

REVIEW OF GROUNDWATER CONTAMINANT MASS FLUX MEASUREMENT

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Abstract : The ability to measure groundwater contaminant flux is increasingly being recognized as crucial in order to prioritize contaminated site cleanups, estimate the efficiency of remediation technologies, measure rates of natural attenuation, and apply proper source terms to model groundwater contaminant transport. Recently, a number of methods have been developed and subsequently applied to measure contaminant mass flux in groundwater in the field. Flux measurement methods can be categorized as either point methods or integral methods. As the name suggests, point methods measure flux at a specific point or points in the subsurface. To increase confidence in the accuracy of the measurement, it is necessary to increase the number of points (and therefore, the cost) of the sampling network. Integral methods avoid this disadvantage by using pumping wells to interrogate large volumes of the subsurface. Unfortunately, integral methods are expensive because they require that large volumes of contaminated water be extracted and managed. Recent work has investigated the development of an integral method that does not require extraction of contaminated water from the subsurface. We begin with a review of the significance and importance of measuring groundwater contaminant mass flux. We then review groundwater contaminant flux measurement methods that are either currently in use or under development. Finally, we conclude with a qualitative comparison of the various flux measurement methods.

Key Words : Groundwater contamination, Hazardous waste site characterization, Hazardous waste site remediation, Mass flux, Flux measurement, Passive flux meter, Natural attenuation, Remediation technology, Integral pump test, Recirculating wells

Significance of Groundwater Contaminant Flux Measurement

Background

Groundwater constitutes about two thirds of the freshwater resources of the world and, if the polar ice caps and glaciers are not considered, groundwater accounts for nearly all usable fresh-

water (UNESCO/WHO/UNEP¹). Even if consideration is limited to only the most active and accessible groundwater aquifers, then groundwater still makes up 95% of total freshwater, with lakes, swamps, reservoirs and rivers accounting for 3.5% and soil moisture accounting for only 1.5% (Freeze and Cherry²). Groundwater has been extracted for domestic use (drinking, cleaning) as well as for agriculture (water for livestock and irrigation) since the earliest times. In the US, where groundwater is important in all regions, about 40% of public water supplies

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overall rely on a groundwater source. In rural areas of the US, 96% of domestic water is supplied from groundwater (UNESCO/WHO/UNEP¹). Also, many of the major cities of Europe are dependent on groundwater.

At the same time that reliance on groundwater is growing throughout the world, groundwater resources are facing an unprecedented risk of contamination due to subsurface releases of chemicals (Einarson and Mackay³). Contaminated groundwater sites can be considered to consist of two parts, the source and the plume. Subsurface source areas typically are created when contaminants are either accidentally or intentionally released on or below the ground from drums, tank, landfills, etc. Many times these releases consist of contaminants such as oils and solvents that exist as separate phase liquids, commonly referred to as nonaqueous-phase liquids (NAPLs), in the subsurface (Figure 1).

These separate phase contaminants migrate through the subsurface, moving by gravity through the vadose, or unsaturated zone, until they reach the water table (Wiedemeier et al.⁴). As the NAPL passes through the vadose zone, it leaves behind residual levels of pure phase contaminant, held between the grains of the porous media by capillary forces (Wiedemeier et al.⁴). NAPLs that are less dense than water, such as

petroleum hydrocarbons, are called light- NAPLs (LNAPLs). LNAPLs will form a layer or pool that floats above the water table, slowly dissolving into groundwater passing below it. NAPLs such as chlorinated solvents are denser than water. These NAPLs, referred to as dense-NAPLs (DNAPLs), will sink below the water table, leaving behind residual droplets (see Figure 1). Eventually, the DNAPL will reach a low permeability layer, where it will spread out, creating a separate phase DNAPL pool (Wiedemeier et al.⁴).

When released as a NAPL, large quantities of contaminants can be trapped in soils as residual droplets and pools. Due to the relatively low water solubility of many NAPL contaminants, the NAPL may persist for decades, only slowly dissolving into passing groundwater, to form contaminant plumes that can extend for miles (Einarson and Mackay³). These plumes can ultimately be transported by flowing groundwater to receptors such as downgradient supply wells or surface water (Einarson and Mackay³). In the United States alone, releases of gasoline fuels containing MTBE (methyl *tert*-butyl ether) may have occurred at more than 250,000 sites, with the potential to contaminate over 9,000 large municipal water supply wells (Einarson and Mackay³).

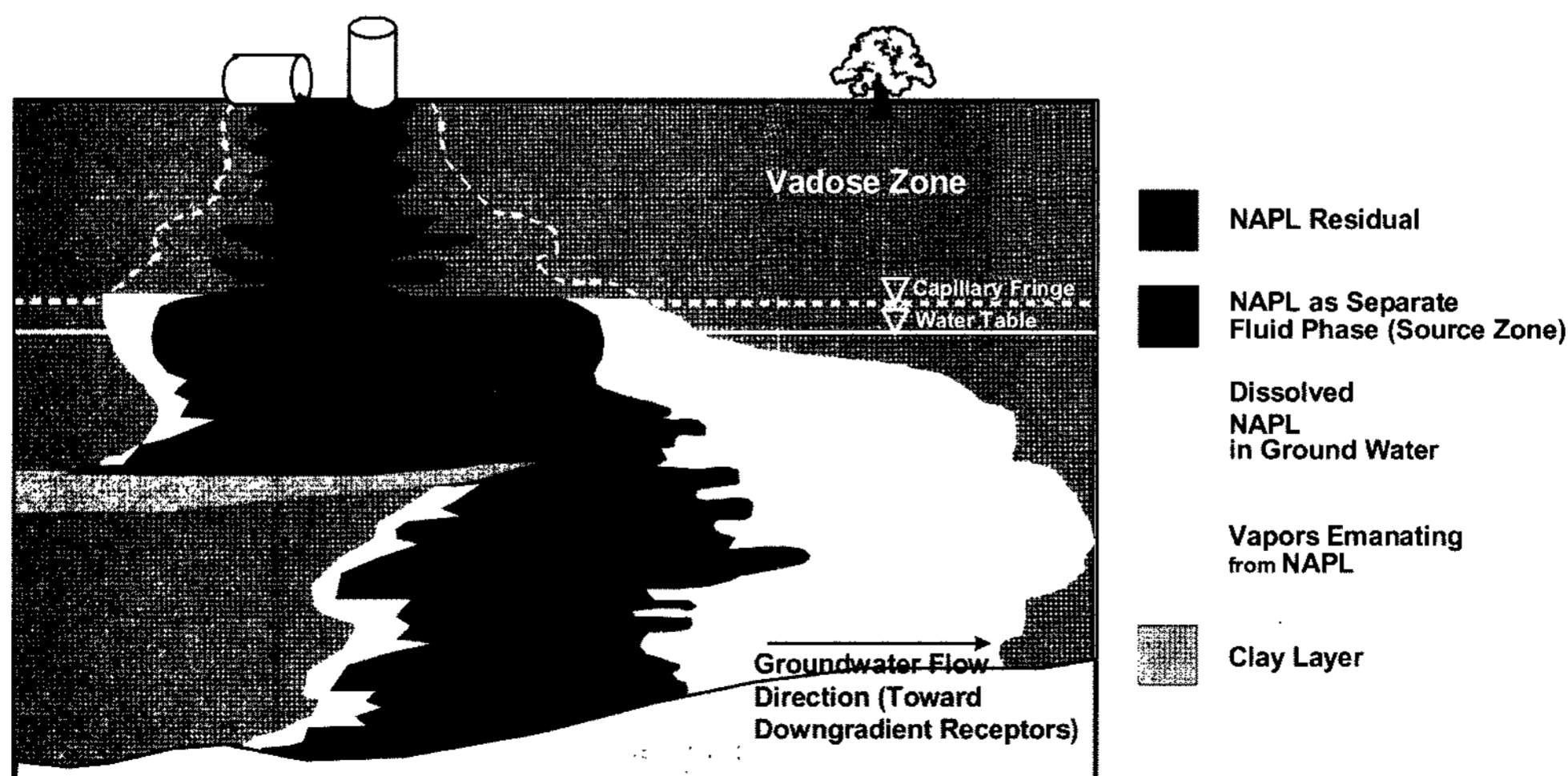


Figure 1. Groundwater contamination source zone (NAPL) and dissolved plume (NRC, 1994).

In 1980, the US government enacted the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) to address the risks posed by past releases of contaminants into soil and groundwater. CERCLA established a multi-decade/multi-billion dollar program to identify, characterize, and remediate contaminated sites.

Due to limited resources, an important component of the CERCLA process is prioritization of sites to be remediated based upon risk to human health and the environment (Einarson and Mackay³). One parameter that is important in quantifying risk is contaminant mass flux (SERDP/ ESTCP⁵, Einarson and Mackay³, API report⁶, Soga et al.¹¹, USEPA⁷). Mass flux is a measure of the rate contaminant mass is transported, in units of mass per time per area of aquifer orthogonal to the direction of groundwater flow. Einarson and Mackay³ argued that contaminant mass flux is more relevant as an indicator of risk at a down-gradient water supply well than contaminant concentration in the plume, even though most of our efforts to date have been focused on quantifying contaminant concentrations in the plume. Einarson and Mackay³ go on to suggest that contaminant mass flux measurements would be more useful than concentration measurements in helping regulators and remediation decision makers prioritize cleanup among numerous contaminant release sites.

In addition to helping assess risk in order to prioritize contaminated site cleanups, mass flux measurements can also be used to (1) quantify how readily a dissolved contaminant is degrading by natural processes (Borden et al.⁸, Bockelmann et al.⁹, Peter et al.¹⁰), (2) evaluate the efficacy of cleanup technologies (SERDP/ ESTCP⁵, Soga et al.¹¹), and (3) determine the source term for use in contaminant transport modeling (Wiedemeier et al.⁴). Contaminant flux measurement has been the subject of considerable research in the past five years, as scientists, regulators, and hazardous waste site managers have begun to realize the importance of measuring contaminant flux, as opposed to “traditional” measurements of contaminant concen-

tration (SERDP/ESTCP⁵).

In this review, we discuss how flux measurements may be used to 1) prioritize contaminated site remediations, 2) quantify how readily a dissolved contaminant is degrading by natural processes 3) evaluate the efficacy of cleanup technologies, and 4) determine the source term for use in contaminant transport modeling. We then review the various methods of flux measurement that are in use or currently under development. We conclude with a qualitative comparison of the various methods.

Reasons for Flux Measurement

Prioritization of cleanup

A contaminant source zone may have the majority of contaminant mass located within low permeability regions. In this case, even though contaminant mass and dissolved concentrations may be large, the flux of contaminant leaving the source zone will be relatively low. Conversely, a smaller source zone in a high permeability region may result in significant contaminant mass flux leaving the area. With this in mind, Einarson and Mackay³ contend that to assess the risk to receptors of groundwater contamination, contaminant mass flux, rather than contaminant concentration, should be evaluated.

In their paper, Einarson and Mackay³ demonstrate how knowledge of the contaminant mass flux emanating from a contaminant source area can be used to estimate the contaminant concentration at a downgradient water supply well. After making a number of simplifying assumptions, Einarson and Mackay³ show that the contaminant concentration in a downgradient water supply well (C_{sw}) pumping at rate Q_{sw} can be calculated as:

$$C_{sw} = M_f \times A \div Q_{sw} \quad (1)$$

where M_f is the contaminant mass flux [$ML^{-2}T^{-1}$] emanating from a contaminant source area whose plume is captured by the supply well and A [L^2] is the area of the plume orthogonal to the groundwater flow direction that is captured by the well.

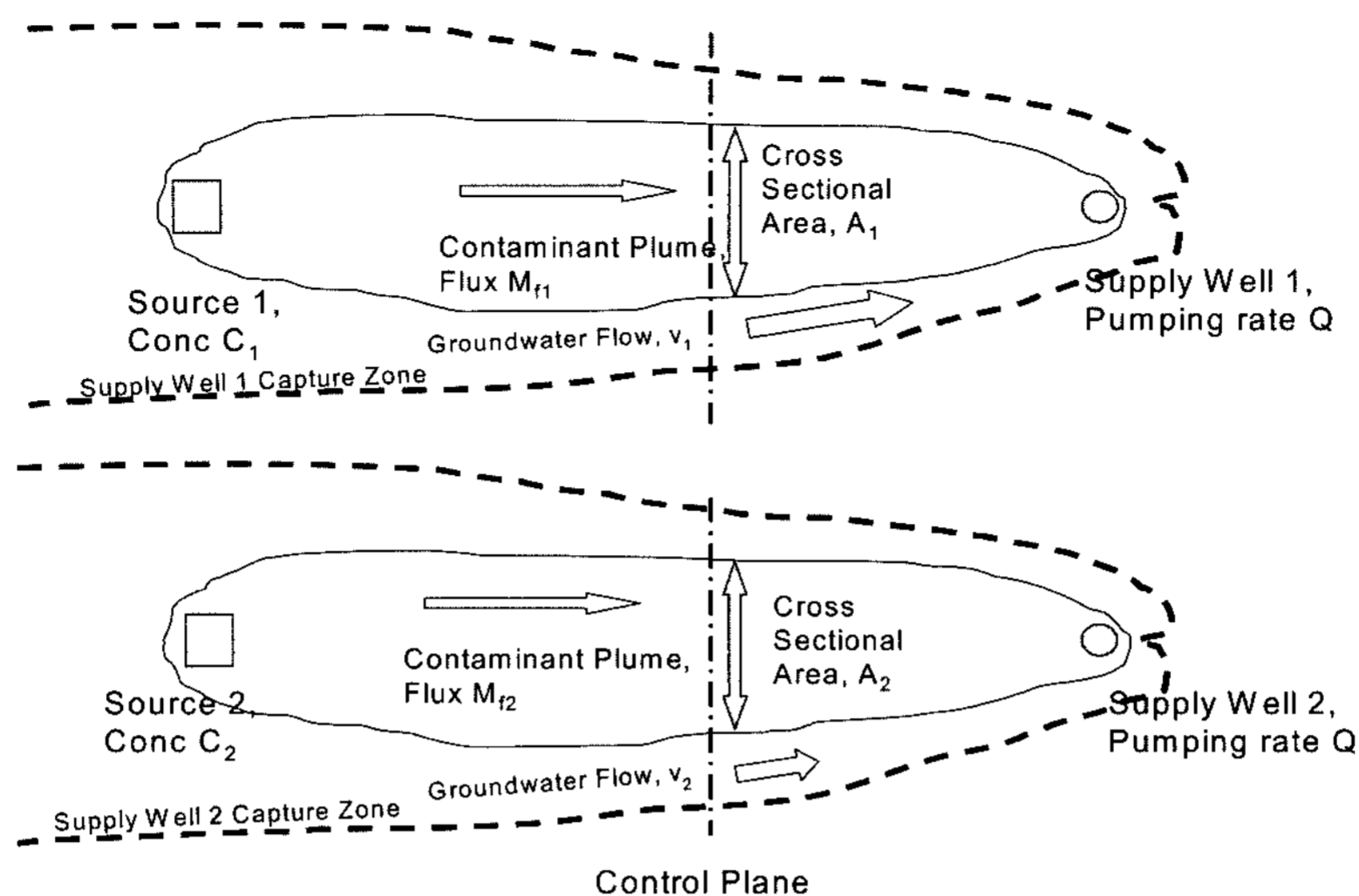


Figure 2. Plan view of two hypothetical contaminated sites (Einarson and Mackay, 2001).

To demonstrate how the measurement of contaminant flux from a source zone is related to risk, and therefore, useful in prioritizing site cleanups, suppose there are two different contaminated sites that have a source zone and supply well at each site (Figure 2) (Einarson and Mackay³).

Just downgradient of Source 1, dissolved concentrations of contaminant are measured at 1 mg/L, while just downgradient of Source 2, contaminant concentrations are 5 mg/L. Let us assume the cross-sectional areas of the two plumes are the same at the control planes shown in Figure 2 ($A_1 = A_2$) and that the groundwater velocities measured at the control planes are 2 m/d and 0.1 m/d for Sources 1 and 2, respectively. Measurements of contaminant flux downgradient of the two sources indicate that the flux from Source 1 is 2 g/(m²-d), while the flux leaving Source 2 is 0.5 g/(m²-d). The plume from each source is captured by a supply well that is pumping at a constant rate Q . In this hypothetical case, even though Source 2 has a higher downgradient contaminant concentration, application of Equation (1) shows that Source 1 will result in a higher concentration in Supply Well 1 than the concentration seen in Supply Well 2 resulting from Source 2. This, of course, is due to the greater mass flux leaving Source 1. Thus, when prioritizing

the two sites for cleanup, a decision maker might decide to address remediation of Site 1 first, even though Site 2 has higher contaminant concentrations.

As described above, it is contaminant mass flux, rather than contaminant concentration, that is more crucial in determining the risk posed by a contaminant source and plume. Thus, ideally, site managers and regulators will have access to accurate flux measurements in order to inform their site management decisions.

Evaluating the efficacy of cleanup technologies

The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) (SERDP/ESTCP⁵) reported that assessing the effects of source zone treatment is one of the highest priorities needs for science and technology within the remediation area. More recently, a SERDP-sponsored Expert Panel Workshop on Reducing the Uncertainty of DNAPL Source Zone Remediation (March 2006) concluded "(g)uidance is needed on when and how to best measure and analyze mass flux data..." (SERDP/ESTCP¹²). As we attempt to evaluate the various source remediation technologies that are being proposed and fielded, we must keep in mind that the measure of technology success is

risk reduction (as opposed to mass reduction, concentration reduction, or some other measure). As demonstrated in the section above, flux reduction can be directly tied to risk reduction, so being able to measure reduction of flux by comparing pre- and post-remediation fluxes, is crucial to being able to evaluate the efficacy of source zone remediation technologies (SERDP/ESTCP⁵), Soga et al.¹¹).

A number of recent studies have been concerned with how application of source remediation technologies may result in flux reduction (Sale and McWhorter¹³), Rao et al.¹⁴), Soga et al.¹¹), Rao and Jawitz¹⁵), McWhorter and Sale¹⁶), NRC¹⁷), Lemke et al.¹⁸). Soga et al.¹¹) focused upon how flux reduction may be a function of the interactions between the remediation technology, source morphology, and subsurface heterogeneities. Some technologies can increase or decrease the long-term contaminant flux in downgradient receptor areas by changing the source morphology during treatment, while other technologies do not affect the mass flux because they treat only the plumes without remediating source areas (Soga et al.¹¹).

Rao et al.¹⁴) conducted three-dimensional particle-tracking model simulations for heterogeneous flow fields and field experiments at the Dover AFB, Delaware to show that significant contaminant flux reductions can be achieved by partial removal of contaminant mass from DNAPL source zones. Rao and Jawitz¹⁵) used a stream tube model to theoretically calculate how reduction of contaminant mass flux is related to reduction of source mass for homogeneous and heterogeneous media. Assuming a homogeneous distribution of DNAPL, and quantifying hydraulic conductivity heterogeneity using the standard deviation of the groundwater velocity distribution (σ), Rao and Jawitz¹⁵) showed that for increasingly heterogeneous media, relatively small source mass reductions could lead to relatively significant flux reductions (Figure 3).

Rao and Jawitz¹⁵) explained this based on the key assumption that DNAPL remediation technologies will preferentially remove or destroy DNAPL in high hydraulic conductivity zones

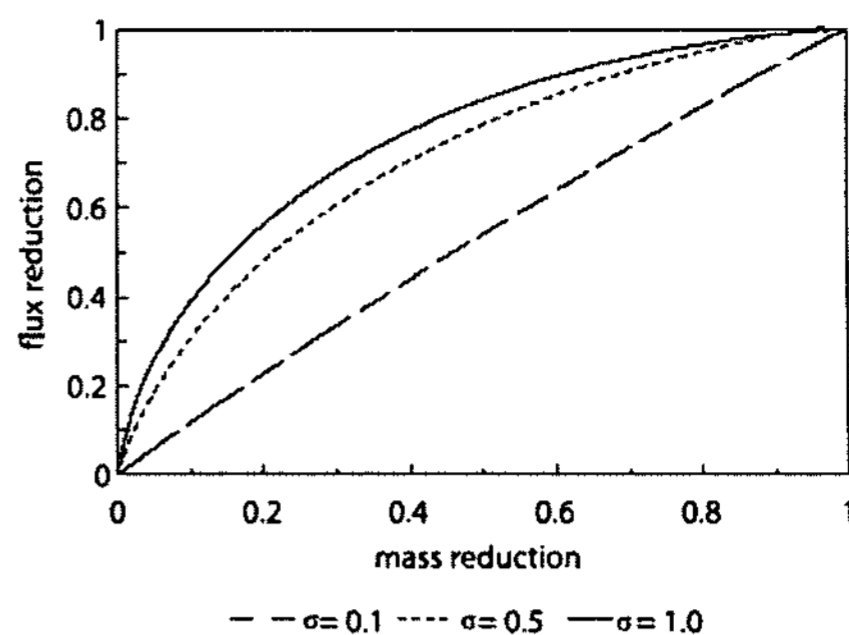


Figure 3. Fractional reductions in contaminant flux as a function of source mass removal for three values of the standard deviation (σ) of the groundwater velocity distribution (Rao and Jawitz¹⁵).

(represented by high velocity stream tubes). Thus, removal of the relatively small fraction of the total DNAPL mass that resides in the high velocity stream tubes can result in relatively large flux reductions, as it is this fraction that contributes the most to mass flux leaving the source area. Even though significant contaminant flux reductions are realized through partial mass reduction in the DNAPL source zone, it is still a matter of debate whether such mass flux reduction is sufficient to achieve adequate risk reduction and regulatory compliance (Rao and Jawitz¹⁵).

A National Research Council report (NRC¹⁷) also showed that mass removal may result in a substantial reduction in mass flux (Figure 4). In agreement with the study by Rao and Jawitz,¹⁵ the NRC¹⁷) suggests that for a given reduction in mass, mass flux reduction in a heterogeneous aquifer may be significantly greater than for a homogeneous formation (Figure 4). Lemke et al.¹⁸) also used modeling to predict that removal of 60 to 99% of contaminant source mass can reduce mass flux under natural gradient conditions by approximately two orders of magnitude. Christ et al.¹⁹) used three-dimensional numerical simulations in a statistically homogenous, non-uniform aquifer, to show that the relationship between source mass reduction and flux reduction was a function of the ratio of DNAPL mass in ganglia to DNAPL mass in pools (specified as the ganglia-to-pool (GTP) mass ratio). Simulations were used to show that at low GTP mass

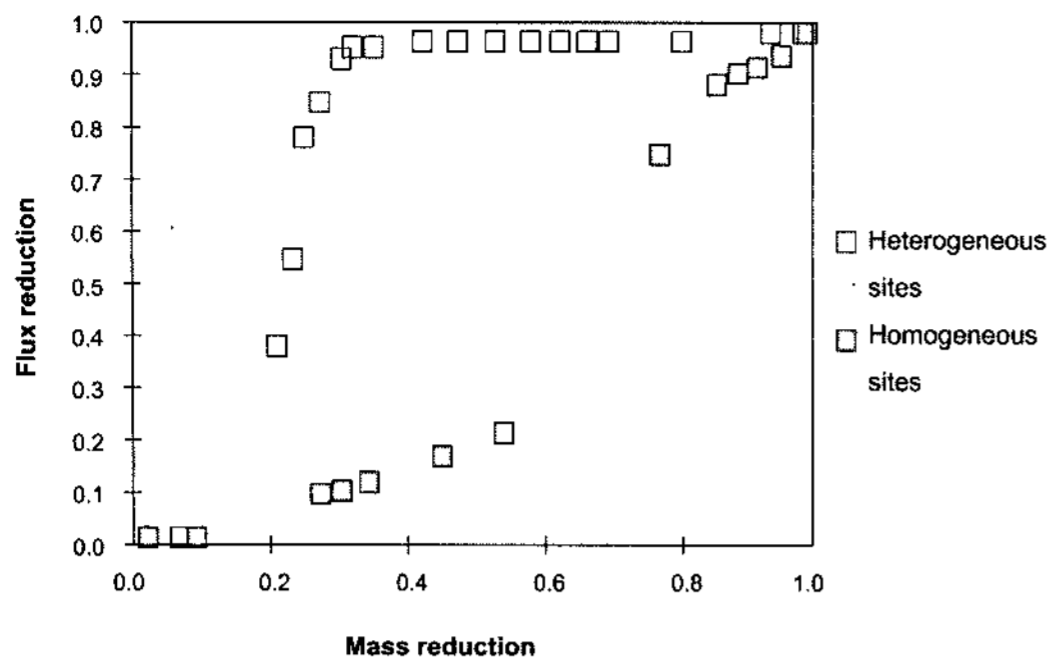


Figure 4. Simulated contaminant flux reduction as a function of mass reduction (NRC¹⁷).

ratios, relatively modest source mass reductions could result in significant flux reductions (Christ et al.).¹⁹

In contrast to the results discussed above (e.g. Rao and Jawitz¹⁵), Sale and McWhorter¹³ used an analytical model with a homogeneous flow field and heterogeneous DNAPL distribution to show that significant flux reductions could only be achieved if there were significant reductions in contaminant mass. This result corresponds to the homogeneous site simulation depicted in Figure 4 (NRC¹⁷). McWhorter and Sale¹⁶ argued that the conclusion that significant flux reduction could be achieved with relatively low mass removal was incorrect because of faulty assumptions employed by Rao and Jawitz.¹⁴ Specifically, Rao and Jawitz¹⁴ assumed: (1) complete depletion of DNAPL within individual stream tubes and (2) no mass transfer between stream tubes. These assumptions can create positive bias in terms of benefits that can be achieved from partial depletion of DNAPL mass. Thus McWhorter and Sale¹⁶ argued that even though the potential benefits of partial mass reduction may include reduced risk, reduced source longevity, reduced site-care requirements, and enhanced natural attenuation, quantification of such benefits as a function of mass removal is necessary. Clearly, the ability to accurately measure contaminant flux is crucial to quantifying the benefits of applying a source remediation technology.

Quantifying natural attenuation (NA)

Natural attenuation is an important strategy

that is used to manage groundwater contamination (SERDP/ESTCP⁵). A number of studies have measured contaminant flux or mass discharge in order to quantify the extent of NA (Borden et al.⁸, Bockelmann et al.⁹, Peter et al.¹⁰).

If one assumes that physical attenuation processes (e.g. dispersion, volatilization, sorption) are steady or small, measurements of mass flux through control planes located perpendicular to the principal contaminant flow direction at different distances from the contaminant source can be used, along with the average travel time between the control planes, to estimate an effective first-order contaminant decay coefficient (Borden et al.⁸). The assumptions of steady-state flow, dispersion, and sorption appear reasonable at many contaminated sites (Bockelmann et al.⁹) and a number of studies have demonstrated that volatilization of organic contaminants is not significant. For example, McAllister and Chiang²⁰ showed that volatilization accounted for only 5-10% of the mass reduction of volatile BTEX compounds. With these assumptions of steady or insignificant physical attenuation processes, measured flux reductions may be regarded as primarily resulting from chemical or biological degradation of the contaminant (Bockelmann et al.⁹).

The rate of NA at a site depends on the site's unique geochemical character. Borden et al.⁸ used mass flux measurements to demonstrate methyl tert-butyl ether (MTBE) and BTEX natural attenuation in a shallow aquifer contaminated by leaking underground storage tanks that contained gasoline and diesel fuel. In the study, flux measurements were used to show that NA was higher near the source area than downgradient and that NA of the BTEX compounds was generally greater than NA of MTBE (Borden et al.⁸). Studies such as these show that mass flux measurement is a powerful tool that can be used to evaluate NA at contaminated field sites, thus providing decision makers with important information that they can use to manage risk.

Modeling fate and transport (source term to

determine downgradient concentration)

Groundwater modeling has developed tremendously over the past 25 years, and we now have the ability to quantitatively estimate groundwater flow and contaminant mass transport in the subsurface (Bedient et al.²¹). The purposes of modeling are as follows (Bedient et al.²¹):

1. Testing a hypothesis, or improving knowledge of a given aquifer system.
2. Understanding physical, chemical, or biological processes.
3. Designing remediation systems.
4. Predicting future conditions or the impact of a proposed stress on a ground water system.
5. Resource management.

After developing a conceptual model of a system, it is necessary to translate the conceptual model into a mathematical model consisting of governing equations and initial and boundary conditions in order that the value of the dependent variable of interest (e.g. contaminant concentration) can be determined as a function of space and time (Wiedemeier et al.⁴). For fate and transport modeling, boundary conditions are specified in terms of contaminant concentrations and/or fluxes (Wiedemeier et al.⁴). It is clear that being able to measure contaminant flux is critical to our ability to appropriately quantify a source term in our model, thereby allowing us to simulate contaminant fate and transport at a site. Proper quantification of the source flux will result in improved modeling and, ultimately, better management decisions at the site.

Flux Measurement Methods

Point Methods

Point flux measurement methods rely on quantification of flux at points within an aquifer. These point measurements may then be used to obtain an average flux, as well as a total mass discharge (units of mass per time) for the area perpendicular to the groundwater flow direction. The disadvantage of point measurements is that

to increase confidence in the accuracy of the measurement, it is necessary to increase the number of points (and therefore, the cost) of the sampling network.

Transect

The conventional method for measuring contaminant mass flux in a plume is to install transects of monitoring wells along control planes that are orthogonal to the direction of groundwater flow. Either single-screen or multilevel groundwater monitoring wells can be used for this purpose (API⁶). Groundwater samples are collected at various points in the control planes, and contaminant concentrations measured at these points. Note that, in order to determine total contaminant mass discharge through the control planes, it is necessary that the monitoring wells sample the entire width and depth of the plume.

Applying the transect method to determine mass flux and discharge is straightforward. After having measured the contaminant concentration (C_i) at the i^{th} sampling point, the advective mass flux, $M_{f,i}$ [M/L^2T], at the point can be calculated as:

$$M_{f,i} = C_i \times q_i \quad (2)$$

where q_i [L/T] is the groundwater specific discharge at well i (Bockelmann et al.⁹). The groundwater specific discharge (also referred to as the Darcy velocity or groundwater flux) is defined by Darcy's Law as the product of the hydraulic conductivity at well i (K_i) and the hydraulic gradient (∇h) ($q = -K_i \nabla h$). We can determine the hydraulic gradient from a potentiometric surface contour map that is constructed based on static water level measurements at the monitoring points. Hydraulic conductivity can be obtained using appropriate slug test or pumping test methods (Weight and Sonderegger²²).

The contaminant mass discharge for individual sampling points, $M_{d,i}$ [M/T], and the total mass discharge through the control plane, M_d [M/T],

are defined as:

$$M_{d,i} = C_i \times q_i \times A_i = M_{f,i} \times A_i \quad (3)$$

$$M_d = \sum_{i=1}^n M_{d,i} \quad (4)$$

where n is the number of monitoring points in the control plane and $A_i [L^2]$ represents the area of the control plane associated with the i^{th} monitoring point. This area may be estimated by constructing Thiessen polygons (polygons whose sides are perpendicular bisectors of lines connecting adjacent monitoring points) in the control planes (Borden et al.⁸⁾, Bockelmann et al.⁹⁾). The average mass flux (M_f) can be obtained by dividing the total mass discharge by the cross-sectional area of the plume at the control plane (A):

$$M_f = M_d / A \quad (5)$$

By combining equations (3), (4), and (5) we also see that average mass flux can be directly calculated from the mass flux measurement at each sampling point as follows:

$$M_f = \frac{\sum_{i=1}^n M_{f,i} A_i}{A} \quad (6)$$

The limitation of the transect method is a result of the fact that sampling is at discrete points across the direction of flow, so a large representative volume of the subsurface is not necessarily interrogated. Increasing the detail of sampling, in order to account for spatial heterogeneities, or the range of sampling, to encompass the entire plume cross-section, requires increasing the number (and therefore cost) of sampling wells (Bockelmann et al.⁹⁾). Guilbeault et al.²³⁾ showed that even for a relatively homogeneous aquifer, vertical well spacing as small as 15 cm and lateral spacings between 1 and 3 m are

needed to characterize small zones of high concentration near a NAPL source.

Borden et al.⁸⁾ evaluated the mass flux of dissolved gasoline constituents (BTEX and MTBE) released from an underground storage tank using this transect method in a Coastal Plain aquifer in rural Sampson County, North Carolina in 1997. Using mass discharge measurements at four control planes, the authors estimated the field scale first-order natural attenuation decay rate of the dissolved contaminants. One advantage of this mass discharge approach to evaluating the rate of natural attenuation is that it does not require fitting a solute transport model to concentrations at individual wells in order to obtain a degradation rate constant. A disadvantage of the approach is that since it is based on sampling at discrete points, the sparser the points, the less reliable the mass discharge estimate compared to estimates based on volume-averaged approaches (such as the IGIM and TRW methods) which will be discussed below (Bockelmann et al.⁹⁾).

Passive Flux Meter (PFM)

This newly-developed method is a point method that involves placing PFMs at points along a control plane to intercept contaminated groundwater. The PFM consists of permeable sorbents and resident tracers (Hatfield et al.²⁴⁾, De Jonge and Rothenberg²⁵⁾). Hydrophobic and hydrophilic permeable sorbents retain dissolved organic and/or inorganic contaminants that are present in the fluid that passes through the PFM. These sorbents have 'resident tracers' which leach into the groundwater at rates proportional to fluid flux. The cumulative volume of groundwater that passes through the flux meter can be calculated using an analytical model that accounts for the mass of resident tracer that has desorbed into the water. Knowing the cumulative volume of groundwater that has passed through the PFM, as well as the time the PFM has been in place and the effective cross-sectional area of the PFM screens, specific discharge of the groundwater can be calculated (Hatfield et al.).²⁴⁾ The con-

taminant mass retained in the flux meter sorbent over the time the PFM has been in place can be used, in combination with the groundwater flux, to determine the contaminant mass flux at the PFM. As this is a point method, the flux measured at each PFM can be summed, using the methods described in Section 2.4.1 (see equations (3) through (6)), to obtain an average flux and a total mass discharge over the plume cross-section.

One advantage of this method over the transect method is that the flux measured by the PFMs is averaged over the time the PFM is in place. This is particularly relevant when discharge varies significantly with time. This temporal averaging may help circumvent overestimation or underestimation of flux that may result from a point measurement in time. Another advantage of the PFM method is that groundwater specific discharge is measured directly. This is in contrast to the transect method, which requires separate measurements of hydraulic conductivity and groundwater gradient in order to apply Darcy's law to determine specific discharge. As with the transect method, properly installed PFMs should intercept the entire width and depth of a plume of dissolved contaminant.

As a point method, the flux meter method has the same disadvantages as the transect method. That is, increasing the detail of sampling, in order to account for spatial heterogeneities, or the range of sampling, to encompass the entire plume cross-section, requires increasing the number (and therefore cost) of installed PFMs. Two other disadvantages are specific to the method itself: (1) a sorbent must be selected that permits sorption of the target contaminant and desorption of the resident tracer, and (2) determination of the area captured by a PFM (for use in equation (6) to calculate the average mass flux) is not straightforward. Selection of a contaminant-appropriate sorbent may require site-specific batch sorption tests and estimation of the capture area associated with a PFM requires application of a formula that requires knowledge of the hydraulic conductivities of the PFM, the well screen/filter pack,

and the aquifer itself (Klammler et al.²⁶), Annable et al.²⁷). Thus, the advantage of not having to know the aquifer hydraulic conductivity in order to use the PFM to measure flux, which was mentioned above, may be lost.

Hatfield et al.²⁴) used the PFM method to measure mass flux of 2,4-dimethyl-3-pentanol (DMP) in an artificial box aquifer (27 cm long by 20 cm high and 18 cm deep). Granular activated carbon (GAC) was used as the sorbent, and various alcohols (ethanol, methanol, isopropyl alcohol, and n-hexanol) were used as resident tracers. DMP mass flux was measured within 5% of the known flux.

De Jonge and Rothenberg²⁵) demonstrated the PFM method for various sorbents and resident tracers in laboratory experiments, using 20 cm by 20 cm unsaturated soil columns. The investigators found that if the correct adsorbent was used in the PFM, fluxes of phenanthrene and glyphosate could be measured with an accuracy of 3.6% ~ 17.8% and 12.4% respectively.

Annable et al.²⁷) performed two field tests of the PFM method at the Canadian Forces Base Borden field site in Ontario, Canada. In both tests, a pumping well was used to induce flow. In the first test, radial flow was induced, and in the second test, flow was linear within a test channel with sheet pile walls on three sides. Trichloroethylene (TCE) and tetrachloroethylene (PCE) were the contaminants in the first test, while MTBE was the contaminant in the second test. The PFMs used GAC as the sorbent and various alcohols as the resident tracers. The PFMs were used to measure groundwater and contaminant (PCE, TCE, and MTBE) mass fluxes. The groundwater and contaminant mass fluxes measured using the PFMs were compared with the "true" mass fluxes measured at the pumping wells. For both tests, it was shown that the PFMs measured groundwater flux within 15% and contaminant mass flux within 30%.

Basu et al.²⁸) used the PFM method to quantify natural attenuation of TCE at a former manufacturing plant located in the Midwestern US. As with earlier evaluations of the PFM

method, activated carbon was used as the sorbent and alcohols were used as the resident tracers. The first-order degradation rate estimated using the PFMs (0.52 yr^{-1}) compared well with the conventional approach, which was used to calculate a rate based upon reduction of TCE concentrations at wells along the plume centerline (0.78 yr^{-1}).

Campbell et al.²⁹⁾ configured a PFM that could be used to quantify the direction, as well as the magnitude, of the groundwater flux. Also, in contrast to earlier PFM evaluations, the contaminant of interest was inorganic (Cr(VI)) rather than organic. To measure groundwater flux direction, the PFM was divided into a center section with three outer sectors. To sorb the inorganic Cr(VI) oxyanions (chromate and bichromate) an anion exchange resin was used as a sorbent. Benzoate was used as the resident tracer. Laboratory experiments were conducted in porous packed bed columns, with known groundwater and Cr(VI) mass fluxes. Results showed an average measurement error for the direction of groundwater flow of $3^\circ \pm 14^\circ$, while the average measurement errors for the groundwater flux magnitude and Cr(VI) mass flux were, respectively, $-8\% \pm 15\%$ and $-12\% \pm 23\%$.

Cho et al.³⁰⁾ and Lee et al.³¹⁾ also investigated the use of the PFM method to measure inorganic anion flux. Cho et al.³⁰⁾ introduced the PNFM (passive nutrient flux meter) to measure nutrient (phosphate) flux in a flow chamber. The investigators used an anion exchange resin as a sorbent and alcohols as resident tracers. Phosphate mass flux and water flux measured by the PNFM were within 6% and 12% of the applied values. Lee et al.³¹⁾ used a PFM with surfactant-modified GAC as a sorbent and alcohol resident tracers to measure perchlorate flux in the field. While the actual values of groundwater and perchlorate mass fluxes in the field were not known, the values measured in two PFM deployments closely matched each other, and the groundwater flux was similar to the groundwater flux measured in a borehole dilution test.

Integral Methods

To avoid the high cost of installing many sampling locations to obtain an accurate flux measurement using point methods, integral methods are used. Integral methods use pumping wells to interrogate large volumes of the subsurface. Unfortunately, integral methods are expensive because they may require that large volumes of contaminated water be extracted and treated.

Integral Groundwater Investigation Method (IGIM)

Spatially integrated contaminant mass discharge (M_d) can be estimated by pumping potentially contaminated water at one or more wells located along a control plane downgradient of a suspected pollutant source zone so as to fully capture the contaminant plume emanating from the source (Bockelmann et al.⁹⁾, Bauer et al.³²⁾). The number and location of the wells, along with pumping rates and times, must be chosen to ensure that the entire plume is captured, in order to determine the total mass discharge across the control plane.

Mass discharge is determined by monitoring contaminant concentration at each of the pumping wells versus time. Under the following assumptions: (1) the flow towards the extraction wells is radially symmetrical, i.e. the natural flow can be neglected during the pumping test; (2) the aquifer is homogeneous with regard to porosity, hydraulic conductivity and thickness, and (3) the concentration does not vary significantly along each of the streamtubes at the scale of the well capture zone, although it may vary from streamtube to streamtube, Bockelmann et al.⁹⁾ described and applied a method at a contaminated site to analytically invert the concentration versus time (CT) measurements to obtain an estimate of mass discharge across a control plane perpendicular to the direction of groundwater flow. Bockelmann et al.⁹⁾ also noted that for a heterogeneous aquifer, where there are detailed measurements of the hydraulic conductivity distribution in space, the CT data can be numerically inverted to estimate mass discharge. If we are able to quantify the cross-sectional area of the plume

captured by the extraction wells, the average mass flux, $M_f \left[\frac{M}{L^2 T} \right]$, can be obtained by dividing the total mass discharge by the cross-sectional area.

Because the IGIM is based on pumping wells, the method can interrogate a large volume of the subsurface with installation of relatively few wells as compared to point methods. The associated disadvantage of this is that extraction of potentially contaminated water can result in safety concerns and water treatment/disposal costs (Bockelmann et al.⁹). Since it is a pumping technique, the IGIM will not work in geologies with low transmissivities. The method also requires capture of the entire plume--incomplete capture will result in underestimation of the mass discharge. On the other hand, if the IGIM well capture zone is too large, contaminant from the plume may mix with large volumes of uncontaminated water, resulting in *CT* responses at the wells where the concentrations are below analytical detection limits. Asymmetrical well capture zones around a well caused by significant heterogeneities lead to uncertain control plane width. Also, preferential flowpaths across the control plane could be overestimated or underestimated by using the average groundwater flux at the scale of the individual well capture zone (Bockelmann et al.⁹).

Bockelmann et al.^{9,33} and Peter et al.¹⁰ applied the IGIM to estimate the NA of a petroleum hydrocarbon contaminant plume at a former gasworks site in Southwest Germany. Bockelmann et al.⁹ quantified mass fluxes and NA rates using the transect and IGIM methods at two control planes. The investigators showed that due to the dependence of the transect method on concentration measurements at points in a relatively sparse monitoring network, there was considerable uncertainty in the flux measurement. Considerable differences (97% ~ 159%) were noted between the fluxes measured by the two methods at the two control planes (Bockelmann et al.⁹). The investigators attributed the differences in the two methods to the fact that the transect

method was inadequate in capturing the plume and geologic heterogeneities and concluded that the IGIM was a viable method for mass flux measurement.

The study by Bockelmann et al.⁹ also quantified NA rate constants using both the IGIM and "centerline" point scale approaches. The centerline approach made use of a long-term tracer test to delineate the contaminant transport path and compare contaminant concentration reduction with the concentration reduction of a conservative tracer along the plume centerline. Both approaches resulted in similar NA rate constant values.

Bauer et al.³² quantified PCE and TCE mass fluxes by using both a numerical inversion code, CSTREAM (Bayer-Raich et al.³⁴), and a simplified analytical approach to interpret IGIM data from an industrialized urban area in Linz, Austria. The results of the numerical and analytical approaches deviated by less than a factor of two.

The IGIM was also evaluated as a component of the European Union-sponsored Integrated Concept for Groundwater Remediation (INCORE³⁵) project at four European cities. The INCORE³⁵ studies involved quantification of chlorinated hydrocarbon contaminant flux at four sites. From the INCORE³⁵ studies, the investigators concluded that the IGIM was capable of quickly and with certainty estimating the average contaminant concentration, spatial distribution of concentration values along a control plane, and mass discharge downgradient of a contamination source zone.

Zeru and Schäfer³⁶ conducted a modeling study of the IGIM to examine how a longitudinal concentration gradient along a contaminant plume affects the estimated contaminant mass flux. The investigators compared the mass flux that was estimated by analytically inverting *CT* data obtained during "virtual" application of the IGIM method to a numerically-generated plume, with the "real" flux, which was obtained from the numerical simulation directly. Results of the modeling study showed that at lower dispersivity values and shorter transport times, the IGIM method overestimates flux, while for higher dis-

persivity values, the method underestimates flux. Better flux estimates were obtained for longer transport times; that is, after the plume advective front passed the locations where the IGIM pumping wells were installed.

Integral Pumping Test (IPT)

Brooks³⁷⁾ recently proposed the IPT method as a way of obtaining an estimate of contaminant mass flux averaged over a large subsurface volume. The method avoids the data analysis complexities of the IGIM, which requires multiple concentration measurements over time, and unlike the IGIM and TRW methods, it does not require separate measurements of hydraulic conductivity and hydraulic gradient.

The IPT method is based on complex potential theory. Mathematical details of the method may be found in Yoon.³⁸⁾ Application of the method assumes steady-state and uniform two-dimensional flow in a homogeneous, isotropic, confined aquifer of uniform thickness.

The IPT method makes use of one or more pumping and monitoring wells. The pumping wells are pumped at different flow rates, and the differences in pumping and monitoring well drawdown for the various pumping rates are measured. Using the pumping well flow rates, drawdown differences, and well locations as input data, and making the assumptions listed above, complex potential theory can be used to directly estimate the regional groundwater flux. The contaminant concentration can then be measured, and multiplied by the groundwater flux, to obtain the contaminant mass flux.

Yoon³⁸⁾ applied the IPT method to measure mass flux in a 9.5 m long by 4.7 m wide by 2.6 m deep artificial confined aquifer filled with relatively homogeneous sand. Yoon³⁸⁾ found that the IPT method underestimated the actual contaminant mass flux by at least 36%. He attributed the error to differences between actual conditions in the artificial aquifer and the method assumptions (particularly, the assumptions of steady-state flow in a homogeneous aquifer).

Tandem Recirculating Wells (TRWs)

TRWs consist of two pumping wells, with each well having an extraction and injection screen. One well operates in an upflow mode, the other in a downflow mode, so that water recirculates between the two wells without being brought to the surface (see Figure 5). While TRWs have been applied in the field for contaminant plume cleanup (McCarty et al.³⁹⁾), and TRW flow models are available (Gandhi et al.⁴⁶⁾), TRWs have not been used in the past for flux measurement. Kim⁴¹⁾ and Huang et al.⁴²⁾ proposed an innovative approach to measure flux by operating TRWs. Since contaminant mass flux can be calculated as the product of the groundwater flux or Darcy velocity (q_0) and contaminant concentration (C), and, by Darcy's Law, Darcy velocity is the product of hydraulic gradient (i) and hydraulic conductivity (K), the following equation can be used to calculate contaminant mass flux (M_f):

$$M_f = K \times i \times C \quad (7)$$

The TRW method involves individually measuring K , i , and C in order to determine contaminant mass flux. Hydraulic gradient may be determined by measuring the piezometric surface at the two TRWs, with the pumps turned off, and a third piezometer. Volume-averaged contaminant concentration in the TRWs can be measured by sampling the contaminated water as it flows through the wells. To measure hydraulic conductivity, an innovative tracer test technique,

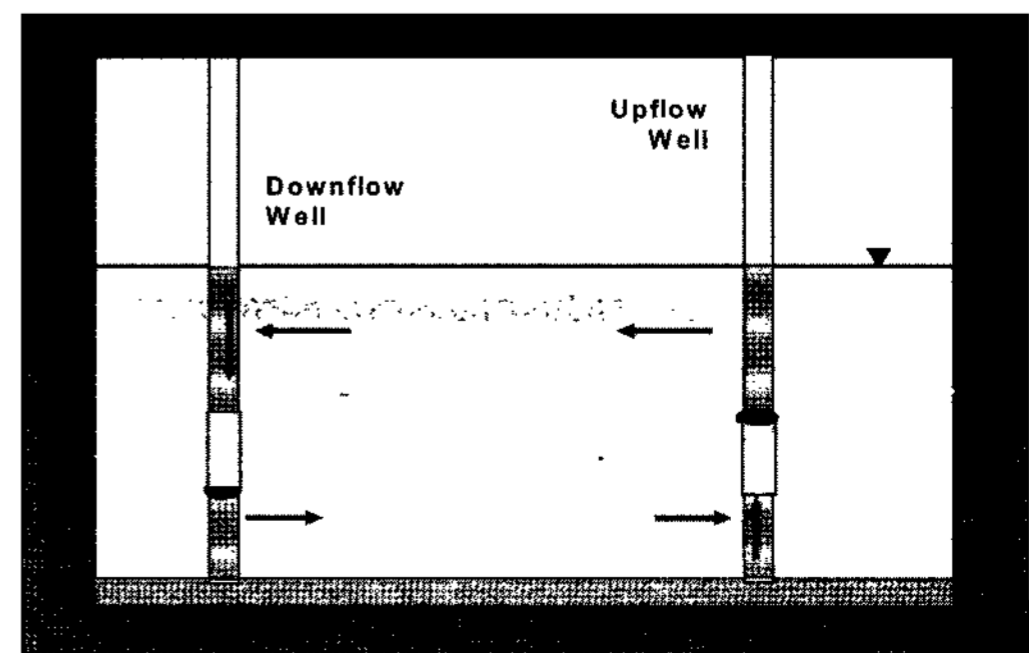


Figure 5. Tandem Recirculating Wells (TRWs).

the interflow measurement approach, was proposed and tested by Kim⁴¹⁾, Yoon³⁸⁾, and Goltz et al.⁴³⁾. This approach uses a tracer test to measure interflow of water between the TRWs, where interflow is defined as the fraction of water flowing into an extraction well screen that originated in one of the two injection screens (see Figure 6). The test consists of injecting a step concentration of one tracer into the upflow well and a step concentration of a second tracer into the downflow well. Subsequently, steady-state tracer concentrations at each of the four screens of the TRW well-pair are measured and based on the concentration measurements, mass balance is used to determine the four interflows between the four well screens. Knowing the four interflows for given TRW pumping rates, inverse modeling can be applied to obtain hydraulic conductivity. The method can be applied assuming isotropic (that is, horizontal and vertical hydraulic conductivities are the same) or anisotropic conductivities. Details of method application may be found in Kim⁴¹⁾, Yoon³⁸⁾ and Goltz et al.⁴³⁾.

The TRW flux measurement method has the benefits of other integral methods, in that a large volume of the subsurface is interrogated. Unlike the other integral methods, though, the costs of treating contaminated water that is extracted from the subsurface are avoided. However, one significant cost of the method, which is not incurred by other methods, is the cost of conducting a long-term tracer test to ensure steady-state

tracer concentrations are obtained at the TRW screens.

Goltz et al.⁴³⁾ conducted an experiment in a 9.5 m long by 4.7 m wide by 2.6 m deep artificial confined aquifer filled with relatively homogeneous sand to measure hydraulic conductivities. Assuming isotropy, which was reasonable in the case of the relatively homogeneous sand aquifer, the investigators used the TRW approach to determine a hydraulic conductivity of 0.16 cm/sec. This compared well with the "actual" conductivity of the aquifer, which was estimated based on previous studies, at 0.17 - 0.20 cm/sec (Bright et al., 2002). When horizontal and vertical conductivities were not constrained to be equal, values of horizontal and vertical conductivity of 0.13 and 0.10 cm/sec were obtained, respectively. The authors attributed the underestimate in conductivities to the fact that anisotropy was assumed for an aquifer that was relatively isotropic (Goltz et al.).⁴³⁾

The TRW method was also applied to measure the flux of a conservative tracer in the artificial aquifer (Huang et al.⁴²⁾). In that test, the measured mass flux of a chloride tracer was within 23% of the actual value.

Comparison of Methods

Table 1 qualitatively compares the different methods in terms of various criteria that are discussed below.

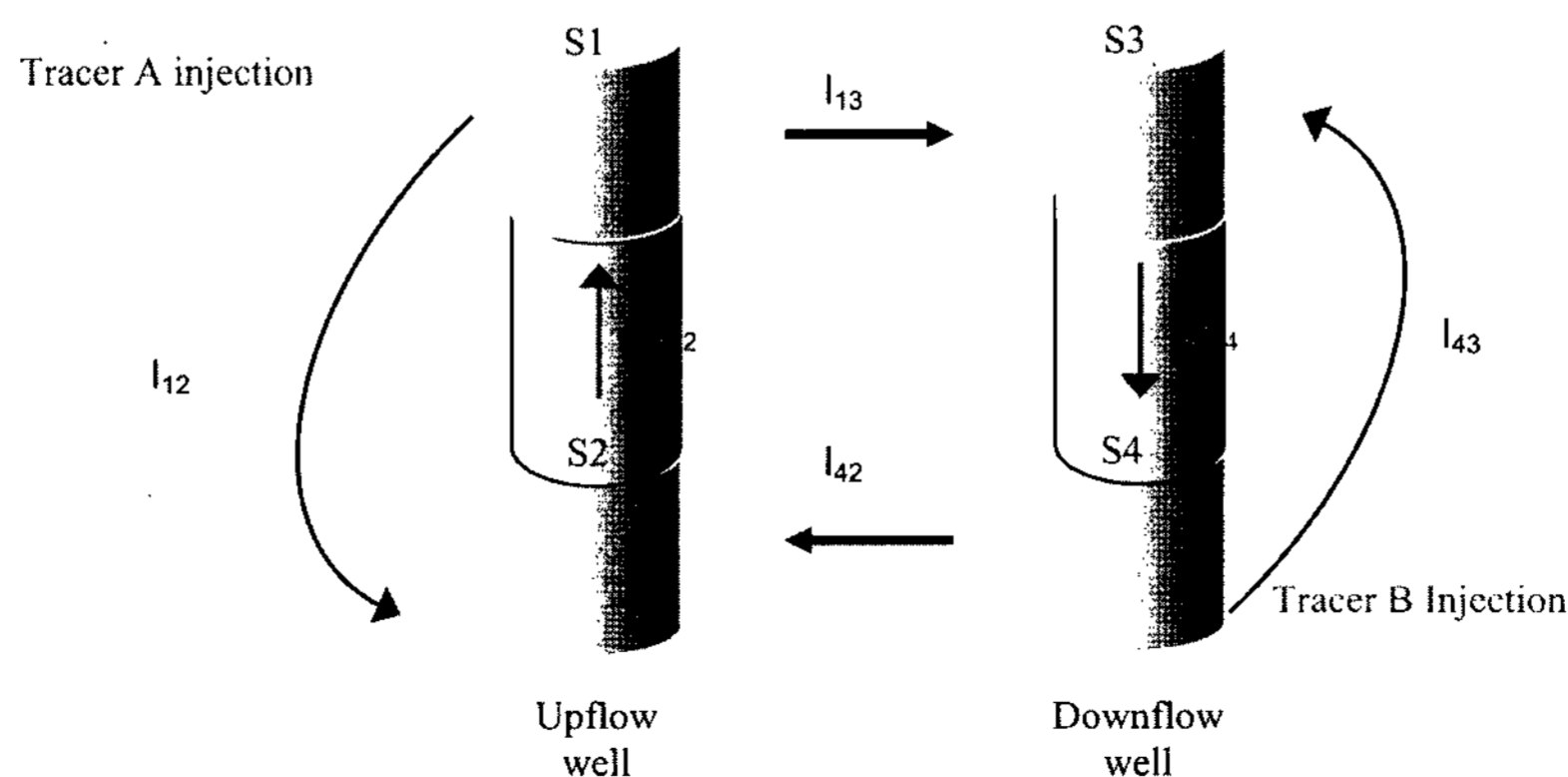


Figure 6. TRW fractional flows and tracer injection screens (Goltz et al.⁴³⁾).

Implementability

This criterion 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 pump 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 IPT method is equally straightforward, requiring installation of standard pumping and monitoring wells. The PFM, IGIM, and TRW methods are somewhat more complex. The PFM method requires quantification of the contaminant which 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 IGIM requires interpretation of the CT data, which is somewhat complex (Bockelmann et al.³³), Zeru and Schäfer³⁶). To implement the TRW 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 Considerations

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

and IPT 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 IGIM methods furthest along, followed by the IPT and TRW methods. The PFM and IGIM 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 TRW 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

Table 2 shows the relative costs of applying each of the flux measurement methods at a hypothetical "template" site (adapted from Kim⁴¹). Costs are normalized to the cost of applying the conventional transect method. The transect method is estimated to be the most expensive method, due to the cost of installing numerous monitoring wells, taking and analyzing water samples, and conducting a pump test to measure hydraulic

Table 1. Comparison of groundwater contaminant flux measurement methods

Methods		Implementability	Regulatory Considerations	Availability	Cost
Point	Transect	1	1	1	4
	PFM	3	2	2	4
Integral	IGIM	3	3	2	2
	IPT	1	3	2	2
	TRW	4	3	4	1

* 1 best; 4 worst

Table 2. Relative costs of applying the different mass flux measurement methods at a template site (Kim, 2005)

Method	Relative Cost
Transect	1.0
PFM	0.99
IGIM	0.78
IPT	0.66
TRW	0.59

conductivity. Note we assume the pump test is done in an uncontaminated portion of the aquifer, to avoid the expense of treating extracted groundwater. The PFM method is slightly less expensive than the transect method at the template site, as the need for a pump test is eliminated. However numerous monitoring wells and extensive sampling are still required. A recent study (ESTCP⁴⁴) found that, in general, the PFM method is less expensive than the transect method as long as 5 or more monitoring wells are required to be installed (Figure 7). Of the three integral methods, the TRW method is the least expensive because there is no need to treat extracted groundwater. The IGIM method is the most expensive integral method, because in addition to treating extracted groundwater, the CT data that are required entail many more analyses of contaminant concentrations than are needed for the other two integral methods.

Figure 7. Unit costs (per linear foot of well screen) of measuring contaminant fluxes by the PFM and transect methods as a function of the number of monitoring wells installed (assumes 10 samples taken per well) (from ESTCP⁴⁴).

Conclusion

The ability to measure groundwater contaminant mass flux is extremely important, in order that contaminated-site managers can prioritize cleanups, evaluate the efficacy of remediation technologies, estimate the rate of natural attenuation of contaminants, and develop a source term for application in contaminant transport models. A number of innovative flux measurement methods are currently being developed and fielded. As discussed above, each method has its own advan-

tages and disadvantages, and areas of application. Ultimately, a site manager must decide on an appropriate flux measurement method to apply, depending on the remedial objective at the site, the hydrogeological and contaminant conditions that are encountered at the site, and the decisions that need to be made, all within regulatory and economic constraints.

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