not be applied in wells that contain NAPLs, as shown by a technology evaluation study performed at one site.

#### **4.4 Transects Based on Isocontours**

At some sites, direct mass flux estimates are not available by any of the methods described in the previous section. In that case, data from existing monitoring well networks can be used to develop mass flux estimates (Nichols and Roth 2004). In this case, monitoring points that are not located in a transect are used to construct a contour map of groundwater concentrations, either by hand or by using computer contouring tools supervised by knowledgeable groundwater personnel. The key point behind the isocontour-based transect approach is that the resulting contour lines represent the hydrogeologist's best estimate of the distribution of concentration in a plume. If there are a sufficient number of monitoring points and if the hydrogeologist's contouring is accurate, the resulting isocontour-based transects would be similar to an actual transect constructed in the field. If there is reason to doubt the accuracy of the contour lines due to a limited number of monitoring well points, then the resulting mass flux estimates will have higher uncertainty. In other words, if a groundwater contour map is accurate enough to be used for regulatory and/or design purposes, then it is likely that there is useful information that can be converted to mass flux and mass discharge estimates.

Figures 4-11 and 4-12 show an example of this method for a single-level monitoring system. In this example, the general method is the same as that described in Section 4.1.1 but with the measurement points being the intersection of contour lines and the isocontour-based transect rather than an actual monitoring point. In this case the width of each polygon is the distance between contour lines on a transect, and the depth is the saturated thickness of the aquifer.

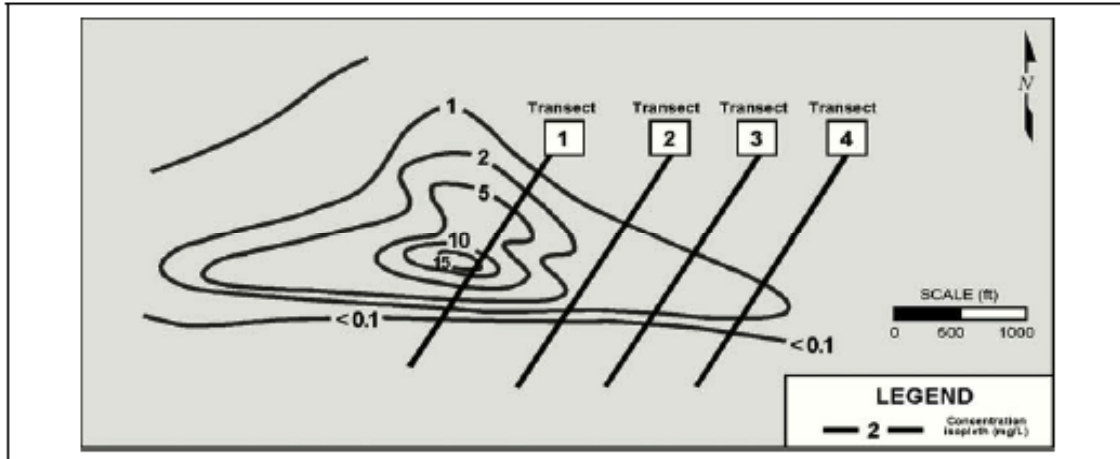


Figure 4-11. Example transects, Dover AFB, Delaware. (Adapted from Einarson 2001.)

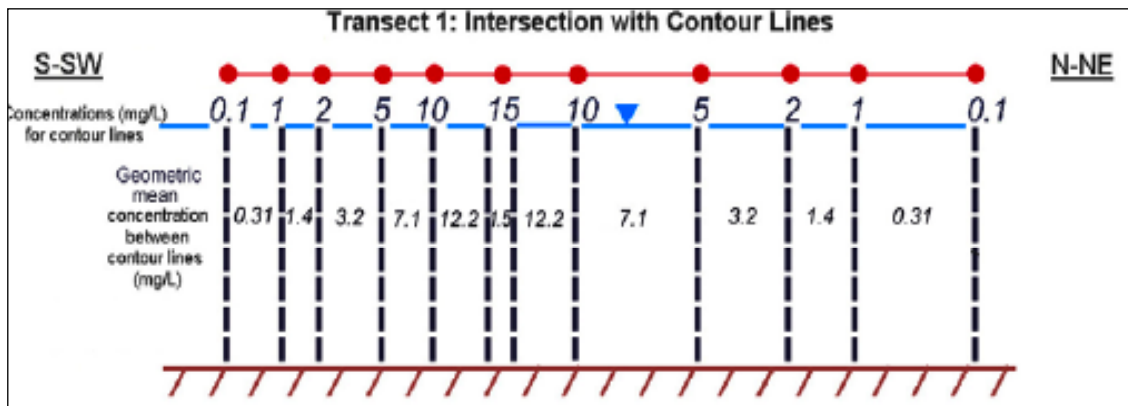


Figure 4-12. Example two-dimensional transect based on isocontour data.

This method may have more uncertainty than high-density multilevel transect data. Care must be taken using this method as contours prepared by either hand or computer that do not sufficiently consider the site-specific geology and controlling preferential pathways often seen in contaminant transport may be misleading. The contours must also take into account vertical variations in flow and transport pathways and distribution. However, useful mass flux estimates may be generated if the monitoring well network is sufficiently dense. The method will be more accurate when the screened interval of the wells in the monitoring network intercepts all or a large fraction of the contaminated plume thickness and when the sample that is collected represents a flow-weighted average concentration. For the last condition, low-flow sampling may not yield a flow-weighted average concentration if the sample is not collecting water from the entire screened interval. Long-screened wells are proposed by some researchers as an inexpensive tool to provide mass discharge data because multiple vertical samples are not needed; rather, the well will represent the flow-weighted concentration of the plume at this location. This method will provide mass discharge information but does not provide any information on the likely maximum concentration at that monitoring point due to the vertical averaging.

#### 4.5 Solute Transport Models

Several solute transport models have dedicated routines to calculate mass flux from the model input data (Nichols and Roth 2004; Farhat, Newell, and Nichols 2006; see Table 4-3). These models require that both groundwater flow data and contaminant data be entered into the model where it is processed to generate output, typically in the form of groundwater concentrations. However, since both flow and concentration data are used in the model, mass flux data can often be obtained from the application of a solute transport model.

**Table 4-3. Solute transport models used for mass flux estimates**

Model	Application and type	Type of mass flux output	Source
BIOSCREEN	Fuel hydrocarbon MNA Analytical	Calculated from a 5 × 11 array of concentration values	<a href="http://www.epa.gov/ada/csmos/models.html">www.epa.gov/ada/csmos/models.html</a>
BIOCHLOR	Chlorinated solvent MNA Analytical	Calculated from a 5 × 10 array of concentration values	<a href="http://www.epa.gov/ada/csmos/models.html">www.epa.gov/ada/csmos/models.html</a>
BIOBALANCE	Chlorinated solvent MNA Analytical	Calculated from a 30 × 30 array of concentration values	<a href="http://www.gsi-net.com/software.asp">www.gsi-net.com/software.asp</a>
MODFLOW/MT3DMS	General Numerical	Calculated at source/sink objects	<a href="http://chl.ercd.usace.army.mil/chl.aspx?p=s&amp;a=ARTICLES!610">http://chl.ercd.usace.army.mil/chl.aspx?p=s&amp;a=ARTICLES!610</a>
MODFLOW/RT3DMS	General, sequential degradation Numerical	Calculated at any transect in model using the rtFlux module	<a href="https://fx.pnl.gov/Files.aspx?EmailID=d9b0eb8e-eb03-45f9-ac65-8fed982667e7">https://fx.pnl.gov/Files.aspx?EmailID=d9b0eb8e-eb03-45f9-ac65-8fed982667e7</a>
MODFLOW/MT3D	General Numerical	Can be calculated externally in spreadsheets using ZoneBudget routine for flow and concentration output	NA
MODFLOW/MT3D	General Numerical	The TOBS Package can calculate the (total) mass flux for selected individual objects such as a section of a river	<a href="http://chl.ercd.usace.army.mil/chl.aspx?p=s&amp;a=ARTICLES!610">http://chl.ercd.usace.army.mil/chl.aspx?p=s&amp;a=ARTICLES!610</a>
REMChlor	Hydrocarbon, chlorinated solvent	Calculated using analytical model	<a href="http://www.epa.gov/ada/csmos/models.html">www.epa.gov/ada/csmos/models.html</a>

Examples of this approach in the literature include the following:

- Clausen et al. (2003) used “MODFLOW coupled with MT3D to conduct a transport simulation. Mass was added to the model at the source until a reasonable match was obtained between the model simulated groundwater plume and the actual plume. Once this was achieved, the model was used to determine the flux rate of RDX to groundwater, which turned out to be approximately 0.1 kg/year.”
- Christensen, Korsgaard, and Riss (2002) used a transient unsaturated zone model to estimate a mass flux of 0.15 kg/year of PCE to groundwater.



- Thuma, Kremesec, and Kolhatkar (2001) used MODFLOW and MT3D to simulate an MtBE plume in Long Island and calculated mass discharge, which was called “mass flux” in their paper, at three locations. The modeled mass discharge near the source zone (310 g/d) was similar to the mass discharge measured via the transect method (250 g/d). Larger differences between the mass discharge generated by the model and the transect method occur because the model may not have captured degradation of MtBE in the downgradient portion of the plume.
- Eberts et al. (2005) used the BIOCHLOR model at a phytoremediation site in Texas to estimate total mass changes over distance. The model indicated that there was a 44% decrease in mass discharge of TCE, referred to in this paper as “mass flux,” partially due to biodegradation related to cottonwood trees.
- Johnson, Truex, and Clement (2006) reported on the use of the rtFlux module in RT3D at a site where mass discharge rates of 160,000 g/d for a no-pumping case and ~8 g/d for a case where pump and treat was used to hydraulically contain a large plume.
- The MODFLOW/MT3D model was applied to a large, multisource industrial site in the Midwest and provided an estimate that ~50,000 g/d of mass discharge of chlorinated compounds would occur without the presence of groundwater containment system. A containment system was predicted to reduce this mass discharge by over 90%.

#### 4.6 Key Considerations Using Models to Obtain Mass Flux

The different types of models are based on different assumptions and calculation techniques. Analytical models make use of simplifying assumptions such as uniform one-dimensional flow fields, simple source characteristics, and other factors that make these models useful for screening or planning purposes. As would be expected, the mass flux estimates from an analytical model also would be better suited for screening or planning purposes as opposed to the case where very detailed mass flux data are required to ensure the reliability of some type of remedial design at large or very complex sites. The accuracy of mass flux data from numerical models would, as expected, be very dependent on the accuracy of the input data for flow and contaminant concentration and mass.

The amount of data available to input into the model is also significant. If there are not enough data to generate node sizes appropriate to the local geology and hydrogeology, the model may oversimplify site conditions. Care must also be taken during model uncertainty assessment and calibration to ensure site conditions are accurately represented.

One study of an MtBE plume on Long Island (Thuma, Kremesec, Kolhatkar 2001) compared the MtBE mass discharge using the transect method to the mass discharged derived from a groundwater solute transport model. The results were similar: 250 g/d for the transect method and 310 g/d for the model (24% relative difference). As mass discharge measurements between sites can vary over many orders of magnitude, these two values (250 and 310 g/d) are very close.

#### 4.7 General Comparison of Five Mass Flux Measurement Methods

A qualitative comparison of five mass flux measurement methods was developed by Goltz et al. (2007) and is presented in Table 4.4. The five methods were as follows:

- transect method (TM)
- passive flux meter (PFM)
- integral pump test (IPT) (The original paper referred to this as integral groundwater investigation method.)
- modified integral pumping test (MIPT) (The original paper referred to this as integral pump test method, or IPT)
- tandem circulation wells (TCW) (The original paper referred to this as tandem recirculation wells, or TRW)

**Table 4-4. Comparison of groundwater contaminant flux measurement methods**  
(Modified from Goltz et al. 2007.)

Methods		Implementability	Regulatory considerations	Availability	Cost
Point	Transect	1 <sup>a</sup>	1	1	4
	PFM	3	2	2	4
Integral	IPT	3	3	2	2
	MIPT	1	3	2	2
	TCW	4	3	4	1

<sup>a</sup> 1 = best, 4 = worst.

Four metrics were evaluated: implementability, regulatory, availability, and cost. No site-specific limitations for any specific method were provided by the authors, suggesting that each method is applicable to a wide range of contaminants and hydrogeologic settings. Additional comments regarding how these methods compared are reproduced below (Goltz et al. 2007):

**Implementability.** This is a measure of how straightforward and simple application of each method would be. The conventional transect method, which consists of installing monitoring wells in order to measure the hydraulic gradient and contaminant concentrations, as well as conducting a pumping test to estimate hydraulic conductivity, is simple to implement. All steps in applying the method are commonly applied in the field and well understood. The MIPT method is equally straightforward, requiring installation of standard pumping and monitoring wells. The PFM, IPT, and TCW methods are somewhat more complex. The PFM method requires quantification of the contaminant which is sorbed onto the sorbent, as well as measurement of the loss of resident tracer. Also, data interpretation requires estimation of the aquifer area associated with each PFM. These measurements require special expertise. The IPT requires interpretation of the (concentration vs. time) data, which is somewhat complex (Bockelmann, Ptak, and Teutsch 2001; Zeru and Schäfer 2005). To implement the TCW method requires construction of special dual-screened wells. The downflow well in particular requires special construction in order to pump water downwards. Also, data interpretation requires somewhat complicated inverse modeling techniques.

**Regulatory.** Both the TCW and PFM methods involve injecting tracers into the aquifer, and this may raise some regulatory concerns. In addition, the TCW method involves circulating contaminated groundwater in the subsurface. If contaminant concentrations vary in space (particularly vertically), this may also concern regulators. The IPT and

MIPT methods are of concern since they require contaminated groundwater extraction. The conventional transect method poses the least regulatory concern.

**Availability.** The transect approach is well understood, has appeared many times in the literature, and involves no special expertise to implement. Therefore, it is readily available from most purveyors of groundwater remediation services. The other methods are all in some stage of technology transfer, with the PFM and IPT methods furthest along, followed by the MIPT and TCW methods. The PFM and IPT methods are well documented in the peer-reviewed literature and could probably be applied by well-trained practitioners who are familiar with the literature. Although the IPT method is new and the method has yet to be documented in the literature, the steps in implementing the method are conventional. Currently, the TCW method is unavailable for field application. The method has yet to appear in the peer-reviewed literature, and implementation would require the assistance of the technology developers.

**Cost.** It is difficult to quantify the cost and the cost/benefit of acquiring detailed mass flux information. It is generally perceived that knowing the mass flux would help regulators and consultant, but it is difficult to quantify these perceived benefits. As more case studies become available, this information may be forthcoming. Please see Kram et al. (2008) for additional information on cost and performance of HRP coupled to the GeoVIS.

Though mass flux is a well-established concept, interest in its use has increased considerably because recent developments have made mass flux estimates more useful and cost-effective (Ptak, Schwarz, and Teutsch 1998; Hatfield et al. 2002a, 2002b). When used in conjunction with traditional techniques that are commonly required by regulatory agencies (e.g., point estimates of concentration, etc.), there may be considerable benefits to be gained by implementing an assessment and remediation plan that includes a flux characterization component. These may include the following:

- reduce the volume of the treatment zone by providing evidence of the high-flux tubes, thereby allowing targeted treatment
- improve the understanding of appropriate active remediation contaminant levels that may and must be achieved by allowing better validation of the natural attenuation capacity of the aquifer system
- improve the estimation of the treatment duration by examining mass flux as a function of time along a downgradient plane

Goltz et al. (2007) did not evaluate one frequently used method, mass discharge estimation using transects based on isocontours (Section 4.4), in their comparison of different mass discharge methodologies. This method has the advantage of being very inexpensive, as most site assessment programs result in isocontour maps of concentration. For certain questions (such as a screening analysis to estimate plume strength), mass discharge estimation using transects based on isocontours is perceived by some practitioners to be a very cost-effective way to obtain useful site data.

## 4.8 Managing Uncertainty

As has been discussed in previous sections, mass flux and mass discharge estimates can be applied in several phases of the site investigation and remediation process. These estimates, while very useful, are also characterized by significant uncertainty due to the method by which they are developed (Section 2.5). The challenge then is to determine the acceptable level of uncertainty for the intended application of mass flux or discharge estimates and how to manage that uncertainty. While what is “acceptable” will be driven by site- and project-specific factors, such as carcinogenicity of the COC and the proximity and sensitivity of potential receptors, there are general constraints in managing or reducing downside risks of uncertainty:

- Level of available funding—Increased sample collection and infrastructure increase capital and labor costs.
- How the flux estimates will be used—Monitoring natural attenuation processes may tolerate more uncertainty than demonstrating compliance.
- Phase of the project—More accurate data may be more useful during certain task or project phases, justifying more sampling and infrastructure installation.
- Project participants’ experience with and confidence in mass flux estimates.

Mass discharge can have a wide range when comparing source strength for different sites. For example, the case studies listed in Appendix A have a range of eight orders of magnitude for mass discharge (0.00078–160,000 g/d) measured at various sites. This is not unexpected because hydraulic conductivity values can range over six or seven orders of magnitude and concentrations can also span a similar range. Therefore, the accuracy of mass flux estimating methods should be considered in this context. In other words, mass flux or mass discharge estimates with uncertainty of an even order of magnitude (factor of 10) can still provide useful information for site management. The data quality objectives related to the use of a mass flux or mass discharge estimate should be determined to ensure that an appropriate method with sufficient data density is used for their development. For example, detailed design projects need more-refined mass flux/discharge estimates, while screening level studies can be successful despite higher uncertainty in the mass flux/discharge estimates.

In highly heterogeneous environments, it may not be cost-effective, or even physically possible, to collect enough samples to obtain a sound estimate using conventional statistical methods. Research is needed to develop statistical approaches that allow for cost-effective determination of integrated mass flux in natural aquifers.

## 5. KEY FINDINGS

This technology overview summarizes the concepts underlying mass discharge and flux, their potential applications, and case studies of the uses of these metrics. Review of the case studies showed that mass discharge and flux estimates have been useful for several site management objectives and that evaluating mass flux and discharge can improve CSMs and lead to more efficient remediation. Specific findings from the case study review include the following:

- **Mass discharge and flux data have improved decision making.** For example, they have been used to trigger transition between technologies.
- **Mass discharge and flux data have reduced remediation costs.** For example, mass flux estimates have been used to identify high-priority layers in stratified aquifers, leading to more cost-effective cleanup.
- **Mass discharge and flux data have been used to prioritize sites.** For example, responsible parties have used mass discharge estimates to identify the sites needing further characterization and remediation within regional flow systems impacted by multiple sources.
- **Mass discharge and flux data have been used to predict remediation performance.** Mass discharge, high-resolution mapping, and available analytical tools have provided the basis for estimation of natural attenuation rates, plume responses to source treatment, and remediation time frames.
- **Transect testing has been by far the most common method used, and transects have proven useful for site management.** Use of well transects has provided more credible estimates of natural attenuation rates than the more typical practice of relying on a line of wells along a flow path because transect data are less susceptible to temporal variations in flow direction and strength
- **Mass flux and discharge estimates can estimate exposure.** Other uses of mass flux and mass discharge data include risk assessment, particularly when evaluating risks to potential downgradient receptors or when assessing the risks of vapor intrusion into buildings located above contaminated groundwater. In many cases, this information is used in the underlying models, but its importance is not recognized, and the estimates may be highly uncertain.

Key conclusions from this overview of mass flux and mass discharge include the following:

- Mass discharge and flux estimates have proven valuable for contaminated site management and should be used more frequently.
- Use will increase rapidly as the benefits of flux and discharge information are more widely recognized.
- A specific estimation method may be better suited to specific site conditions and objectives, so it is important to consider the advantages and limitations of the methods available.
- Useful mass discharge and flux estimates often can be developed from existing site data and/or limited site sampling, often for relatively little cost.
- All methods of mass flux and discharge estimation involve uncertainty that should be recognized and quantified, to the extent practicable, when considering use of the parameters. However, concentration-only data may have similar, or greater, uncertainty.

- Strategies to manage uncertainty include precharacterization and sampling in stages.
- Mass discharge can also have an important role in regulatory decisions and may have advantages over concentration data for some purposes. Examples include deciding when to shift from aggressive treatments to natural attenuation, evaluating DNAPL source remediation efforts, or even for determining when no further action is required at a site.

## 6. RESEARCH NEEDS

- Research is needed to develop statistical approaches and models that allow for cost-effective estimation of mass flux and mass discharge in contaminated aquifers and a delineation of the associated uncertainty.
- Additional methods should be developed to improve the reliability of various mass flux and mass discharge measurement techniques.
- Additional studies comparing new mass measurement methodologies with the transect method should be conducted.
  - comprehensive comparison of key methods and method categories to each other (point vs. point, boring vs. boring, transect vs. transect, and mixed comparisons [e.g., three-dimensional distributions based on points/borings vs. three-dimensional distributions based on transects])
- New method-specific “application” guidance documents should be prepared as new methods and technologies to measure mass flux and mass discharge have been validated.
- Refine the methodologies used to convert discharge estimates obtained using a transect to predicted concentration ranges at a receptor. This is a key to refining the exposure rate at the receptor as compared to the following:
  - exposure rates dependent upon only concentration-based estimates
  - regulatory standards (e.g., drinking water MCLs)This could serve to bridge the current gap between engineering performance metrics based on reduction of mass and regulatory performance metrics based on a linkage to anticipated reduction in concentration at a receptor.
- More work should be performed evaluating the use of mass flux and discharge estimates over time to determine the age of the release and the total mass of the release.
- Development of plume classification systems that rely on the mass flux/mass discharge concepts.
- Determine the accuracy and reliability of mass flux/mass discharge measurements made with rapid screening tools (such as the MIP and advanced piezocone).
- Studies to determine whether long-screen wells (screen intervals of 5 feet or more) are accurately averaging the mass flux information into a single concentration measurement and

to determine the overall accuracy and applicability of mass flux/mass discharge measurements from transects using long-screened wells.

- Develop focused methods to accurately measure mass discharge from specific sources, such as diffuse, low-strength sources associated with low-permeability compartments that have been charged with contaminants via matrix diffusion.

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## **Appendix A**

### **Mass Flux Case Study List**



**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
1	Annable et al. 2005	CFB Borden, Ontario	PCE and TCE	Site characterization—Evaluated depth-specific mass flux and specific discharge using PFM.	Pumping well, passive flux meter (PFM)	Not applicable (n/a)	n/a
			MtBE	Site characterization—Evaluated depth-specific mass flux and specific discharge using transect method (TM) with PFM and TM with multilevel sampling (MLS) wells and identified increasing mass discharge with distance from initial source due to transient conditions.	TM, PFM	n/a	n/a
2	Barbaro and Neupane 2006	Dover AFB, Delaware	VOCs	Site characterization—Used $M_d$ values calculated from two transects to evaluate natural attenuation along the flow path.	TM	Detailed three-dimensional plume delineation improved conceptual site model (CSM) and provided more reliable determination of plume attenuation rate between two transects.	Used a uniform specific discharge across both transects based on relatively uniform head distribution, lithology, and aquifer thickness in the vicinity of the two transects.
3	RTDF 1998	Dover AFB, Delaware	Total chlorinated organics	Site characterization—Used multiple transects to evaluate the degree to which natural attenuation was occurring downgradient of a source zone.	Indirect—synthetic transect from contours	n/a	n/a

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
4	Basu et al. 2006	Former electronic parts manufacturing plant, midwestern United States	TCE	Site characterization and evaluation of remediation alternatives— Measured mass flux and mass discharge to characterize (a) site hydrogeology, (b) source strength, (c) vertical delineation of specific discharge and contaminant flux at well locations, and (d) degradation rates. Isoconcentration contours and depth-specific Darcy flux were used to estimate mass discharge at three transects transverse to groundwater flow for the purpose of calculating a biodegradation rate. Depth-integrated mass flux was calculated at various locations along a cross section parallel to groundwater flow.	PFM and isoconcentration contour transects	Depth-discrete flux monitoring indicates that the zone of higher permeability and lower concentrations needs to be considered as a target zone for remediation because it represents a relatively large portion of the source strength, which shows that focusing remediation only in the zone of high concentrations may be “suboptimal.” Detailed contaminant flux vertical profiles revealed valuable information about the upgradient source distribution that could not be determined using conventional monitoring well data. High-resolution profiles of specific discharge versus depth determined using the PFM provide valuable information about variability in hydraulic conductivity that may affect the distribution of injected solutions during remediation.	PFM was used to quantify specific discharge at approximately 0.3 m intervals. The average specific discharge determined using the PFM for shallow, intermediate, and deep zones were compared to specific discharge estimates based on average single-well response tests for monitoring wells completed in corresponding horizons.
5	Basu et al. 2009	Former manufacturing site, Australia	TCE	Site characterization—Used $M_d$ values to compare mass discharge from source zone to $M_d$ in plume about 175 m downgradient to evaluate potential for natural attenuation of TCE. Determined that higher $M_d$ in plume relative to smaller source zone $M_d$ is because of declining source concentrations and six-year travel time between the source and plume control plane transects.	Transects using PFMs	Flux-based site management approach in heterogeneous aquifer resulted in improved CSM, which will lead to improved effectiveness of site remediation measures. Mass flux and specific discharge measurements were used to demonstrate that residual DNAPL mass was present in low-permeability zones and that source treatment was unwarranted.	PFMs were used to quantify specific discharge at approximately 0.3 m intervals over different periods of time to allow for assessment of seasonal fluctuations.

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
6	Bauer et al. 2004	Linz, Austria	PCE, TCE	Risk prioritization based on regional characterization of relative strengths of multiple source zones at different sites—Used the integral pumping test (IPT) method to evaluate mass discharge at three transects. Purpose was to quantify the relative strength of multiple source zones contributing to a dissolved plume. Two to five pumping wells were used on each transect. Water generated during pumping tests was disposed to the sewer system without treatment. Source zones between transects were identified as being stronger than upgradient sources.	IPT	Basin-wide mass discharge analysis determined which source zones should be targeted for further characterization and remediation and identified which portions of the aquifer could be excluded from further investigation and remediation.	n/a
7	Beckett, Stanley, and Walsh 2005	Fuel release site, Morro Bay, California	MtBE	Mass discharge framework used to evaluate potential threat of MtBE plume to nearby water supply wells.	n/a	n/a	n/a
8	Bockelmann, Ptak, and Teutsch 2001	Former manufacturing site near Stuttgart, Germany	BTEX, polycyclic aromatic hydrocarbons (PAHs)	Site characterization—Evaluated natural attenuation between two transects situated at distances of 140 and 280 m downgradient of the source zone. Mass discharges at each transect were used to estimate first-order biodegradation rates. Each transect included four pumping wells, and the average travel time between the two transects under static conditions is 70 days.	IPT based on wells along transects	Mass discharge estimated using the IPTs facilitated the estimation of natural attenuation rates in a highly heterogeneous aquifer with a curvilinear flow path. Changes in mass discharge of electron acceptors and metabolic by-products between transects was also evaluated to provide additional lines of evidence for biodegradation.	n/a

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
9	Bockelmann et al. 2003	Former manufacturing site near Stuttgart, Germany	BTEX, PAH	Site characterization—Compared the mass discharge across two transects using two approaches: (a) integrating mass flux estimated at each well based on point-source concentrations and (b) IPT method. Also estimated plume attenuation rates for BTEX and PAH species between three transects using three methods: (a) conventional concentration vs. distance attenuation estimates along the flow path, which was determined based on a natural gradient tracer test; (b) mass discharge at each transect based on integrated mass flux; and (c) mass discharge based on IPTs. Transects are 30, 140, and 280 m downgradient of the source zone. Each transect incorporated four monitoring wells with approximate spacing of 30–40 m between. Investigators determined that mass discharge estimates using monitoring well concentrations and well spacing of 30–40 m at this site resulted in significantly different discharge estimates than the IPT method (up to 159% difference).	TM	Evaluated uncertainty when using large spacing between wells along transect for estimating mass flux.	n/a

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
10	Borden et al. 1997	Sampson County, North Carolina	MtBE, BTEX	Site characterization—Installed four transects up to 177 m downgradient of the source zone to delineate vertical and horizontal contamination and to facilitate estimation of biodegradation rates along the flow path. Five to six clusters of monitoring wells were installed along each transect. At each location, typically three wells were installed at different elevations, each having a 1.5 m screen length. The well screen length was selected to facilitate a flux-averaged evaluation over 1.5 m. The use of mass discharge to estimate biodegradation rates reduced uncertainty by eliminating the effect of vertical and transverse dispersion and mitigating the effect of nonideal well placement. Temporal variations in mass discharge were also evaluated over a two-year period.	TM	Using mass discharge to estimate plume attenuation rates between transects overcame previous limitations in estimating a biodegradation rate along the nonlinear flow path. Used medium-resolution vertical sampling with flux-averaged concentrations in 1.5 m well screens to estimate mass discharge and plume attenuation at each transect. Further vertical delineation was not required for this study.	n/a
11	Brooks et al. 2008	Hill AFB, Utah	TCE and cis-1,2-DCE	Remediation performance monitoring—Compared the mass discharge at a transect approximately 10–15 m downgradient of the source zone before and after remediation to assess performance efficiency. Multiple methods were used for mass discharge estimates to reduce uncertainty. Ten monitoring wells situated on the transect with approximate spacing of 3 m.	PFM, modified integral pump test (MIPT), TM	Demonstrated that source treatment resulted in a significant reduction in mass discharge from the source. Multiple methods were used to estimate mass discharge to reduce the uncertainty of the remediation performance assessment. High-resolution mass flux delineation indicates a potential reduction in source zone permeability due to stimulated biodegradation that occurred as a result of source treatment.	PFM and IPT

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
12	Brooks et al. 2008	Fort Lewis, Washington	TCE and cis-1,2-DCE	Remediation performance monitoring—Compared the mass discharge at a transect approximately 6 m downgradient of the source zone before and after remediation to assess performance efficiency. Multiple methods were used for mass discharge estimates to reduce uncertainty. Ten monitoring wells situated on the transect with approximate spacing of 5 m.	PFM, MIPT, TM	Demonstrated that source treatment resulted in a significant reduction in mass discharge from the source. Multiple methods were used to estimate mass discharge the reduce the uncertainty of the remediation performance assessment. High-resolution mass flux delineation indicates a potential reduction in source zone permeability due to stimulated biodegradation that occurred as a result of source treatment.	PFM and IPT
13	Brusseau et al. 2007	Tucson International Airport area, Arizona	TCE	Remediation performance monitoring—Used mass removal data from an operating pump-and-treat system to confirm the presence of NAPL in the source zone and evaluated the transient relationship between mass flux reduction and source mass depletion.	n/a	Mass removed by the pump-and-treat system over 19 years was reported to be higher than the initial estimate of dissolved-phase mass, suggesting that NAPL is present in the source zone. Partitioning interwell tracer testing to measure source mass indicates that a 90% reduction in mass flux occurred with only a 50% reduction in source mass. This detailed characterization helps to improve the effectiveness of site management decisions.	n/a
14	Burton et al. 2002	Beach Point, Maryland	Chlorinated solvents and heavy metals	Risk assessment—Evaluated potential risks associated with discharge of chlorinated solvents and heavy metals from the Beach Point surficial aquifer to Bush River, a tributary of Chesapeake Bay.	n/a	Groundwater discharge was used to evaluate dilution in the surface water body and the applicability of a Maryland “regulatory mixing zone,” i.e., a localized discharge zone in which local water quality standards may be exceeded.	n/a
15	Buscheck, Nijhawan, and O’Reilly 2003	Gas station, Tahoe City, California	MtBE	Mass discharge used to evaluate potential impact to downgradient river.	n/a	n/a	n/a

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
16	Buscheck, Nijhawan, and O'Reilly 2003	Fuel terminal, San Jose, California	MtBE	Mass flux measured to select optimal rate of dissolved oxygen addition to PRB with diffusive emitters.	n/a	n/a	n/a
17	Buscheck, Nijhawan, and O'Reilly 2003	Unnamed site	MtBE	Mass discharge measured at three transects to evaluate natural attenuation of plume.	n/a	n/a	n/a
18	Buscheck, Nijhawan, and O'Reilly 2003	10 fuel release sites in California	MtBE	Mass discharge values used to prioritize remediation. Shows sites with high $M_d$ values are not necessarily the sites with the highest concentrations.	n/a	n/a	n/a

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
19	USEPA 2009	Well 12A Superfund Site, Tacoma, Washington	Chlorinated solvents	Remedial action objectives and remediation performance monitoring —Based on computer modeling results, it was determined that a future reduction in mass discharge from the source zone of 90% would be sufficient to meet MCLs at the compliance wells, allowing for a future transition from active source remediation to MNA in the plume. Based on this work, an RAO developed for the site is a 90% reduction in mass discharge from the source zone. A transect of monitoring wells will be used to evaluate changes to mass discharge during active remediation and to assess changes in mass flux at other wells closer to the source zone. The compliance transect includes six horizontal locations with approximate spacing of 400 ft between locations, and each location includes two to three nested wells. The distribution of mass flux changes over time will be used to optimize the active remediation of the source zone. The PFM will be used to assess mass flux in monitoring wells.	TM using PFM	Use of a mass discharge reduction as an interim remediation goal provides a single metric for evaluating the integrated effect of source treatment and is directly related to the source strength that affects plume response to remediation. A mass discharge reduction goal can also be readily compared to the range of mass discharge reductions documented as being achievable for various technologies under site-specific conditions.	PFM



**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
20	Chapman and Parker 2005	Industrial site, Connecticut	TCE	Site characterization and remediation performance monitoring—Measured the mass discharge across a transect of MLS wells to evaluate the distribution of mass in the plume and assess the influence of source zone isolation conducted six years earlier.	TM	High-resolution vertical sampling resulted in an important refinement to the CSM because the zone of concentrated source strength in the aquifer is thinner than what was apparent based on conventional monitoring well data. A mass balance demonstrated that 3,000 kg of TCE was stored in the aquitard over a distance of 280 m downgradient from the source. Based on a conservative comparison to mass discharge across the plume transect after the DNAPL source had been isolated, the authors determined that it would take longer than 80 years for TCE mass stored in the aquitard to be removed. The measured mass discharge at the transect was also used in a mass balance to demonstrate that substantial mass depletion had occurred in the source zone due to natural dissolution over four decades prior to source zone isolation.	Specific discharge was applied as a uniform value along the transect because the variability of <i>K</i> in the mildly heterogeneous aquifer was much smaller than the variability in TCE concentrations.

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
21	Chapman et al. 2007	Industrial site, Connecticut	TCE, cis-1,2-DCE	Site characterization—Evaluated processes contributing to natural attenuation of chlorinated solvents across three transects situated between the DNAPL source zone and a river. The three transects were located 280–700 m downgradient from the source zone. The mass discharge investigation was conducted to facilitate the characterization of processes causing the natural attenuation of TCE and by-products along the groundwater flow path and to support a detailed mass balance assessment.	TM	A detailed mass discharge assessment significantly improved the CSM for contaminant transport pathways and the relative quantitative contribution of multiple attenuation processes. The mass balance included quantitative prediction of the relative mass discharged to local drainage streams versus the mass discharged from groundwater to a downgradient river. The mass balance also included quantification of mass loss through volatilization in local surface-water ponds.	Specific discharge was applied uniformly across all three transects.
22	Chapman et al. 1997	Former gasoline station, Ontario	BTEX	Remediation performance monitoring—Three transects were installed using MLS wells along each transect. The purpose of the transects was to evaluate the reduction in BTEX mass flux downgradient of a treatment zone consisting of passive wells containing oxygen-releasing compound between the first and second transect. Several monitoring events were conducted to evaluate changes to source mass discharge and treatment efficiency in the biobarrier over time.	TM	Mass discharge estimated at transects 2 and 3 was used to evaluate the degree to which natural attenuation was occurring downgradient of the biobarrier. The mass discharge calculations indicated that other organic and inorganic species represented significant sinks of oxygen which reduced the efficiency of BTEX treatment.	Specific discharge was applied as a uniform value along both transects. “Given the relatively small variation in flow velocity observed and the number of other unknowns, the assumption of a uniform velocity field is justified for these first-approximation estimates. The assumption of a uniform velocity field is not expected to significantly bias the conclusions drawn from these mass flux estimates, since the conclusions are based on differences between Fences 1 and 2.”
23	Einarson et al. 2005	MtBE release site, Calistoga, California	MtBE	Mass discharge calculations suggest release from one site responsible for chemical impacts detected in supply well.	n/a	n/a	n/a

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
24	Einarson and MacKay 2001	Port Hueneme, California	MtBE	Transect of MLS wells.	TM	n/a	n/a
25	Einarson and MacKay 2001	Site 1, Alameda Naval Air Station	cis-1,2-DCE	Transect of MLS wells.	TM	n/a	n/a
26	Einarson and MacKay 2001	Unnamed	MtBE	Transect of MLS wells.	TM	n/a	n/a
27	Einarson and MacKay 2001	Vandenberg AFB, California	MtBE	Transect of MLS wells.	TM	n/a	n/a
28	Guilbeault, Parker, and Cherry 2005	Florida	TCE	Site characterization—Measured the mass discharge across a transect downgradient of a source zone.	TM	High-resolution sampling improved the CMS with respect to hot-spot locations. Three distinct local high-concentration zones were identified with concentrations ranging 4%–15% of solubility. Approximately 60% of the source mass discharge was in <5% of the transect area, and 80% of the mass discharge was in <10% of the transect area.	Specific discharge was applied as a uniform value along the transect because the variability of <i>K</i> in the mildly heterogeneous aquifer was much smaller than the variability in concentrations.
29	Parker et al. 2008	Florida	TCE	Remediation performance monitoring—Estimated the change in mass discharge across a transect due to the implementation of a hydraulic control remedy downgradient of the source zone. The estimate of mass discharge change due to the source zone containment system was based on temporal changes in groundwater concentrations at multilevel wells along the transect, assuming that there was no change in groundwater specific discharge across the transect.	TM	The estimated mass discharge occurring in the plume after the source zone had been hydraulically isolated was used to demonstrate that the mass stored in a thin clay layer is much higher than the mass discharge rate. This comparison was used to illustrate that back-diffusion from a thin clay represents a long-term process likely to sustain concentrations in the plume above MCLs.	n/a

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
30	Guilbeault, Parker, and Cherry 2005	Ontario	PCE	Site characterization—Measured the mass discharge from the source zone across a transect.	TM	High-resolution sampling improved the CSM with respect to hot-spot locations. Four distinct local high-concentration zones were identified with concentrations as high as 16% of solubility. Approximately 60% of the source mass discharge was in <5% of the transect area, and 80% of the mass discharge was in <10% of the transect area.	Specific discharge was applied as a uniform value along the transect because the variability of <i>K</i> in the mildly heterogeneous aquifer was much smaller than the variability in concentrations.
31	Guilbeault, Parker, and Cherry 2005	New Hampshire	PCE	Site characterization—Measured the mass discharge from the source zone across a transect.	TM	High-resolution sampling improved the CSM with respect to hot-spot locations. Fifteen distinct local high-concentration zones were identified with concentrations 1%–62% of solubility. Approximately 60% of the source mass discharge was in <5% of the transect area, and 80% of the mass discharge was in <10% of the transect area.	Used two specific discharge zones: one above and one below a clay layer. The hydraulic conductivity of the clay layer is orders of magnitude less than the sand layers, so the clay layer was ignored in the mass flux and mass discharge calculations, and the thickness of the clay was subtracted in the areal elements where it was present.
32	D’Affonseca et al. 2008	Coal tar site near Hamburg, Germany	Naphthalene	Site characterization—Used a transect with three well clusters over a total width of 60 m, with three vertical well screens at each cluster location. Also used the IPT with one extraction well having a capture zone width of 15 m. The purpose was to evaluate DNAPL architecture in the source zone. Two- and three-dimensional modeling of multicomponent DNAPL depletion was conducted, and simulated mass discharge was compared to estimated values based on field data.	TM, IPT	Vertical delineation of mass flux confirmed that one portion of the source zone was contributing a majority of the discharge making up the total source strength. Modeling illustrated that the mass flux of naphthalene has likely reached its peak and will begin to decline over time. Field and model data were used to evaluate the potential benefits and limitations of partial mass removal on downgradient mass discharge trends.	Specific discharge was applied uniformly across the transect.

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
33	DiFillippo and Brusseau 2008	Several sites, North America	Various	Remediation performance assessment—Evaluated the relationship between mass discharge reduction and source mass depletion for 21 remediation projects.	Various	n/a	n/a
34	Ellis, Mackat, and Rivett 2007	River Tame, U.K.	Inorganic parameters	Regional characterization—Estimated mass discharge of various inorganic parameters from the Birmingham Aquifer to River Tame.	n/a	Provided a quantitative comparison of the degree of base flow loading to the river relative to contributions from other sources of surface water.	n/a
35	Ford, Wilklin, and Hernandez 2006	Superfund site, Massachusetts	Arsenic	Site characterization—Used arsenic mass flux calculations to compare the relative contribution of groundwater discharge and sediment dissolution/desorption to arsenic in surface water.	Synoptic sampling	n/a	n/a
36	Goltz et al. 2009	Test site, New Zealand	Bromide and nitrate	Measurement method validation—Used an artificial aquifer with dimensions of $9.5 \times 4.7 \times 2.6$ m to validate TCW methods and to compare to the MIPT method.	TCW, MIPT	n/a	n/a
37	Imbrigiotta et al. 1997	Picatinny Arsenal, New Jersey	TCE	Conducted a detailed mass balance to assess relative contributions of various processes representing gains and losses for plume mass. The mass discharge to a brook downgradient from the source zone was included in the mass balance assessment.	Hand calculations	n/a	n/a
38	Johnson, Truex, and Clement 2006	Unidentified site	Unknown	Remedial design—Demonstrated an example application where RT3D was used to estimate the plume mass discharge corresponding to different remedial alternatives.	Modeled	n/a	n/a

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
39	Kao and Wang 2001	Gasoline spill site, Garysburg, North Carolina	BTEX	Site characterization—Used mass discharge estimates from three transects at distances of 8, 48, and 88 m downgradient of the source zone to estimate natural biodegradation rates.	TM	Plume attenuation rates were estimated based on declines in mass discharge between transects, independent of transverse horizontal and vertical dispersivity estimates.	Specific discharge was applied uniformly across all transects.
40	Landmeyer et al. 2001	Gasoline station near Beaufort, South Carolina	MtBE	Site characterization—Used mass discharge estimates across three transects adjacent to a creek receiving groundwater discharge. Results showed that MtBE was undergoing extensive biodegradation in a small oxic zone caused by mixing of groundwater and surface water adjacent to the creek.	TM	n/a	n/a
41	Pitz 1999	South Puget Sound, Washington	Nitrate	Site characterization—Estimated nitrate mass loading to South Puget Sound by groundwater discharge.	Recharge zone method	Nitrate mass discharge estimates facilitate tracking of annual changes in nutrient loading to South Puget Sound.	n/a
42	Ricker 2008	Former wood treating site, Louisiana	Naphthalene	Site characterization—Estimated temporal changes to dissolved plume mass and the potential for downgradient migration of the plume center of mass, as part of a plume stability evaluation.	n/a	Analysis of plume stability based on individual well trends can be challenging when some wells show a decreasing trend and other wells show an increasing or stable trend. This study demonstrated the application of plume dissolved mass and the center of mass location over time to demonstrate that the naphthalene plume is shrinking over time.	n/a
43	Semprini et al. 1995; Weaver Wilson, and Kampbell 1997	St. Joseph, Michigan	Total ethenes	Site characterization—Used multiple transects to evaluate natural attenuation rates along the groundwater flow path.	TM	Estimated natural attenuation rates based on mass discharge are independent of dispersivity estimates and less susceptible to transient fluctuations in groundwater flow direction and uncertainty in the location of the plume centerline.	Not specified

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
44	Thomson, Hood, and Farquhar 2007	CFB Borden, Ontario	TCE, PCE	Remediation performance assessment—Used a transect of MLS wells to compare pre- and post-treatment mass flux distribution and mass discharge.	TM	n/a	n/a
45	Thomson, Hood, and Farquhar 2007	Coal tar creosote source, Borden, Ontario	PAHs, BTEX	Remediation performance assessment—Conducted a mass balance to evaluate efficiency of permanganate injections and evaluated changes to mass discharge associated with source treatment.	n/a	A detailed mass balance involving permanganate and contaminated species was critical to evaluating the efficiency of remedial injections. Temporal fluctuations in mass discharge and plume mass provided valuable information regarding the effectiveness of source treatment and the corresponding influence on downgradient plume response.	n/a
46	Thuma, Kremesec, and Kolhatkar 2001	Long Island	MtBE	Site characterization—Calculated mass flux across several transects downgradient from the source zone using monitoring well concentration data and compared these data to calculations from a solute transport model to validate the model calibration.	TM, solute transport model	Mass flux data were used to demonstrate natural attenuation due to biodegradation was occurring along the groundwater flow path. Using mass discharge as a model calibration target provides an important metric that may help to improve the representativeness of the calibrated model.	n/a
47	Kingston 2008 (Table 5.5)	Thermal Treatment Site 1	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
48	Kingston 2008 (Table 5.5)	Thermal Treatment Site 2	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
49	Kingston 2008 (Table 5.5)	Thermal Treatment Site 3	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
50	Kingston 2008 (Table 5.5)	Thermal Treatment Site 4	Total VOCs	Remediation performance assessment.	TM	n/a	n/a

**Table A-1. Mass flux/discharge measurement methods**

Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
51	Kingston 2008 (Table 5.5)	Thermal Treatment Site 5	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
52	Kingston 2008 (Table 5.5)	Thermal Treatment Site 6	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
53	Kingston 2008 (Table 5.5)	Thermal Treatment Site 7	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
54	Kingston 2008 (Table 5.5)	Thermal Treatment Site 9	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
55	Kingston 2008 (Table 5.5)	Thermal Treatment Site 11	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
56	Kingston 2008 (Table 5.5)	Thermal Treatment Site 12	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
57	Kingston 2008 (Table 5.5)	Thermal Treatment Site 14	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
58	Kingston 2008 (Table 5.5)	Thermal Treatment Site 15	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
59	Kingston 2008 (Table 5.5)	Thermal Treatment Site 16	Total VOCs	Remediation performance assessment.	TM	n/a	n/a
60	Kingston 2008 (Table 5.5)	Thermal Treatment Site 18	Total VOCs	Remediation performance assessment.	TM	n/a	n/a



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Case study ID	Reference	Site	Constituents	Use	Mass flux/discharge measurement method	Benefits of mass flux/mass discharge estimates	Method used to estimate specific discharge
61	Troldborg et al. 2008	Naerum Supply Well Field, Denmark		Risk prioritization and forensic evaluation—A model decision support tool is applied to evaluate the site(s) causing contamination at a water supply well field. Estimated source mass discharge from multiple sites are input to a regional groundwater model to evaluate the relative risks and contribution to pollution at the water supply wells.	Groundwater flow and transport models	Prioritization of site cleanup is based on a quantitative assessment of relative risks to the downgradient receptors for multiple sites. This method also identified the sites most likely to be contributing to pollution at the water supply wells.	n/a

**Table A-2. Mass flux/discharge methods and configuration**

Case study ID	Reference	Sample collection device for mass flux estimation	Method used to estimate specific discharge	# transects perpendicular to ground-water flow	Width of transect(s) (m)	# transects parallel to ground-water flow	Horizontal spacing along transects	# vertical wells on transects	Vertical well screen lengths (m)	Vertical interval between screens (m)
2	Barbaro and Neupane 2006	Direct-push rig used to vibrate drill rods to deepest sampling depth (12–15 m bgs). Stainless steel well screen was then exposed to aquifer. Samples extracted with peristaltic pump using Teflon tubing. Then drill rod with exposed screen was pulled up to next sampling depth. Stability of drill string indicated that borehole collapsed below sampling depth, which “minimized cross contamination.”	Used a uniform specific discharge across both transects based on relatively uniform head distribution, lithology, and aquifer thickness in the vicinity of the two transects.	7	130–380	Not applicable (n/a)	40–45 m	3–4	1.2	2.4

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Case study ID	Reference	Sample collection device for mass flux estimation	Method used to estimate specific discharge	# transects perpendicular to groundwater flow	Width of transect(s) (m)	# transects parallel to groundwater flow	Horizontal spacing along transects	# vertical wells on transects	Vertical well screen lengths (m)	Vertical interval between screens (m)
5	Basu et al. 2009	<i>Longitudinal transect along plume centerline:</i> PFMs installed in wells for time-integrated mass flux measurements for periods of 6 and 72 days. <i>Source and plume transects perpendicular to flow:</i> PFMs installed in wells for time-integrated mass flux measurement over 20 days. PFMs also deployed in a two-screen well nest during three flux sampling periods described above to measure seasonal variability in groundwater flux distribution.	PFMs were used to quantify specific discharge at approximately 0.3 m intervals over different periods of time to allow for assessment of seasonal fluctuations.	2	13–40	1	<i>Source transect:</i> 3–6 m spacing, <i>plume transect:</i> 15–21 m spacing	Total of 2–3 screens in each well nest over two aquifers separated by a 1–2-m-thick clay confining unit	2–6	2–5
9	Bockelmann et al. 2003	Groundwater samples from permanent wells	Not specified	3	n/a	n/a	30–39	1	n/a	n/a
10	Borden et al. 1997	Groundwater samples from permanent wells	Not specified	4	n/a	n/a	10–16	3	1.5 m well screens to provide flux-averaged concentrations across screen, for purpose of estimating mass discharge at the transect	0–1 m on cross section parallel to groundwater flow

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Case study ID	Reference	Sample collection device for mass flux estimation	Method used to estimate specific discharge	# transects perpendicular to ground-water flow	Width of transect(s) (m)	# transects parallel to ground-water flow	Horizontal spacing along transects	# vertical wells on transects	Vertical well screen lengths (m)	Vertical interval between screens (m)
11	Brooks et al. 2008	PFM sorbent was silver-impregnated granular activated carbon. PFMs were constructed to match the saturated thickness in each well, and multiple PFMs (1.5 m long) were deployed as needed in wells to cover well screen intervals longer than 1.5 m. Each	PFM, IPT	1	n/a	n/a	3	1	3-m-long screens completed across the entire saturated thickness of the aquifer	n/a
12	Brooks et al. 2008	PFM sock was divided into 25-cm-long segments separated using Norprene rubber washers to prevent vertical water flow in the PFM and section the device upon retrieval.	PFM, IPT	1	n/a	10	6.1	1	7.5	n/a
19	USEPA 2009	Passive flux meters	PFM	1	500	n/a	100	2	n/a	n/a
20	Chapman and Parker 2005	“Groundwater samples were collected using a peristaltic pump and dedicated sampling tubes. After purging at least two tubing volumes, the pump was shut off (maintaining the vacuum at surface), the sample tube withdrawn from the multilevel point, the pump reversed or suction released, and groundwater in the sample tube pumped or drained into a 25-mL VOA vial....”	Specific discharge was applied as a uniform value along the transect because the variability of <i>K</i> in the mildly heterogeneous aquifer was much smaller than the variability in TCE concentrations.	1	485	n/a	Average: 24 m, minimum: 7 m, maximum: 47 m	4–8	0.10–0.15	0.3–1

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21	Chapman et al. 2007		Specific discharge was applied uniformly across all three transects.	3	485–590	n/a	Average spacing on transects ranged from 24 m upgradient to 41 m down-gradient	MLSs: 4–8, Waterloo profiler: varied, piezometers: 3–5	MLSs: 0.10–0.15, Waterloo profiler: depth-discrete, piezometers: 0.10–0.15	MLSs: 0.3–1, Waterloo profiler: 0.15–0.6, piezometers: 3–4 screens over 3 m thickness or 3–5 screens over 2 m thickness

**Table A-2. Mass flux/discharge methods and configuration**

Case study ID	Reference	Sample collection device for mass flux estimation	Method used to estimate specific discharge	# transects perpendicular to ground-water flow	Width of transect(s) (m)	# transects parallel to ground-water flow	Horizontal spacing along transects	# vertical wells on transects	Vertical well screen lengths (m)	Vertical interval between screens (m)
22	Chapman et al. 1997	Groundwater samples from permanent wells	Specific discharge was applied as a uniform value along both transects. "Given the relatively small variation in flow velocity observed and the number of other unknowns, the assumption of a uniform velocity field is justified for these first-approximation estimates. The assumption of a uniform velocity field is not expected to significantly bias the conclusions drawn from these mass flux estimates, since the conclusions are based on differences between Fences 1 and 2."	3	2	n/a	0.3	6	n/a	0.15
28	Guilbeault, Parker, and Cherry 2005	Waterloo profiler (temporary) and permanent multilevel wells	Specific discharge was applied as a uniform value along the transect because the variability of <i>K</i> in the mildly heterogeneous aquifer was much smaller than the variability in concentrations.	1	40	n/a	Average of 3 m	Average of 25 vertical samples per profile location	Depth-discrete	Varies, minimum spacing of 0.15

**Table A-2. Mass flux/discharge methods and configuration**

Case study ID	Reference	Sample collection device for mass flux estimation	Method used to estimate specific discharge	# transects perpendicular to ground-water flow	Width of transect(s) (m)	# transects parallel to ground-water flow	Horizontal spacing along transects	# vertical wells on transects	Vertical well screen lengths (m)	Vertical interval between screens (m)
30	Guilbeault, Parker, and Cherry 2005	Waterloo profiler (temporary) and permanent multilevel wells	Specific discharge was applied as a uniform value along the transect because the variability of <i>K</i> in the mildly heterogeneous aquifer was much smaller than the variability in concentrations.	1	72	n/a	Average of 5 m	Average of 10 vertical samples per profile location	Depth-discrete	Varies, minimum spacing of 0.15 m
31	Guilbeault, Parker, and Cherry 2005	Waterloo profiler (temporary)	Used two specific discharge zones: one above and one below a clay layer. The hydraulic conductivity of the clay layer is orders of magnitude less than the sand layers, so the clay layer was ignored in the mass flux and mass discharge calculations, and the thickness of the clay was subtracted in the areal elements where it was present.	1	27	n/a	Average of 2 m	Average of 12 vertical samples per profile location	Depth-discrete	Varies, minimum spacing of 0.15 m
32	D’Affonseca et al. 2008	Groundwater samples from permanent wells	Specific discharge was applied uniformly across the transect.	1	60	n/a	30	3	3.7	9
39	Kao and Wang 2001	Groundwater samples from permanent wells	Specific discharge was applied uniformly across all transects.	3	32	n/a	8	4	0.6	1.2

**Table A-2. Mass flux/discharge methods and configuration**

Case study ID	Reference	Sample collection device for mass flux estimation	Method used to estimate specific discharge	# transects perpendicular to ground-water flow	Width of transect(s) (m)	# transects parallel to ground-water flow	Horizontal spacing along transects	# vertical wells on transects	Vertical well screen lengths (m)	Vertical interval between screens (m)
43	Semprini et al. 1995; Weaver, Wilson, and Kampbell 1997	Auger with 5 ft well screen, collected samples at continuous 5 ft intervals	Not specified	4	115–200	1	19–50	Various	1.5	0 (continuous 5 ft sample intervals using a slotted auger)

**Table A-3. Mass flux/discharge estimates pre- and post-treatment**

Case study ID	Constituents	Treatment process	Pretreatment mass discharge (kg/y)	Post-treatment mass discharge (kg/y)	% reduction pre vs. post
41	Nitrate		Nitrate: 160,000–190,000	Not applicable (n/a)	n/a
8	BTEX, PAH	Natural attenuation between transects due to biodegradation. Pre- and post-treatment represent mass discharge values from transects at distances of approximately 140 m (pretreatment) and 280 m (post-treatment) downgradient from the source zone.	Chloride: 38,832 Total BTEX: 0.7 Total PAH: 12 NO <sub>3</sub> : 88 Mn(II): 254 Fe(II): 770 SO <sub>4</sub> : 79,351	Chloride: 37,588 Total BTEX: 0.04 Total PAH: 5 NO <sub>3</sub> : 274 Mn(II): 161 Fe(II): 1,142 SO <sub>4</sub> : 77,468	Chloride: 3% Total BTEX: 94% Total PAH: 58% NO <sub>3</sub> : –211% Mn(II): 37% Fe(II): –48% SO <sub>4</sub> : 2%
51	Total VOCs	Thermal treatment.	680	82	88%
37	TCE	Natural attenuation via biodegradation and volatilization.	<i>Gains:</i> Desorption: 550 Infiltration: <1 DNAPL dissolution: unknown <i>Losses:</i> Biodegradation: 360 Discharge to surface water: 50 Volatilization: 50 Dispersion: <1 Sorpton: <1	n/a	n/a

**Table A-3. Mass flux/discharge estimates pre- and post-treatment**

Case study ID	Constituents	Treatment process	Pretreatment mass discharge (kg/y)	Post-treatment mass discharge (kg/y)	% reduction pre vs. post
20	TCE	A sheet pile enclosure was installed around the DNAPL source zone. Mass discharge was estimated across the transect at a distance of 280 m downgradient from the source zone six years after source isolation. The investigators estimated that the mass discharge prior to source zone isolation was 10 times higher than the post-isolation mass discharge, based on the observed magnitude of changes in TCE concentrations in monitoring wells over this time period.	360 (estimated)	36 (measured)	90% (Complete restoration was not obtained due to back-diffusion from the silt aquitard to the aqueous plume outside the isolated source zone.)
43	Total ethenes	Natural attenuation via biodegradation. Pre- and post-treatment mass discharge values represent calculations for transects situated 130 and 855 m downgradient of the source zone (i.e., separation distance of 745 m over which natural attenuation was evaluated).	TCE: 120 DCE: 130 Vinyl chloride: 17 Ethene: 7.6 Total ethenes: 280 Methane: 66 Chloride: 1,500	TCE: 0.95 DCE: 10 Vinyl chloride: 1.7 Ethene: 0.16 Total ethenes: 13 Methane: 47 Chloride: 5,300	TCE: 99.2% DCE: 92% Vinyl chloride: 90% Ethene: 98% Total ethenes: 95% Methane: 29% Chloride: -250%
12	TCE	Thermal treatment and multiphase extraction.	PFM: 240 MIPT: 170 TM: 220 Average: 210	PFM: 0.84 MIPT: 0.55 TM: 0.69 Average: 0.69	PFM: 99.6% MIPT: 99.7% TM: 99.7% Average: 99.7%
4	TCE	Natural attenuation between transects due to reductive dechlorination. Pre- and post-treatment represent mass discharge values from transects at distances of approximately 0 m (pretreatment) and 31 m (post-treatment) downgradient from the source zone.	MW8-99 (x = 0): 201 MW2-98 (x = 12m): 133	MW-13I (x = 31m): 100	50% over 31 m downgradient from source zone
32	Naphthalene	n/a	176	n/a	n/a
3	Total chlorinated organics	n/a	100	n/a	n/a
12	cis-1,2-DCE	Thermal treatment and multiphase extraction.	PFM: 49 MIPT: 82 TM: 92 Average: 74	PFM: 1.4 MIPT: 0 TM: 0 Average: 0.47	PFM: 97% MIPT: 100% TM: 100% Average: 99.4%



**Table A-3. Mass flux/discharge estimates pre- and post-treatment**

Case study ID	Constituents	Treatment process	Pretreatment mass discharge (kg/y)	Post-treatment mass discharge (kg/y)	% reduction pre vs. post
46	MtBE	Natural attenuation via biodegradation. Pre- and post-treatment mass discharge values represent the calculated flux at transects situated approximately 1000 and 4400 feet downgradient of the source zone.	91	4	95.6%
48	Total VOCs	Thermal treatment.	60	4.9/21	65%/92%
24	MtBE	n/a	55	n/a	n/a
47	Total VOCs	Thermal treatment.	52	0.19	99.63%
49	Total VOCs	Thermal treatment.	49	0.13	99.73%
28	TCE	n/a	31–45	n/a	n/a
21	TCE, cis-1,2-DCE	Natural attenuation in via biodegradation and discharge to the on-site pond and drainage creeks where dilution and volatilization occurred. Mass discharge values represent Transects 1 and 3, separated by a distance of 420 m and a travel time of several years.	TCE: 36 cis-1,2-DCE: 0.84	TCE: 0.07 cis-1,2-DCE: 0.11	TCE: 99.80% cis-1,2-DCE: 86.96%
50	Total VOCs	Thermal treatment.	32	2.1	93%
11	TCE	Surfactant-enhanced aquifer restoration (SEAR).	PFM: 28 MIPT: 28 TM: 28 Average: 28	PFM: 2.2 MIPT: 1.4 TM: 2.6 Average: 2.1	PFM: 92% MIPT: 95% TM: 91% Average: 93%
39	BTEX	Natural attenuation via biodegradation. Mass discharge values for pre- and post-treatment represent transects at distances of 8 and 88 m downgradient of the source zone.	Benzene: 11 Toluene: 5.2 Ethylbenzene: 1.5 m- and p-xylene: 1.9 o-xylene: 1.7 1,2,4-trimethylbenzene (TMB): 1.1 Total BTEX: 22.3	Benzene: 1.6 Toluene: 0.064 Ethylbenzene: 0.29 m- and p-xylene: 0.16 o-xylene: 0.080 1,2,4-TMB: 0.56 Total BTEX: 2.8	Benzene: 85% Toluene: 98.8% Ethylbenzene: 81% m- and p-xylene: 92% o-xylene: 95% 1,2,4-TMB: 48% Total BTEX: 88%
30	PCE	n/a	20.5	n/a	n/a
31	PCE	n/a	15	n/a	n/a
25	cis-1,2-DCE	n/a	11	n/a	n/a
53	Total VOCs	Thermal treatment.	9.4	0.027	99.71%
59	Total VOCs	Thermal treatment,	9.3	0.017	99.82%
6	PCE, TCE	n/a	PCE: 8.2 TCE: 0.82	n/a	n/a
52	Total VOCs	Thermal treatment.	4.6	0.073	98.41%
27	MtBE	n/a	0.44–2.5	n/a	n/a

**Table A-3. Mass flux/discharge estimates pre- and post-treatment**

Case study ID	Constituents	Treatment process	Pretreatment mass discharge (kg/y)	Post-treatment mass discharge (kg/y)	% reduction pre vs. post
5	TCE	n/a	Source: 1.1 Plume (x = 175 m): 2.1	n/a	n/a
54	Total VOCs	Thermal treatment.	1.7	0.6	65%
26	MtBE	n/a	1.5	n/a	n/a
11	cis-1,2-DCE	SEAR	DCE below level of quantification	PFM: 1.1 MIPT: 0.73 TM: 1.4 Average: 1.1	n/a
60	Total VOCs	Thermal treatment.	1.3	2.8	-115%
58	Total VOCs	Thermal treatment.	1.2	0.054	96%
2	VOCs	Natural attenuation between transects (possibly oxidation of cis-DCE under iron-reducing conditions). Pre- and post-treatment represent mass discharge values from transects at 91 m (pretreatment) and 335 m (post-treatment) downgradient from the source zone.	PCE: 0.19 TCE: 0.35 cis-DCE: 0.20	PCE: 0.20 TCE: 0.38 cis-DCE: 0.07	PCE: n/a TCE: n/a cis-DCE: 65%
44	TCE, PCE	In situ chemical oxidation with potassium permanganate recycling for 485 days followed by 180 days of enhanced flushing in the source zone via groundwater extraction.	TCE: 0.31 PCE: 0.32	TCE: 0.0026 PCE: 0.036	TCE: 99.2% PCE: 89%
40	MtBE	Natural attenuation via biodegradation. Mass discharge values for pre- and post-treatment represent transects separated by less than 6.5 m adjacent to the creek.	0.51	0.019	96%
55	Total VOCs	Thermal treatment.	0.40	0.03	93%
57	Total VOCs	Thermal treatment.	0.097	0.061	37%
56	Total VOCs	Thermal treatment.	0.019	$1.80 \times 10^{-7}$	100.00%
29	TCE	n/a	n/a	n/a	90%–99% (Complete restoration was not obtained due to back-diffusion from the silt and clay lenses to the aqueous plume outside the contained source zone.)

**Table A-3. Mass flux/discharge estimates pre- and post-treatment**

Case study ID	Constituents	Treatment process	Pretreatment mass discharge (kg/y)	Post-treatment mass discharge (kg/y)	% reduction pre vs. post
10	MtBE, BTEX	Natural attenuation via biodegradation and volatilization. Mass discharge reduction efficiency represent the difference in mass discharge between the source zone and a transect located 88 m downgradient of the source zone.	n/a	n/a	Toluene: >99% Ethylbenzene: >99% m- and p-xylene: >99% o-xylene: 89% Benzene: 87% MtBE: 74%

## **Appendix B**

### **Overview of Comparison Studies with Passive Flux Meters**

## OVERVIEW OF COMPARISON STUDIES WITH PASSIVE FLUX METERS

The Environmental Security Technology Certification Program conducted a study of the PFM at four sites, including the CFB Borden Site, NASA's L-34 Site, Port Hueneme Site, and Indian Head Site. At each site, experiments were designed to provide independent estimates of both groundwater and contaminant fluxes that could be compared to fluxes measured by PFMs. The following section is based on information from ESTCP (2006a, 2006b, 2006c, 2007).

In each experiment, the PFM was constructed and installed in a monitoring well in approximately 30 minutes. The PFM consisted of carbon sorbent, packed in a sock (with tracers), and separated with impermeable dividers along the length of the sock. Each PFM was 1.5–1.6 m in length and was exposed to the groundwater for a period of 3–7.3 weeks. When the PFMs were removed, they were immediately placed in a PVC tube to prevent losses of VOCs. After removal, each 20–25 cm interval of sorbent was mixed and analyzed. The process of extraction and sampling required approximately 20 minutes per meter.

Groundwater samples were collected by pumping or bailing the monitoring well prior to sampling. Samples were collected in 40 mL volatile organic analysis (VOA) vials, placed in coolers containing dry ice, and transported to Purdue University or The University of Florida. Alcohol tracers had holding times of <14 days. The 150–160 cm PFMs were segmented into 5–60 cm sections and transferred to containers. Samples were thoroughly mixed, placed in 250 mL wide-mouth jars, put in a cooler, and transported to Purdue University or The University of Florida. The sorbent samples had a 28-day holding time.

All samples collected were analyzed at either The University of Florida or Purdue University. Volatile organics (including tracers) were analyzed for by directed liquid injection on gas chromatographs. The detection limits were 1 mg/L. Headspace analysis (using 50 µg/L detection limits) was used if low concentrations were detected. USEPA Method 314.1 with a detection limit of 1 µg/L was used to analyze for perchlorate. Simple regression analysis was used to assess the data at individual monitoring wells. Spatial analysis was performed to assess the spatial mean and variance of contaminant/water fluxes evaluated over transects or within a plume.

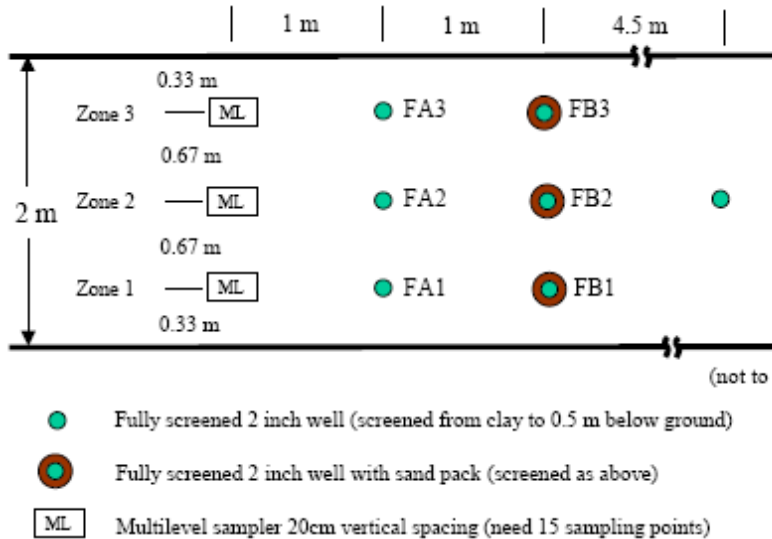
### CFB BORDEN SITE

The CFB Borden site was tested in three locations. The geology at the site consisted of surficial sand (approximately 3.5 m thick) overlying a clayey aquitard. The aquifer conductivities at the site ranged 0.1–15 m/d.

#### First Test

The first test used an existing sheet pile–enclosed flume for flow gate. The flume was 15 m long × 2 m wide. The test gate allowed for controlling subsurface flow, monitoring MtBE concentrations with MLSs and measuring both water and MtBE fluxes using PFMs installed in monitoring wells with different constructions. The saturated thickness of the aquifer in the gate was about 1.5 m. Steady flow was established from one pumping well located in the closed end of the flume.

Two transects were set up, consisting of three 5.1 cm, fully screened wells with installed PFMs (Figure B-1). Three monitoring wells had sand packs; the other three did not. The water flux measurements determined with the PFMs were compared with the measured flow rate of the extraction well. The PFMs also were used to measure MtBE fluxes, which were then compared to those estimated by an existing network of MLSs. The first flux measurements were made after an exposure period of one week (August 13–17, 2002) in the monitoring wells with sand packs. The second flux measurement was made after a period of one week (August 17–22, 2002) in the monitoring wells without sand packs.



**Figure B-1. Configuration of PFM, first Borden test.**

The measured groundwater flux at any monitoring well and the induced flux in the gate ( $8.23 \pm 0.66$  cm/d) varied less than 11.2% (Table B-1). The maximum coefficient of variation for measured water fluxes was 0.6 in wells constructed with a filter pack and  $<1.3$  for simple screened wells. For screened monitoring wells, the integrated water flux obtained from averaging results of three PFMs compared to the induced flow rate was  $-2.3\%$ ; for wells constructed with filter packs, the integrated water flux was  $0.7\%$ . For the last field test involving the plume interception well, water fluxes were estimated within 2% of the extraction flow rate.

**Table B-1. Water flux measurements by PFM to the steady induced flux in the flow gate**

Zone	Well with Filter Pack			Well Without Filter Pack		
	Average (cm/d)	CV	% Difference <sup>a</sup>	Average (cm/d)	CV <sup>b</sup>	% $\Delta$ Difference <sup>a</sup>
1	7.62	0.6	7.7	9.21	1.3	6.5
2	8.82	0.4	-6.9	8.24	1.2	-11.2
3	8.08	0.4	1.8	7.71	1.0	-0.1
Gate Average	8.17	0.4	0.7	8.42	1.2	-2.3

<sup>a</sup> Based on a water flux of 8.23 (CV = 0.08) cm/d determined from extraction well and  $\% \Delta = 200 * (8.23 - PFM) / (PFM + 8.23)$   
<sup>b</sup> Coefficient of variation

Total MtBE fluxes, obtained from integrating PFM measurements from the monitoring wells without sand packs, compared within 16.63% of integrated calculations from MLS. For the monitoring wells containing sand packs, total MtBE fluxes were within 1.18% of integrated calculations using depth-averaged MtBE concentrations from six flux wells and three MLS wells (Table B-2).

**Table B-2. Depth-averaged MtBE concentration from MLSs and flux wells, mg/L**

zone	MLS* 8/16/2002	MLS* 8/13/2002	FA-wells 8/13/2002	FB-wells 8/13/2002
1	2.14(1.02)	2.69 (0.91)	2.36	4.45
2	2.16(1.23)	3.03 (1.08)	2.79	6.94
3	1.29(1.46)	2.82 (1.38)	2.37	5.95

\* Coefficient of variation in parentheses

Second Test

The second field test took place in a controlled-release plume consisting of a mixture of 45% PCE, and 45% TCE by weight, which extended 80 m in length. For this study, 17 fully screened monitoring wells (measuring 3.2 cm) were installed 1 m downgradient of the MLS well transect No. 13. TCE and PCE data collected by the MLSs was compared to data from the PFMs. Also water flux measurements made by the PFMs were compared to those made by a BHD test (Table B-3).

**Table B-3. Comparison of measured groundwater fluxes in monitoring wells located in the forested area**

Well	Method of Measured Groundwater Fluxes (cm/d)		
	Passive Flux Meter	Borehole Dilution (BHD)	% Δ*
13-7-1	2.2	2.0	-7.7
13-7-2	2.9	2.6	-10.1
13-7-3	3.9	3.5	-10.9
13-7-4	2.3	2.1	-5.2
13-7-5	3.9	3.6	-6.5
13-7-6	4.0	3.4	-16.7
13-7-7	5.0	5.1	1.7
13-7-8	3.8	3.3	-13.7
13-4	3.6	2.9	-24.2
13-5	6.4	6.0	-6.7
13-6	7.2	6.6	-8.8
13-9	5.2	5.6	7.7
13-13	4.9	5.5	10.3
13-15	2.3	2.1	-8.8
13-19	5.5	5.6	2.1
<b>Average Absolute Difference</b>			<b>9.4</b>
<b>Standard Deviation</b>			<b>5.7</b>

\*  $\% \Delta = 200 * (PFM - BHD) / (PFM + BHD)$

Relative concentration differences between MLS and PFM data were 3.2% for TCE and 13% for PCE when averaged over the thirteenth sampling transect (Table B-4). However, when

comparing flux-averaged concentration measurements made by the MLSs and the PFM measurements at individual wells, the variation was greater than 35% (Table B-5).

**Table B-4. TCE and RCE concentration from MLSs**

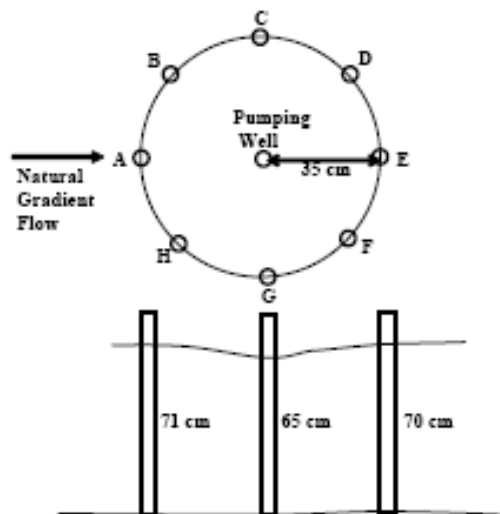
MLS Well	TCE		PCE	
	Concentration [mg/l]	Coefficient of Variation	Concentration [mg/l]	Coefficient of Variation
MLS-5	0.30	0.59	0.65	0.30
MLS-6	0.39	1.59	0.68	0.77
MLS-7	0.53	1.80	0.65	1.45
MLS-9	0.82	1.84	1.85	1.41
MLS-11	0.50	1.88	3.44	1.12
MLS-14	0.41	1.56	4.15	0.71
MLS-15	0.45	1.60	5.65	0.73
MLS-18	0.23	1.89	7.70	0.97
MLS-19	0.22	1.72	7.01	1.14
MLS-20	0.38	1.52	8.43	1.10
MLS-23	0.62	1.35	12.95	1.60
MLS-24	1.30	0.97	12.53	1.93
Transect Average	0.51	1.53	5.48	1.10

**Table B-5. Flux-averaged TCE and PCE concentration from PFMs**

Flux Well	TCE		PCE	
	Flux-averaged Concentration [mg/l]	Coefficient of Variation	Flux-averaged Concentration [mg/l]	Coefficient of Variation
well 13-5	0	0	0.25	1.34
well 13-6	0.08	2.45	0.18	1.28
well 13-7	0.18	2.17	0.39	1.57
well 13-9	0.42	1.68	0.73	1.37
well 13-11	0.11	0.87	0.94	0.84
well 13-13	0.35	1.37	1.34	0.91
F-13-14	0.29	0.94	1.10	0.88
well 13-15	0.55	1.21	5.31	1.04
well 13-17	0.61	1.45	10.33	0.98
well 13-18a	0.60	1.78	7.00	1.46
F-13-18	0.83	1.92	5.82	0.80
well 13-19	0.59	0.87	10.91	1.09
well 13-21	1.96	0.98	15.08	1.14
well 13-23	1.08	0.69	27.23	0.92
well 13-25	1.09	0.89	2.17	0.56
Transect Average	0.58	1.28	5.92	1.09

Third Test

The third field test took place in the same controlled-release plume used for the second field test. For this test, a ring of eight 3.2 cm fully screened monitoring wells were placed evenly apart at a radial distance of 35 cm from an active plume interception well (Figure B-2). The purpose was to compare the measured contaminant and water fluxes obtained from the ring of PFMs to contaminant mass discharges measured at the interception well. The PFMs were spaced at 1 m intervals, and vertical resolution of sorbent sampling was 20–25 cm.



**Figure B-2. Configuration of Borden third test PFMs.**

The PFM measurements of groundwater flux were compared to known fluxes and to measurements made by BHD test. Previous studies reported groundwater fluxes ranging 5–8 cm/d. The average PFM-measured flux was 6.62 cm/d with an estimated coefficient of variation of 0.33. Measured water fluxes were based on PFMs deployed for 7.3 weeks. TCE and PCE were respectively measured by PFMs to be 9%–32% of mass flow rates at the wellhead (Table B-6). A BHD was also conducted in one of the PFM wells, which showed a strong correlation between PFM-measured fluxes and BHD test results. The average absolute relative difference in measurements was 9.4%.



**Table B-6. Comparison of integrated PFM measurements of water flux and PCE and TCE mass flows**

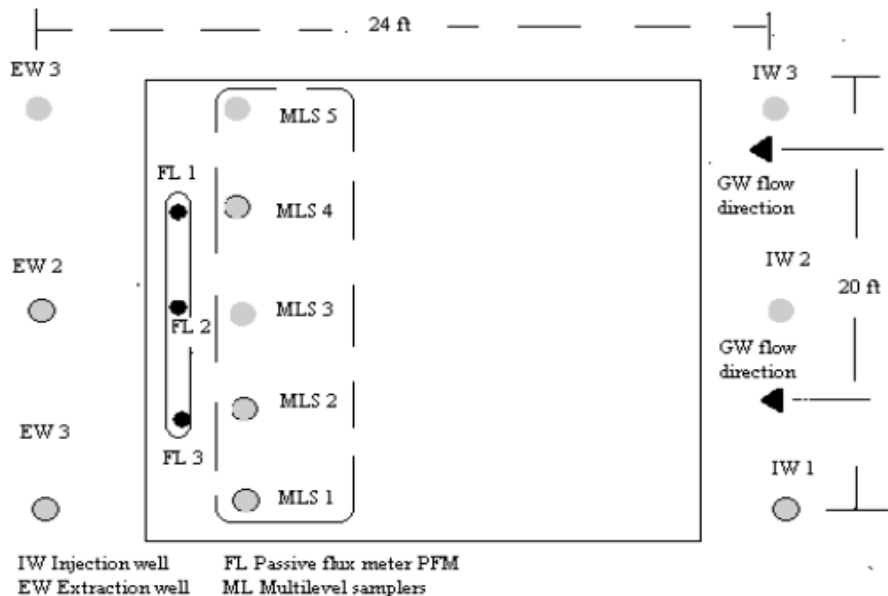
	PFM	Extraction Well <sup>a</sup>	% Error <sup>b</sup>
Water Flux [cm/hr]	0.97	0.99	-1.59
TCE Mass Flow [mg/hr]*	104.05	113.83	-8.59
PCE Mass Flow [mg/hr]*	129.64	97.92	32.40

<sup>a</sup> Product of the PFM measured water flux and the PFM derived flux-averaged contaminant concentration  
<sup>b</sup> 100\*(PFM-Extraction Well)/(Extraction Well)

**NASA’s LC-34**

NASA’s LC-34 site was used for testing the PFMs in a biologically simulated environment. The geology at the site is composed of surficial sand and shell deposits that extend to a depth of 45 ft, where clay is encountered. The surficial soils can be divided into three units: the Upper Sand Unit (USU), the Middle Fine-Grained Unit (MFGU), and the Lower Sand Unit (LSU). The aquifer exists within the MFGU 22–30 ft below ground surface (bgs). The sediments in the surficial aquifer are relatively permeable. The vertical hydraulic conductivity ranges from  $10^{-3}$  to  $10^{-2}$  cm/s. The hydraulic conductivity ranges from  $1.44 \times 10^{-2}$  to  $1.21 \times 10^{-2}$  cm/s in the USU, from  $8.28 \times 10^{-2}$  to  $5.43 \times 10^{-2}$  cm/s in the MFGU, and  $1.21 \times 10^{-2}$  to  $4.10 \times 10^{-2}$  cm/s in the LSU. The difference between the three upper units and the CU is 4–6 orders of magnitude ( $10^{-7}$  to  $10^{-8}$  cm/s). Previous measurements of vertical hydraulic conductivity of the CU range from  $1.5 \times 10^{-7}$  to  $4.5 \times 10^{-8}$  cm/s with an average of  $5.89 \times 10^{-8}$  cm/s.

Three injection and three extraction wells were used to form a flow cell. Five MLS wells, with five sampling locations, were located within the cell (Figure B-3). The PFM flux monitoring was conducted in three wells installed upgradient of the central extraction well (EW-2). All wells were screened over the interval 16–26 ft bgs.



**Figure B-3. Configuration of NASA LC-34 PFM test.**

There were four sampling events at the site. The first provided a background measurement prior to bioremediation and was conducted after four weeks of steady water flow. TCE and degradation by-products were quantified. The second sampling event occurred during ethanol injection performed to stimulate biological activity. The third round of sampling

occurred after injection of TCE-degrading microbes. The final sampling event occurred after several weeks with no additional treatment in the intervening time. The work was conducted over a one-year period.

Prior to bioaugmentation, the PFM measurements of the groundwater fluxes were within 6%–19% of the controlled flow rate through the test cell. Following site remediation, percent differences ranged 4%–30%. Site bioactivity appeared to degrade the resident tracer ethanol. The less degradable and more highly sorbed alcohols appeared to give more reliable assessments of water flux.

Prior to remediation, integral average flux plane calculations made by PFMs and MLSs differed 0%–23%. TCE flux comparisons differences ranged 7%–113%. The average difference for local flux was 41%.

During biostimulation and after bioaugmentation, the contaminant flux estimates using PFMs and MLSs varied significantly (17%–186%). Measurements of TCE flux differences ranged 0%–200%. The average difference for local flux was 125%. The integrated fluxes measured at the extracted well and over the PFM flux plane varied 32%–190%. The PFMs showed higher vinyl chloride and ethene fluxes than those derived from extraction well data and MLS samples, suggesting that that the PFM sorbent (activated carbon sorbent) may have trapped highly volatile compounds or that TCE and DCE degraded to vinyl chloride and ethene while sorbed on the activated carbon.

## **PORT HUENEME SITE**

The Port Hueneme site is a shallow, unconfined, sandy aquifer contaminated with MtBE. At this site PFMs were installed in selected wells in cell cluster B, which contained wells designed with and without filter packs, installed by drilling or direct-push methods. These well clusters were located near each other, allowing groundwater flow and MtBE flux to be compared. Results were compared for both groundwater flow and MtBE flux. To evaluate the performance of wells commonly installed by drillers, wells with a 20-40 mesh sand pack surrounding 0.010-inch slotted schedule 40 PVC pipe were installed. To evaluate the performance of nonpack wells that are installed by direct-push equipment, wells were installed with a 0.010-inch slotted schedule 40 PVC pipe without filter packs. Samples were collected in vertical intervals of approximately 30 cm to determine flux distributions. Four clusters of wells were installed, consisting of the following five types of wells:

- ¾-inch-diameter pushed wells—no filter pack (#1 wells)
- ¾-inch-diameter pushed wells—ASTM specifications (#2 wells)
- ¾-inch-diameter pushed wells—“conventional” (0.010 slot, 20-40 sand) (#3 wells)
- 2-inch-diameter pushed wells—ASTM specifications (#4 wells)
- 2-inch-diameter drilled wells—ASTM specifications (#5 wells)

Groundwater fluxes estimated by aquifer conductivities and hydraulic gradients were compared to PFM measurements. The PFM measurements in ¾-inch wells compared favorably; however, the measurement in the 2-inch wells did not compare as well. (Possibly the drilling process used

to install the 2-inch well loosened soil in the vicinity of the well, increasing the hydraulic conductivity.) There is a possibility that PFMs could be more sensitive to local conductivity changes than could be detected with the pneumatic slug test.

Measurements of fluxes collected with PFMs were within a factor of 2 of each other, which is likely due to the site heterogeneity. The study indicated that pushed wells measured significantly lower fluxes than 2-inch wells. Due to the site heterogeneity, flow variations between the wells were significant. As a result, the contaminant fluxes were not expected to compare between wells, regardless of well type. A comparison of flux-averaged concentrations showed no significant difference between well types.

## **THE INDIAN HEAD SITE**

The Indian Head site was selected for testing PFMs designed with silver-impregnated granular activated carbon (SM-SI-GAC) as the sorbent, in a shallow aquifer contaminated with perchlorate. At the site, the top 2–4 ft of surficial deposits consisted of fill material, including organic material, gravel, and silty sand. The underlying 11–13 ft consisted of mottled light to olive brown clayey to sandy silts. At a depth of approximately 15 ft bgs, a 1–1.5-ft-thick layer of sand and gravel was encountered. The sand and gravel layer was underlain by a gray clay layer, which extended to a depth of at least 20 ft bgs (the maximum depth studied). Depth to groundwater ranged approximately 6.5–10.25 ft bgs. The average hydraulic gradient was 0.023 ft/ft. Slug test results indicated an average hydraulic conductivity of approximately 0.012 ft/min within the aquifer. Based on these values, the estimated groundwater flux was 0.4 ft/d.

PFMs were installed in four existing, screened, 2-inch monitoring wells. The site was divided into two zones: near source zone and plume. All monitoring wells had 10 ft screens, and two 5 ft socks were installed in each well to cover the whole screened interval. The PFMs were used twice, once for a period of three weeks and the second for a period of 6.3 weeks, and the flux measurements were compared. Before any well was used for flux measurements, it was developed and left for approximately one week to equilibrate with the flow field before a PFM was installed.

Groundwater fluxes measured with PFMs were comparable to fluxes determined by BHD tests. The groundwater flux measurements from the first sampling and second sampling events varied 21%–35%. For monitoring wells 1, 3, and 4, perchlorate fluxes respectively varied 22%, 193%, and 0% between the two sampling events. Results also indicated that the SM-SI-GAC was stable physically, chemically, and biologically for a maximum of 44 days and that the alcohol tracers and captured perchlorate on it were not biodegradable.

## **CAPE CANAVERAL**

Figure B-4 is an example of output from the BIOCHLOR analytical model (Aziz et al. 2000) showing mass flux results at a site located on Cape Canaveral Air Station, Florida. The mass flux data, in units of mg/d, are shown at the bottom of the table located in the upper half of the output

screen. The source flux is about 210,000 mg/d (about 77 kg/ year). At a point about 1085 ft downgradient, however, the modeled mass flux is only 83 mg/d (about 0.030 kg/year), or a 99.96% reduction.

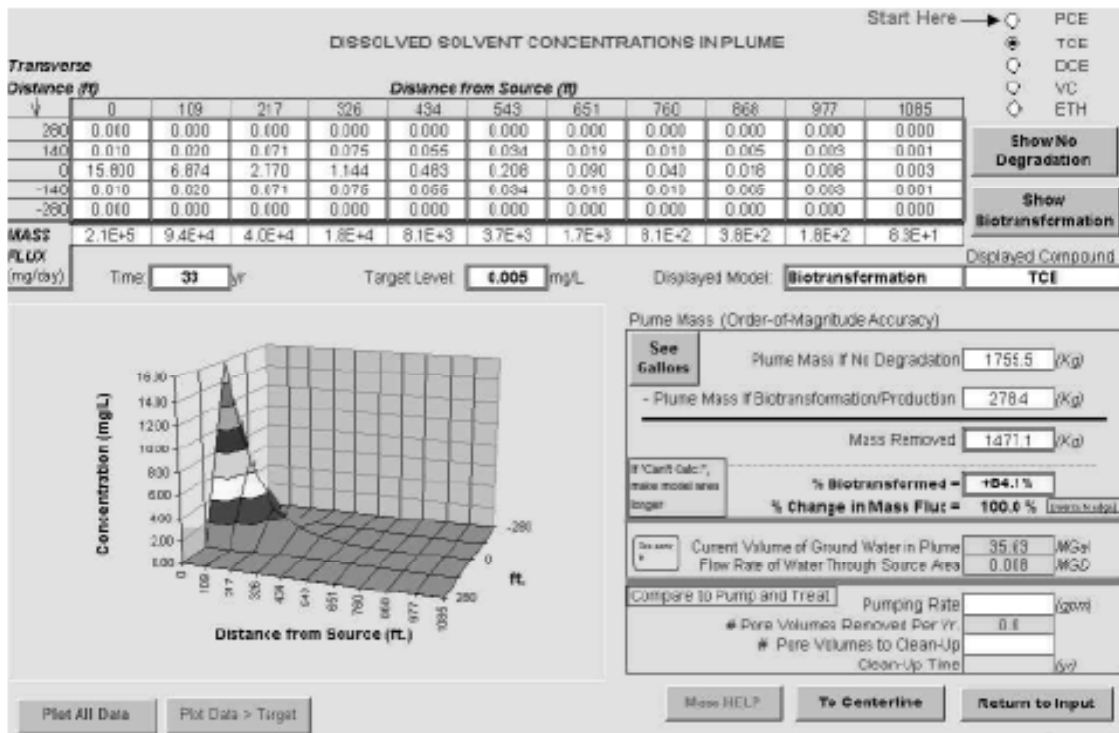


Figure B-4. BIOCHLOR output showing mass flux data.

## **Appendix C**

### **Integrated DNAPL Site Strategy Team Contacts**

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## **Appendix D**

### **Glossary**

## GLOSSARY

- advection.** Transport of a solute by the bulk motion of flowing groundwater.
- aliphatic compounds.** Acyclic or cyclic, saturated or unsaturated carbon compounds, excluding aromatic compounds.
- amendment.** Substrate introduced to stimulate the in situ microbial processes (vegetable oils, sugars, alcohols, etc.).
- anisotropy.** The property of being directionally dependent, as opposed to “isotropy,” which means homogeneity in all directions.
- bioaugmentation.** The addition of beneficial microorganisms into groundwater to increase the rate and extent of anaerobic reductive dechlorination to ethene.
- bioremediation.** Use of microorganisms to biodegrade contaminants in soil and groundwater.
- biostimulation.** The addition of an organic substrate or nutrients into groundwater to stimulate anaerobic reductive dechlorination.
- chlorinated ethene.** Organic compounds containing two double-bonded carbons and possessing at least one chlorine substituent.
- compliance monitoring.** The collection of data which, when analyzed, can allow for the evaluation of the contaminated media against standards such as soil and or water quality regulatory standards, risk-based standards, or remedial action objectives.
- chlorinated solvent.** Organic compounds with chlorine substituents that commonly are used for industrial degreasing and cleaning, dry-cleaning, and other processes.
- conceptual site model (CSM).** A hypothesis about how contaminant releases occurred, the current state of the source zone, and current plume characteristics (plume stability).
- control plane.** The location of the control plane, or response boundary, is defined as a location within the source area, upgradient or immediately downgradient of the source area where changes in the plume configuration are anticipated due to the implementation of the DNAPL source zone treatment. The response boundary should not be confused with the term “point of compliance,” which the Environmental Protection Agency defines as the point where media-specific standards (e.g., maximum contaminant levels, risk-based cleanup goals) must be achieved.
- dense, nonaqueous-phase liquid (DNAPL).** A water-immiscible organic liquid that is denser than water (e.g., tetrachloroethene).
- DNAPL architecture.** The spatial distribution of DNAPL mass and source zone hydraulic conductivity distribution, and the correlation between DNAPL mass and hydraulic conductivity in the subsurface.
- desorption.** The converse of “sorption.”
- diffusion.** The process of net transport of solute molecules from a region of high concentration to a region of low concentration caused by their molecular motion in the absence of turbulent mixing.
- dilution.** A reduction in solute concentration caused by mixing with water at a lower solute concentration.
- dispersion.** The spreading of a solute from the expected groundwater flow path as a result of mixing of groundwater.

**flux.** Rate of flow of fluid, particles, or energy through a given surface.

**hydraulic conductivity.** The capability of a geologic medium to transmit water. A medium has a hydraulic conductivity of unit length per unit time if it will transmit in unit time a unit volume of groundwater at the prevailing viscosity through a cross section of unit area, measured at right angles to the direction of flow, under a hydraulic gradient of unit change in head through unit length of flow.

**hydraulic gradient.** The change in hydraulic head per unit distance in a given direction, typically in the principal flow direction.

**inorganic compound.** A compound that is not based on covalent carbon bonds, including most minerals, nitrate, phosphate, sulfate, and carbon dioxide.

**in situ bioremediation.** The use of biostimulation and bioaugmentation to create anaerobic conditions in groundwater and promote contaminant biodegradation for the purposes of minimizing contaminant migration and/or accelerating contaminant mass removal.

**integrated contaminant mass flux.** See mass discharge, cumulative mass flux, total mass flux, integrated mass flux (ITRC 2008a). The total quantity of a migrating substance that moves through a planar transect within the system of interest and oriented perpendicular to the direction of  $x$  movement. If the transect is at the entry point to the system, the integrated mass flux is the loading. If the transect is at the exit point from the system, the integrated mass flux is the discharge. Note that these terms have units of mass per time (kg/year, g/d, or the like) and represent an extension of the traditional engineering definition of flux (e.g., kg/year/m<sup>2</sup>) in which the transect area is accounted for to allow mass balance calculation of plume- or system-scale behavior.

**mass balance.** Quantitative estimation of the mass loading to the dissolved plume from various sources, as well as the mass transport, phase transfer, degradation, and the attenuation capacity for the dissolved plume.

**mass discharge** ( $M_d$ , mg/d). Contaminant load past a transect (mass per time) (also called “cumulative mass flux” and “mass discharge,” or confusingly, “mass flux” by some groups).

**mass flux** ( $J$ , mg/d/m<sup>2</sup>). Contaminant load (per unit area per time), a general term where mass flux and/or mass discharge type calculations are performed.

**mass loading.** Contaminant released to the environment (in this case the aquifer or unsaturated zone) from the source material.

**mass transfer.** The irreversible transport of solute mass from the nonaqueous phase (i.e., DNAPL) into the aqueous phase, the rate of which is proportional to the difference in concentration.

**monitored natural attenuation (MNA).** The term “natural attenuation” refers to naturally occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants. When scientists monitor or test these conditions to make sure natural attenuation is working, it is called “monitored natural attenuation” (USEPA 2001a).

**natural attenuation.** Naturally occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media.

**process monitoring.** The collection of information documenting the operation of a system's engineered components.

**performance monitoring.** The collection of information which, when analyzed, allows for the evaluation of the performance of a system on environmental contamination.

**plume.** A zone of dissolved contaminants. A plume usually originates from a source and extends in the direction of groundwater flow.

**pool.** An accumulation of DNAPL above a capillary barrier.

**response boundary.** See "control plane."

**saturated zone.** Subsurface environments in which the pore spaces are filled with water.

**seepage velocity.** The rate of movement of fluid particles through porous media along a line from one point to another.

**sorption.** The uptake of a solute by a solid.

**source strength.** Mass discharge at the source zone.

**source zone.** The subsurface zone containing a contaminant reservoir sustaining a plume in groundwater. The subsurface zone is or was in contact with DNAPL. Source zone mass can include sorbed and aqueous-phase contaminant mass as well as DNAPL.

**specific discharge.** An apparent velocity calculated from Darcy's law, represents the flow rate at which water could flow in an aquifer if the aquifer were an open conduit.

**substrate.** A molecule that can transfer an electron to another molecule and/or provide carbon to the microorganism. Organic compounds, such as lactate, ethanol, or glucose, are commonly used as substrates for bioremediation of chlorinated ethenes.

**volatilization.** The transfer of a chemical from its liquid phase to the gas phase.

## **Appendix E**

### **Acronyms and Symbols**

## ACRONYMS

AFB	Air Force Base
ASTM	American Society of Testing and Materials
BTEX	benzene, toluene, ethylbenzene, and xylenes
BHD	borehole dilution
bgs	below ground surface
COC	contaminant of concern
CPT	cone penetrometer testing
CSM	conceptual site model
DCE	dichloroethene
DNAPL	dense, nonaqueous-phase liquid
ECOS	Environmental Council of the States
ERIS	Environmental Research Institute of the States
ESTCP	Environmental Security Technology Certification Program
GMS	Groundwater Modeling Software
gpm	gallons per minute
HRP	high-resolution piezocone
IPT	integral pump test
ITRC	Interstate Technology & Regulatory Council
LC	Launch Complex
MCL	maximum contaminant level
MIP	membrane interface probe
MIPT	modified integral pump test
MLS	multilevel sampler
MNA	monitored natural attenuation
MtBE	methyl tertiary-butyl ether
NAPL	nonaqueous-phase liquid
NASA	National Aeronautics and Space Administration
PAH	polycyclic aromatic hydrocarbon
PCE	perchloroethene
PFM	passive flux meter
PZ	piezometer
RAO	remedial action objective
RI	remedial investigation
SEAR	surfactant-enhanced aquifer restoration
SERDP	Strategic Environmental Research and Development Program
TCE	trichloroethene
TCW	tandem circulating well
TM	transect method
TMB	trimethylbenzene
TRW	tandem recirculating well
USEPA	U.S. Environmental Protection Agency
VOA	volatile organic analysis
VOC	volatile organic compound



## SYMBOLS

$A$	area of the control plane
$A_i$	area of the polygon
$A_j$	flow area through polygon
$b$	uniform thickness, aquifer thickness
$C$	contaminant concentration
$^{\circ}\text{C}$	degrees Centigrade, Celsius
$C_F$	averaged $A_j$ area associated with an individual measurement ( $\text{m}^2$ )
$C_F$	flux averaged concentrations
$C_j$	concentration of constituent at polygon
cm	centimeter
$C_n$	individual concentration
$C_o$	initial dissolved aqueous resident tracer concentration individual measurement point in the pore fluid transect ( $\mu\text{g/L}$ )
$C_{sw}$	contaminant concentration in water extracted from the supply well (mass/volume)
d	day
ft	foot, feet
g	gram
$i$	hydraulic gradient
$i_j$	hydraulic gradient at individual point (cm/cm)
$J$	mass flux (mass/time/area)
$J_c$	time-averaged advective contaminant mass flux
$J_i$	mass flux measurement at location $i$
$K$	hydraulic conductivity
kg	kilogram
kg/year	kilograms per year
$K_j$	individual hydraulic conductivity at polygon term
$K_n$	individual $K_j$ hydraulic conductivity term at individual point (cm/sec)
$K_{ow}$	octanol-water partition coefficient
$K_p$	Kreundlich equilibrium partition
$K_{sp}$	mineral solubility product
L	liter
$L$	length
$L^2$	area
$L^3$	volume
$L^3/L^2/t$	volume per area per time ( $\text{L}/\text{m}^2/\text{d}$ )
m	meter
$M$	mass
$M_c$	mass of contaminant sorbed
$M_d$	mass discharge (e.g., g/area)
$M_{dj}$	mass discharge through polygon
mg	milligram
$M_r$	relative mass of tracer remaining in the PFM sorbent
$M/t$	mass per time (e.g., g/d)
$M/L^2/t$	mass per area per time (e.g., $\text{g}/\text{m}^2/\text{d}$ )

$P_b$	bulk density of the sorptive matrix
$q$	groundwater velocity, specific discharge, average
$Q$	groundwater flux discharge
$q_j$	specific discharge through polygon
$q_0$	Darcy groundwater flux, Darcy groundwater velocity
$q_{sw}, Q_{sw}$	pumping rate of supply well
$r$	radius of the PFM cylinder
$R_d$	retardation of the resident tracer on the PFM sorbent
$R_{dc}$	retardation of the contaminant on the PFM sorbent
$t$	time
$T$	aquifer transmissivity (volume/time sampling duration)
$w$	mass discharge of plume near water supply well (mass/time)
$\alpha$	convergence or divergence of flow around the PFM
$\Delta h$	head difference between the pumping well and the observation well
$\Delta x$	distance between pumping well and observation well
$\mu\text{g/L}$	micrograms per liter