

Spatially-Averaged, Flow-Weighted Concentrations – A More Relevant Regulatory Metric for Groundwater Cleanup

Murray Einarson
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Mass and Flux Distributions from DNAPL Zones in Sandy Aquifers

by Martin A. Guilbeault^{1,2}, Beth L. Parker^{1,3}, and John A. Cherry¹

Abstract

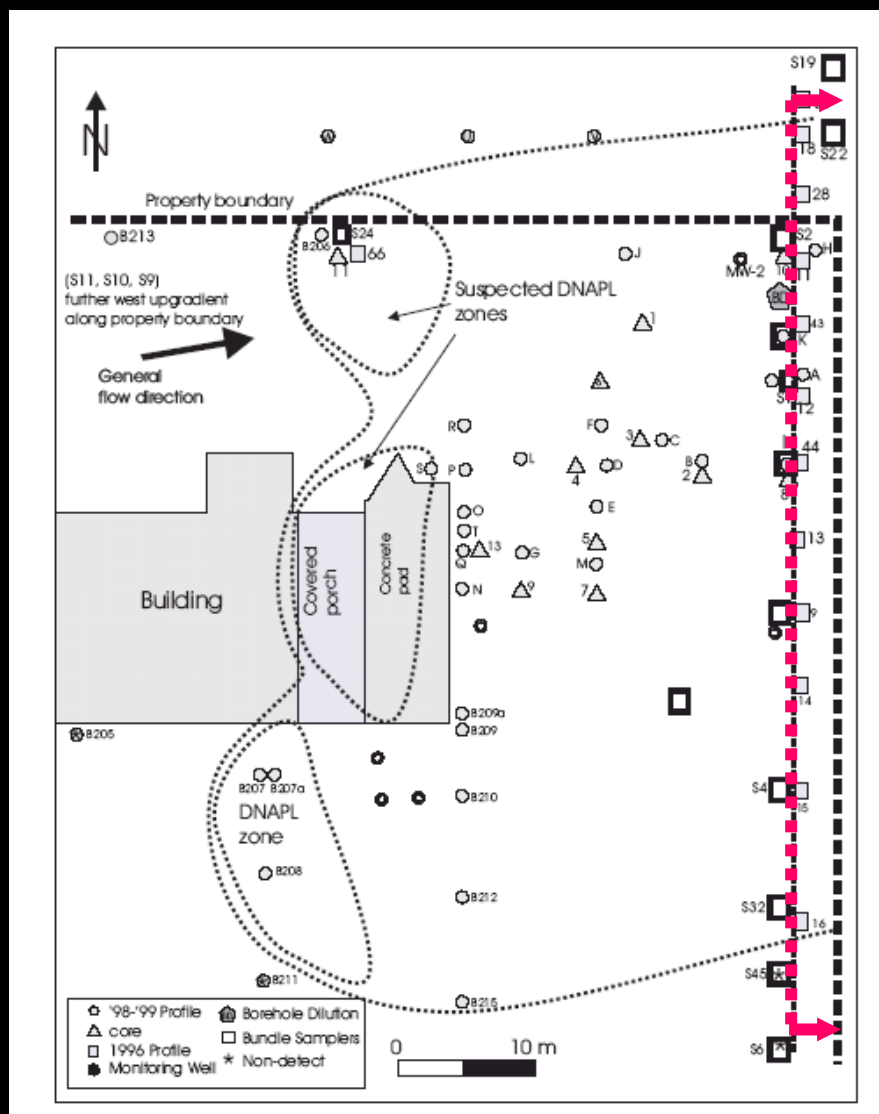
At three industrial sites in Ontario, New Hampshire, and Florida, tetrachloroethylene (PCE) and trichloroethylene (TCE), released decades ago as dense nonaqueous phase liquids (DNAPLs), now form persistent source zones for dissolved contaminant plumes. These zones are suspended below the water table and above the bottoms of their respective, moderately homogeneous, unconfined sandy aquifers. Exceptionally detailed, depth-discrete, ground water sampling was performed using a direct-push sampler along cross sections of the dissolved-phase plumes, immediately downgradient of these DNAPL source zones. The total plume PCE or TCE mass-discharge through each cross section ranged between 15 and 31 kg/year. Vertical ground water sample spacing as small as 15 cm and lateral spacing typically between 1 and 3 m revealed small zones where maximum concentrations were between 1% and 61% of solubility. These local maxima are surrounded by much lower concentration zones. A spacing no larger than 15 to 30 cm was needed at some locations to identify high concentration zones, and aqueous VOC concentrations varied as much as four orders of magnitude across 30 cm vertical intervals. High-resolution sampling at these sites showed that three-quarters of the mass-discharge occurs within 5% to 10% of the plume cross sectional areas. The extreme spatial variability of the mass-discharge occurs even though the sand aquifers are nearly hydraulically homogeneous. Depth-discrete field techniques such as those used in this study are essential for finding the small zones producing most of the mass-discharge, which is important for assessing natural attenuation and designing remedial options.

Introduction

Chlorinated solvents are the most prevalent organic contaminants found in ground water (Stroo et al. 2003), and in the dissolved phase they are typically mobile and recalcitrant, particularly trichloroethylene (TCE) and tetrachloroethylene (PCE). Schwillie (1984, 1988) was the first to recognize that chlorinated solvent plumes (i.e., zones of

plumes comprised of other types of organic contaminants (Mackay and Cherry 1989). Although the processes governing subsurface DNAPL and plume behavior are known (Cohen and Mercer 1993; Pankow and Cherry 1996) and numerous solvent contaminated sites have been investigated, DNAPL masses at field sites are not often quantified. (Feenstra 2003). Heterogeneity imposes severe limits for

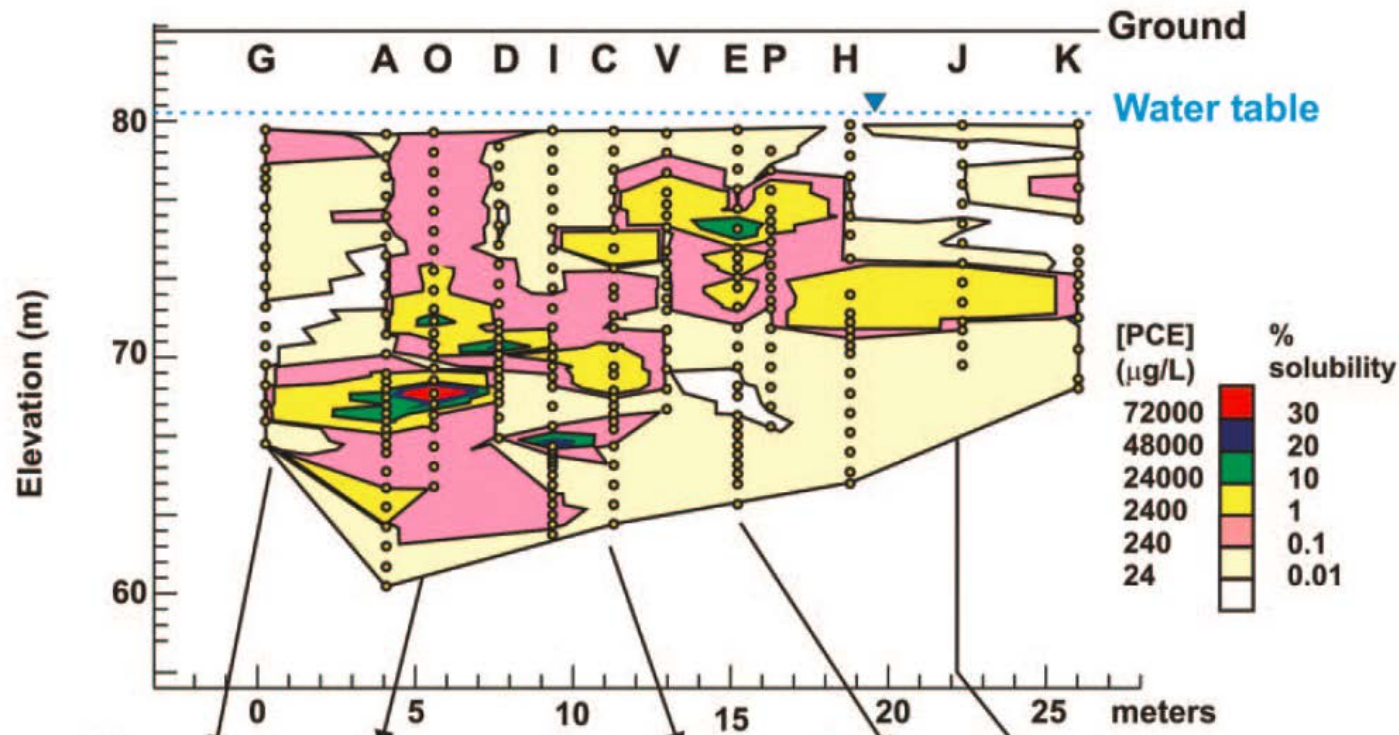
Industrial Site, New Hampshire



(Source: Guilbeault, Parker, & Cherry, 2005)

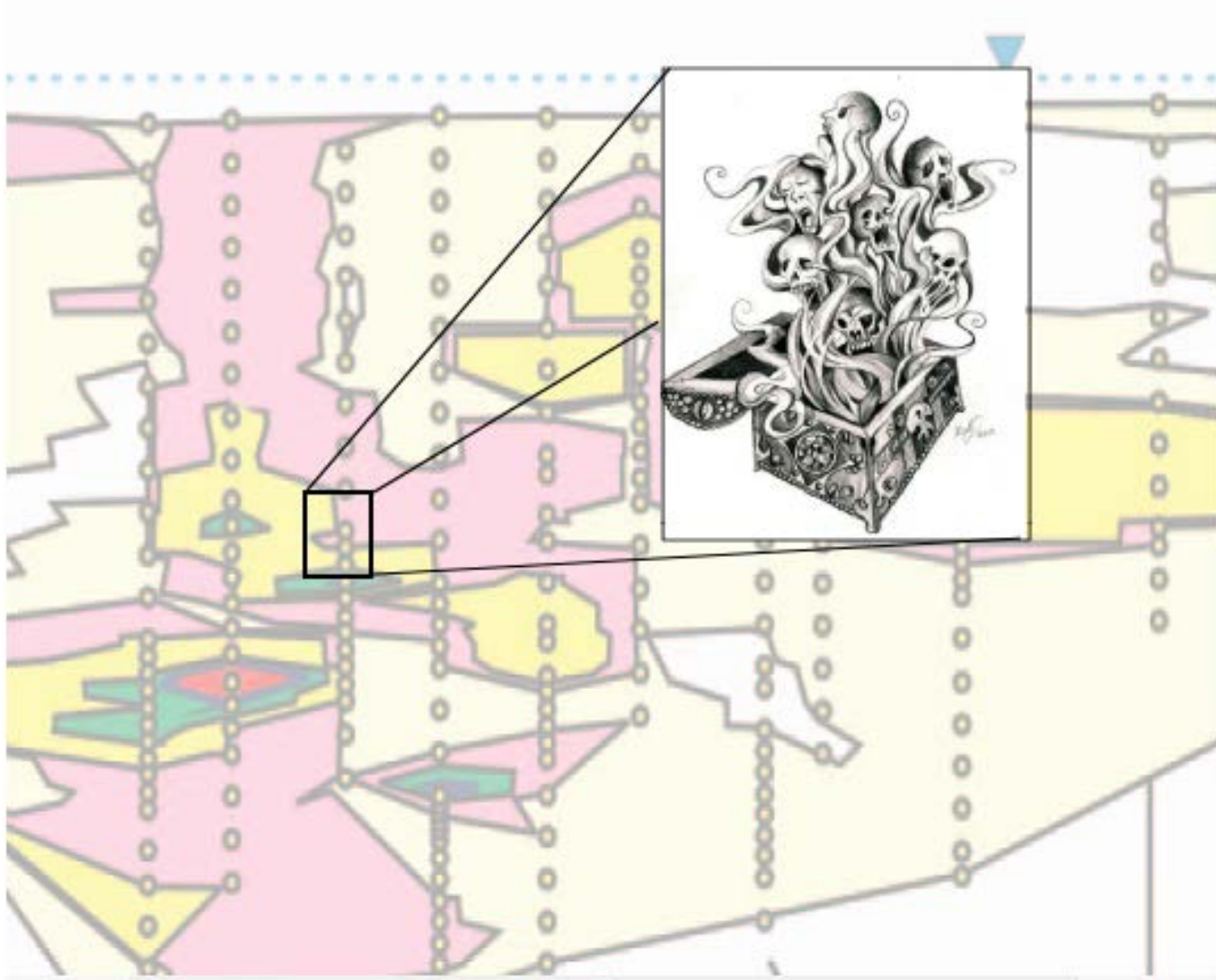
Field Research & HRSC has brought a new awareness of the heterogeneity of solutes in dissolved plumes

New Hampshire PCE Site



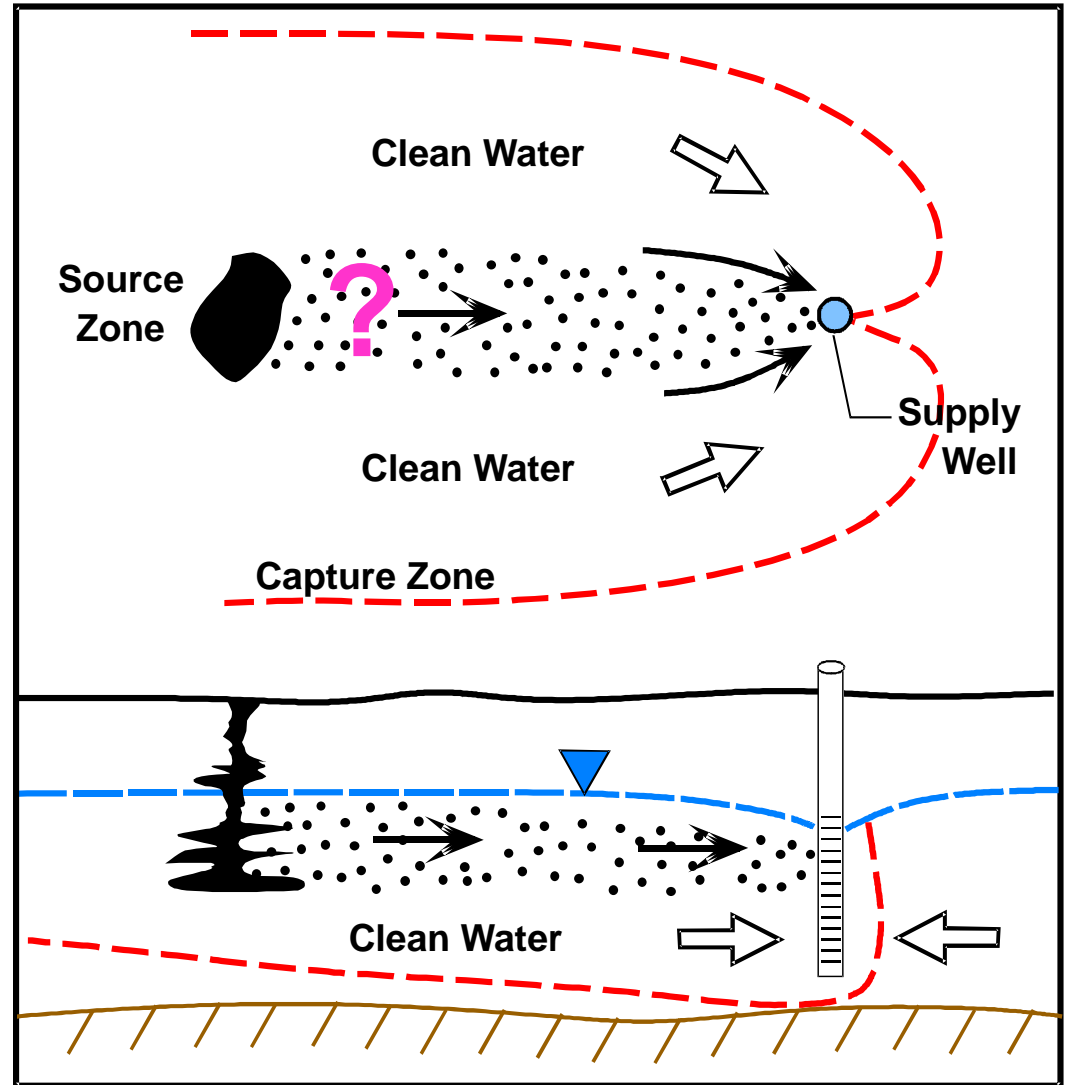
(Source: Guilbeault et al. 2005)

Has HRSC opened up Pandora's Box?
Which concentrations do you pick?!?



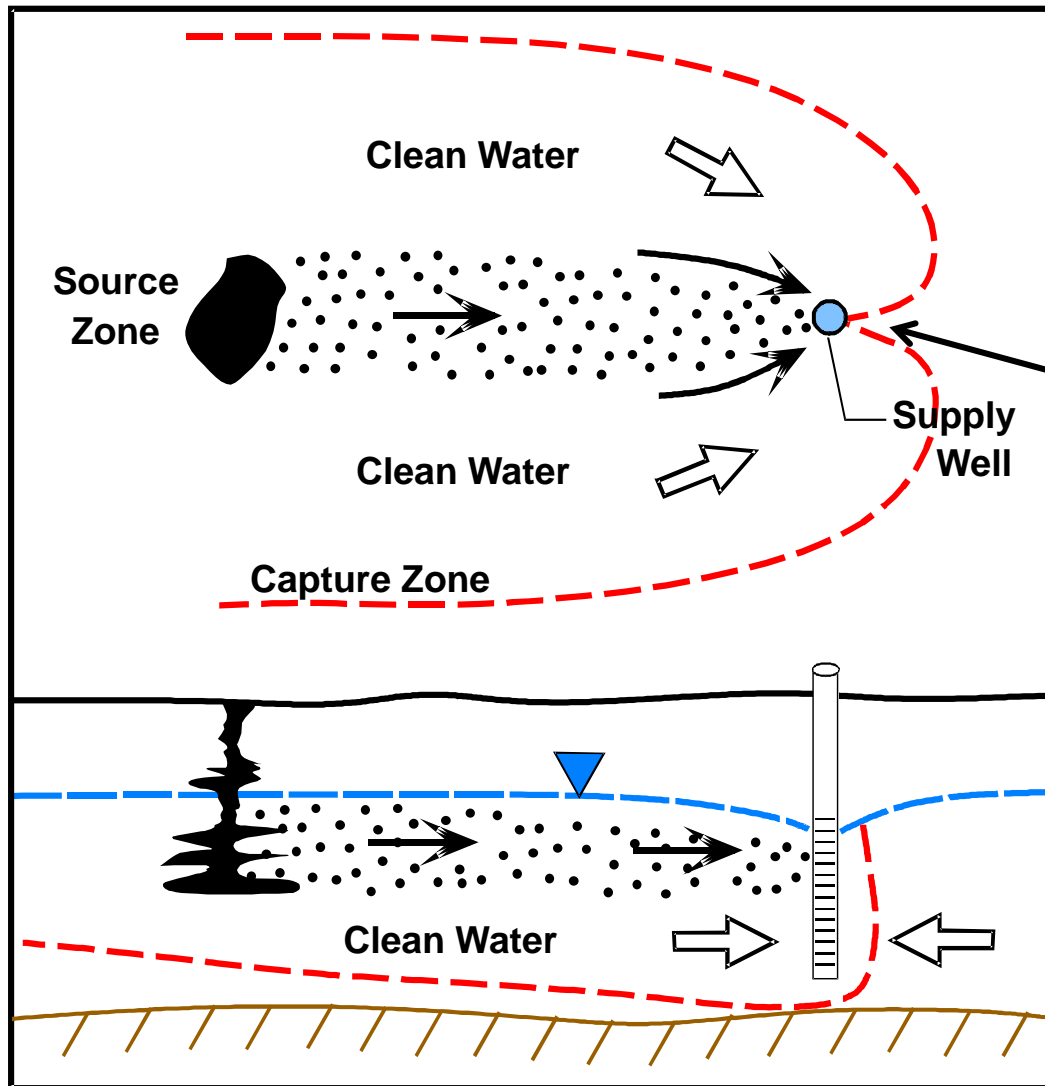
Impact to a supply well from a point-source chemical release

Problem: Traditional site assessments that focus on defining contaminant concentrations don't facilitate predictions of possible future impacts to downgradient supply wells!



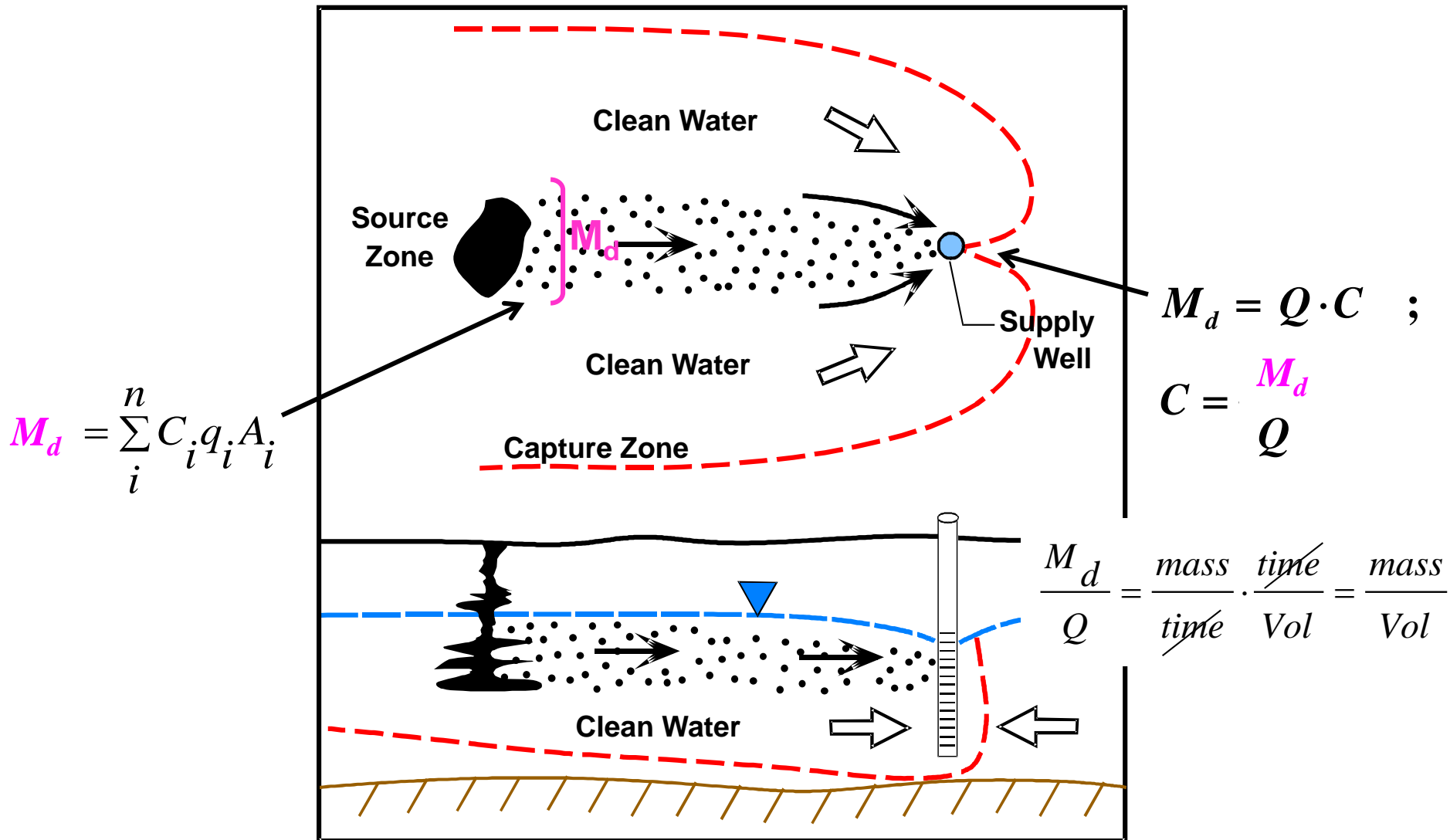
Contaminant Mass Discharge

Contaminant *mass discharge* provides the link between the plume and the supply well



$$M_d = Q \cdot C$$

Contaminant Mass Discharge (M_d)



Example calculation of predicted impact to downgradient supply well

$$M_d \times \frac{1}{Q_w} = C_w$$

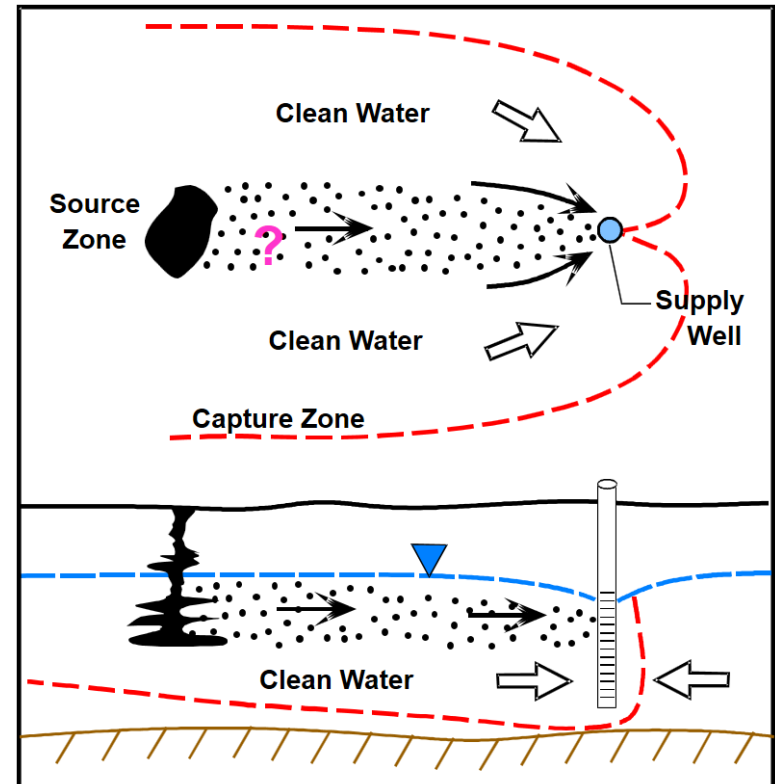
$$\frac{m}{t} \times \frac{t}{v} = C_w$$

M_d = mass discharge

Q_w = Pumping rate

C_w = Concentration in well

$$\frac{11.5 \text{ g}}{d} \times \frac{\text{min}}{300 \text{ gal}} \times \frac{1 d}{1440 \text{ min}} \times \frac{10^6 \text{ ug}}{g} \times \frac{1 \text{ gal}}{3.79 \text{ L}} = \frac{7 \text{ ug}}{L}$$



Transect method (Alameda Point, CA)

$$M_d = \sum_i^n C_i q_i A_i$$

where :

C_i = average concentration

q_i = specific discharge

A_i = cross sectional area

$$M_d \cong \frac{40 \text{ g}}{d}$$

For K determination:

- slug tests
- borehole dilution tests
- constant head injection tests
- pore-pressure dissipation tests
- empirical methods (grain size distribution)

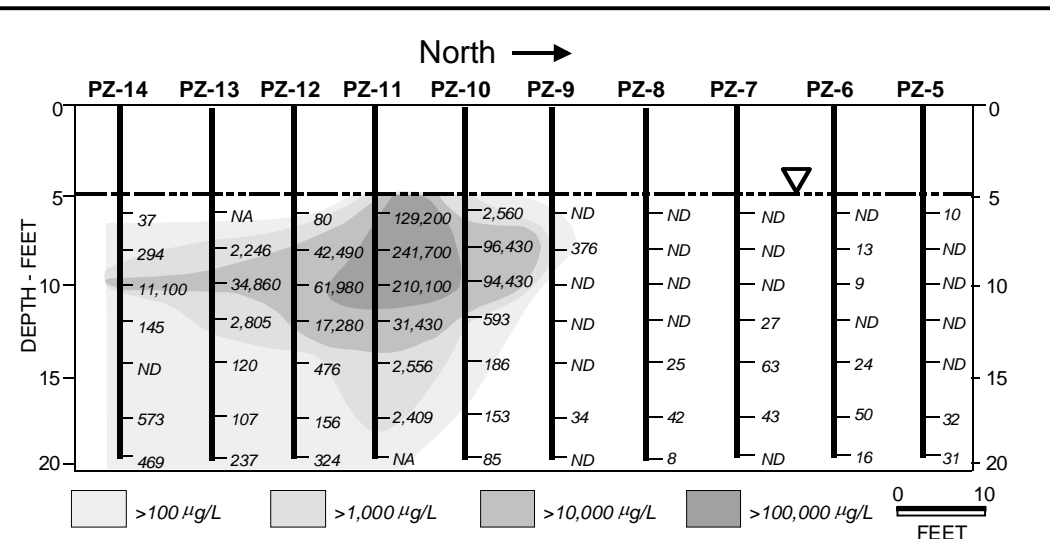


Figure 4a

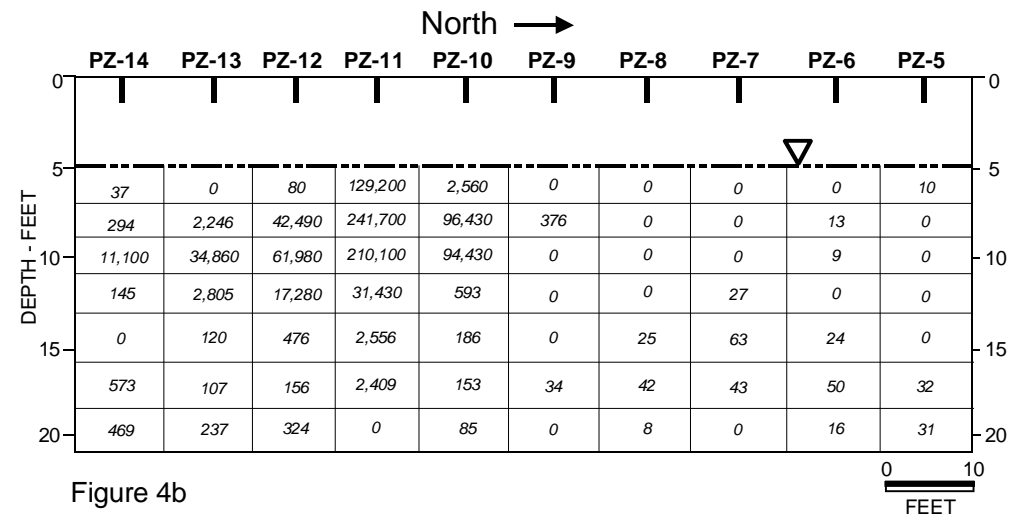
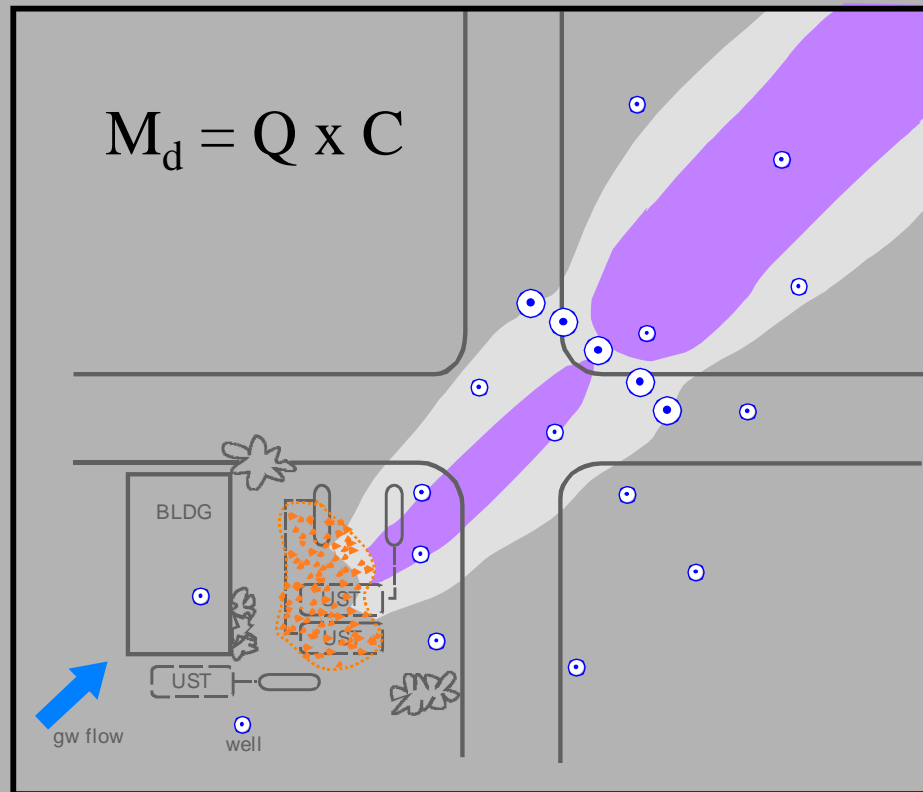


Figure 4b

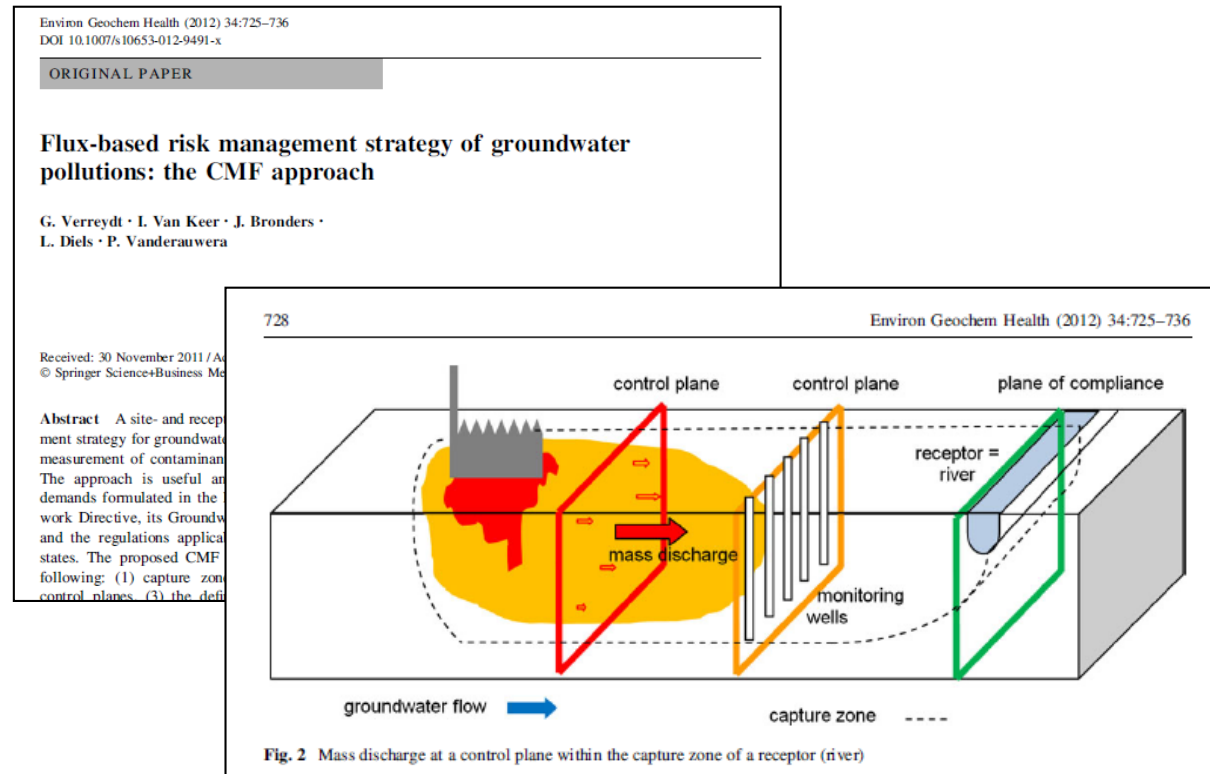
✓ Calculate M_d from existing pump
& treat records!



(Steady-state pumping method)

International adopters of Mass Discharge Framework

- Germany (“Emission Based” Cleanup)
- Province of British Columbia
- Australia
- Netherlands



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Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites

Committee on Future Options for Management
in the Nation's Subsurface Remediation Effort

Water Science and Technology Board

Division on Earth and Life Studies

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Technology Development to Support Long-Term Management of complex Sites

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reviews have evaluated the variety of tools available to quantify the magnitude and spatial distribution of DNAPL (e.g., NRC, 2005; Mercer et al., 2010). These tools range from low-cost methods to infer the presence of DNAPL (as reviewed by Kram et al., 2001) to more extensive methods designed to delineate the spatial distribution of NAPL saturation to guide source zone remediation (e.g., Saenton and Illangasekare, 2004; Moreno-Barbero and Illangasekare, 2005, 2006). For the latter purpose, the partitioning interwell tracer test (PITT) has proven to be relatively effective (e.g., Annable et al., 1998; Brooks et al., 2002), although its deployment is hindered by high cost and need for relatively sophisticated interpretive tools.

As it is unlikely that complete removal of contaminant source material will be feasible for many complex sites, the transition to long-term management will depend not only on the amount of source mass removed, but on the rate at which mass is transferred between the source and plume compartments during the post-remediation period. One of the most promising recent developments in source zone management is the development of tools for measuring contaminant *mass flux*, either at localized monitoring points or as an integrated *mass discharge* across a control plane. Such knowledge of contaminant discharge is particularly useful in evaluating the potential for downgradient natural attenuation processes.

Conceptually, contaminant discharge is a calculated parameter that reflects both temporal and spatial averaging of the product of groundwater discharge (length per area per time) and contaminant concentration (mass per volume). Field methods include synoptic sampling (e.g., Einarson, 2006), passive flux meters (Annable et al., 2005; Basu et al., 2006), steady-state pumping (e.g., Buschek, 2002), recirculation flux measurements (Goltz et al., 2007), integral pumping tests (Bockelmann et al., 2001; Bauer et al., 2004), and modified integral pumping tests (Brooks et al., 2008). The use of flux measurements as an alternative to concentration-based metrics offers several advantages relevant to long-term management, including less sensitivity to spatial/temporal variability and correspondence with screening models that attempt to correlate source zone mass removal with downgradient plume behavior.

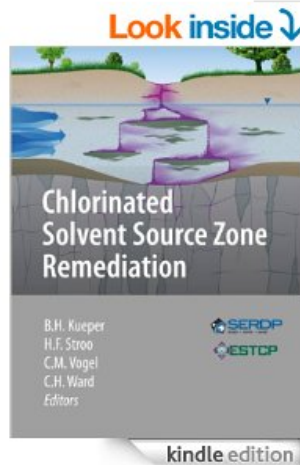
Several recent reviews have explored the relative performance of various techniques for measuring mass flux, which appear to be highly site-specific (EPA, 2009; ITRC, 2010; Kavanaugh and Deeb, 2011). Additional field research is needed to support the more widespread adoption of flux-based performance metrics, including (1) further clarification of the range of uncertainty associated with mass flux and mass discharge measurements, (2) continued refinement of specific aspects of the various techniques, including a better definition of the necessary preliminary site characterization, and (3) new measurement techniques.

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CHAPTER 7

FLUX-BASED SITE ASSESSMENT AND MANAGEMENT

Michael D. Annable,¹ Michael C. Brooks,² James W. Jawitz,¹ Kirk Hatfield,¹
P. Suresh C. Rao³ and A. Lynn Wood²

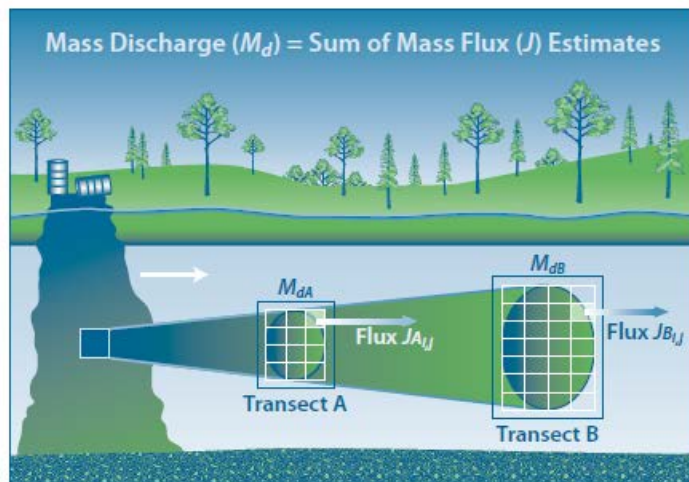
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7.1 INTRODUCTION

Characterization of dense nonaqueous phase liquid (DNAPL) contaminated sites poses significant challenges, but continual advances have led to improvements in both site characterization methods and decision making in recent years. In the area of site risk/liability characterization there has been increased interest in shifting from a focus on concentration measurements to quantifying flux of both contaminants and groundwater and estimation of source mass (Einarson and Mackay, 2001; API, 2002, 2003; ITRC, 2003; Kavanaugh and Rao, 2003; NRC, 2004). As a result of this shift, new approaches have been developed for measuring both flux and mass discharge at DNAPL-contaminated sites. Flux-based data can be used to determine site mass discharge, conduct plume, and source mass balances and track changes in mass over time. This information can support reassessment of the site (risk/liability) conceptual model and allows quantitative evaluation of the importance

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

But, concentration metrics are established in our regulatory systems



Md values can be converted to spatially-averaged, flow-weighted concentrations!

Flow-Weighted Constituent Concentrations

Flow-weighted constituent concentrations are obtained by multiplying the flow (typically hourly values over a 24-h period) times the corresponding constituent concentration, summing the results, and dividing by the summation of the flows as given Eq. (3-12).

$$C_w = \frac{\sum_{i=1}^n C_i Q_i}{\sum_{i=1}^n Q_i} \quad (3-12)$$

where C_w = flow-weighted average concentration of the constituent

n = number of observations

C_i = average concentration of the constituent during i th time period

Q_i = average flowrate during i th time period

Whenever possible, flow-weighted constituent concentrations should be used because they are a more accurate representation of the actual wastewater strength that must be treated. Determination of the simple arithmetic average and flow-weighted constituent concentrations is illustrated in Example 3-7.

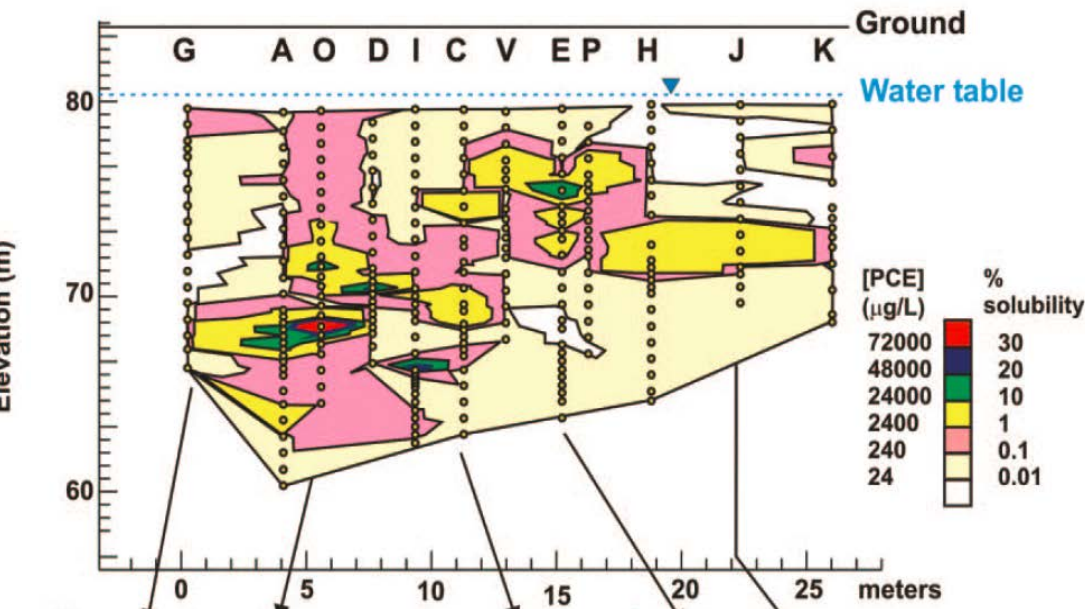
Calculating a spatially-averaged, flow-weighted concentration (C_A)

$$M_d = 15 \text{ kg/y} = 41 \text{ g/d}$$

$$Q_p = \text{plume volumetric discharge} = 3.27 \text{ gpm} (6,497 \text{ m}^3/\text{y})$$

$$C_A = M_d/Q_p = 15 \text{ kg/y} / 6,497 \text{ m}^3/\text{y} = 0.0023 \text{ kg/m}^3 \\ = 0.0023 \text{ g/L} = 2.3 \text{ mg/L} = 2,300 \text{ ug/L} \checkmark$$

New Hampshire PCE Site



This concentration metric is useful for calculating maximum concentration in a supply well

$$C_A \times Q_p/Q_{\text{well}} = C_{\text{well}}$$

Case 1: $Q_w = 3.27 \text{ gpm}$
 $0.0023 \text{ kg/m}^3 \times 6,497 \text{ m}^3/\text{y} / 6,497 \text{ m}^3/\text{y} = 2,300 \text{ ug/L}$

Case 2: $Q_w = 327 \text{ gpm}$:
 C_{well} would be 23 ug/L

Forthcoming article in Fall 2017 GWMR

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Ground Water
Monitoring & Remediation

Guest Editorial

Spatially Averaged, Flow-Weighted Concentrations – A More Relevant Regulatory Metric for Groundwater Cleanup?

by Murray Einarson

Passage of the Safe Drinking Water Act in 1974 established maximum contaminant levels (MCLs) for many chemical compounds in drinking water in the United States. When CERCLA (i.e., “Superfund”) legislation was passed a few years later, MCLs became de facto cleanup standards for contaminated sites in the United States. As stated in CERCLA 121(d)(2)(A):

...Remedial action shall require a level or standard of control which at least attains Maximum Contaminant Level Goals established under the Safe Drinking Water Act and water quality established under section 304 or 303 of

The last 35 years has also brought new technologies and insights into contaminant hydrogeology. High-resolution geophysical methods, and direct-push sensors and sampling systems are now available to quickly define the subsurface distribution of contaminants in three dimensions. Scores of investigations confirm that the distribution of contaminants in the subsurface is typically complex, with much residual mass residing in fine-grained strata. A seminal field study demonstrating the extreme spatial variability of concentrations in dissolved plumes of chlorinated solvents at three industrial sites was performed by Guibeaault et al. (2005). Figure 1 is from

should be used for judging regulatory compliance? What about the contamination that is sequestered in the fine-grained fraction? Is that not logically less important in a risk assessment since the flux of contaminants from such low permeability media is low (and perhaps insignificant) compared to the flux from higher flow zones? Shouldn't contaminants trapped in low permeability sediments somehow be given less “weight” than contaminant mass in the high-flow zones that actually convey contaminants to downgradient water supply wells?

What is clearly needed is a spatially averaged, flow-weighted concentration that considers the significance of where

Thank you!

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