

# 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 Comprehensive Environmental Response, Compensation and Liability Act (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 Clean Water Act, where such goals or criteria are relevant and appropriate under the circumstances of the release or potential release.

Experience remediating sites in the last 35 years, however, shows that cleaning up groundwater to MCLs has been challenging, if not impossible, at many sites. Once released into the subsurface, the distribution of the contaminant typically becomes very complex and heterogeneous. The mass preferentially flows in high permeability zones, and eventually becomes sequestered in adjacent fine-grained deposits due to molecular diffusion. Diffusion of the contaminants back out of the fine-grained fraction is rate limited, and, in the case of the fine-grained deposits, may take centuries

or millennia to reach MCLs (National Research Council 2013).

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 Guilbeault et al. (2005). Figure 1 is from Guilbeault et al.’s paper that shows the distribution of Tetrachloroethylene (PCE) along a sampling transect at a contaminated site in New Hampshire. That transect is oriented perpendicular to the plume axis downgradient from a Dense Chlorinated Non-Aqueous Phase Liquid (DNAPL) source zone. Inspection of Figure 1 shows PCE concentrations as high as 148700  $\mu\text{g/L}$  in one of the plume cores. Moreover, PCE concentrations range more than four orders of magnitude between samples that are only a few meters apart.

The discovery of the heterogeneous distribution of solute concentrations in the subsurface has created a regulatory conundrum. We now know that there are myriad solute concentrations in the subsurface at most contaminated sites. Which concentrations should be

compared to MCLs for cleanup? All of them? There are literally thousands or even millions of point concentrations in the subsurface—which ones 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 the mass is distributed. This concentration value should be spatially averaged and flow-weighted to give more consideration to the mass that resides in the high flow zones. This is possible via a simple manipulation of the mass discharge equation. This modification results in a spatially averaged, flow-weighted concentration metric ( $C_A$ ) that could replace point concentrations as a more meaningful cleanup metric at sites with contaminated groundwater. Let us explore contaminant mass discharge first.

Contaminant mass discharge ( $M_d$ ) has units of mass per time and is the integration of mass flux ( $J$ ) across a vertical control plane or “transect” perpendicular to the groundwater flow direction, thus quantifying the total rate at which dissolved contaminant

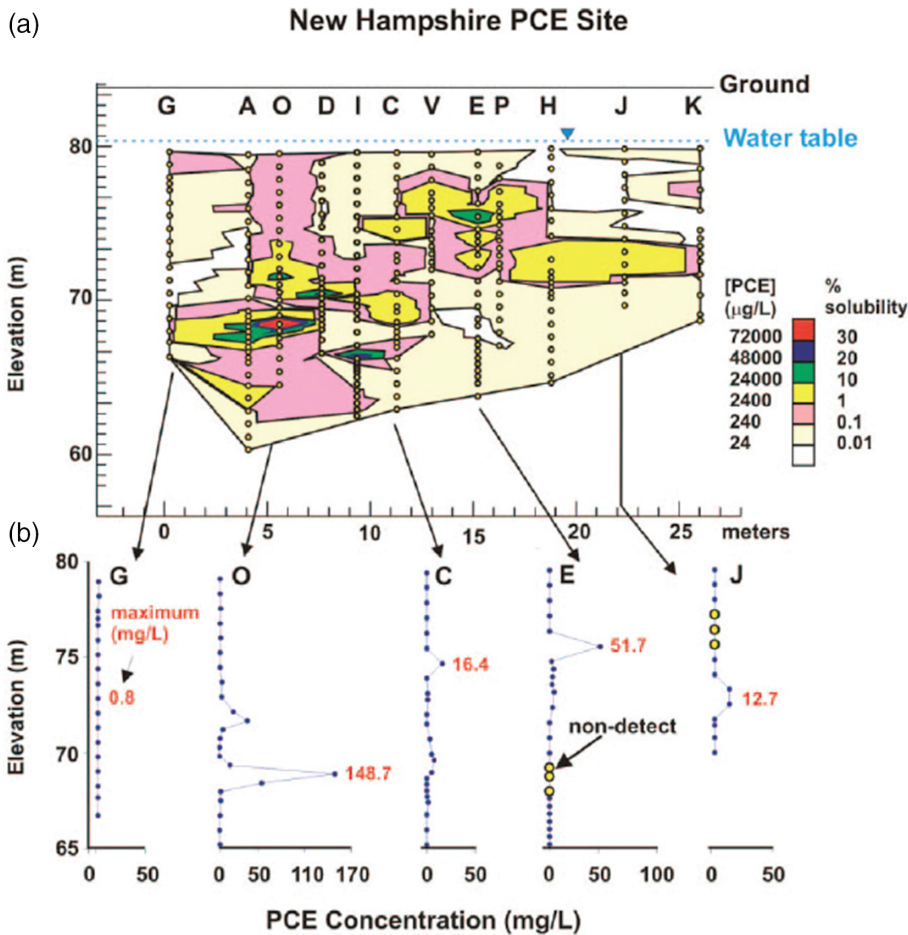


Figure 1. PCE concentrations measured in sampling transect downgradient of a PCE DNAPL source (Guilbeault et al. 2005).

mass conveyed by groundwater flow at any given time:

$$M_d = \int_A J dA \quad (1)$$

with

$$J = q_0 C = -KiC \quad (2)$$

where  $M_d$  is the contaminant mass discharge (M/T),  $A$  is the cross-sectional area of the contaminant plume ( $L^2$ ) perpendicular to  $J$  or the hydraulic gradient,  $J$  is the local contaminant mass flux (M/T/ $L^2$ ),  $q_0$  is the Darcy groundwater flux ( $L^3/L^2/T$ ),  $K$  is hydraulic conductivity (L/T),  $i$  is the hydraulic gradient (dimensionless), and  $C$  is the concentration of the contaminant (M/ $L^3$ ).

Mass discharge is a particularly useful parameter for risk evaluations and prioritization of cleanup because the potential impact to a downgradient supply well can be estimated by dividing the mass discharge value by the pumping rate of the supply well (Einarson and Mackay 2001). The same relationship holds for plumes discharging into well-mixed surface water bodies (Ford 2005).

This simple relationship is expressed as:

$$C_{\text{well}} = \frac{M_d}{Q_{\text{well}}} \quad (3)$$

where  $C_{\text{well}}$  is the average solute concentration in water pumped from well (M/ $L^3$ ), and  $Q_{\text{well}}$  is the pumping rate of well that fully captures plume ( $L^3/T$ ).

The use of mass loading or mass discharge as a metric for assessment and remediation of subsurface contamination is gaining popularity in the United States (Buscheck 2002; American Petroleum Institute 2003; ITRC 2010; Suthersan et al. 2010; Mercer et al. 2010; Newell et al. 2011; National Research Council 2013; Annable et al. 2014; EPA 2014; Hadley et al. 2014; Horneman et al. 2017) and in other parts of the world (Bockelmann et al. 2003; King 2006; Clements et al. 2009; Verreydt et al. 2012). Regulatory acceptance of the mass loading framework, however, has been slow in

the United States, primarily because concentration-based standards are so established in statutes, regulations, and practice.

Fortunately, spatially averaged, flow-weighted concentration values can be easily calculated from mass discharge values. Such calculations are common in waste water and process engineering (e.g., Tchobanoglous et al. 2004). In the groundwater environment, this is simply the contaminant mass discharge divided by the groundwater discharge of the dissolved plume:

$$C_A = \frac{M_d}{Q_p} \quad (4)$$

where  $C_A$  is the average solute concentration in plume (M/ $L^3$ ), and  $Q_p$  is the groundwater discharge of plume flowing through the cross-sectional area ( $A$ ) ( $L^3/T$ ).

Thus, a spatially averaged, flow weighted concentration can be calculated by dividing the contaminant

mass discharge by the groundwater discharge of the plume. This yields one concentration value ( $C_A$ ) that reflects not only the spatial average but is also weighted toward the more permeable flow zones that actually convey contaminants to potential groundwater receptors.

In the example for the New Hampshire site cited above (Figure 1), the authors state in their publication that the calculated mass discharge of PCE is 15 kg/year (Guilbeault et al. 2005). On table 2 of their publication, the authors list the average darcy flux ( $q$ ) and cross-sectional area of the plume ( $A$ ) that, when multiplied together, yields a groundwater discharge value of 6497 m<sup>3</sup>/day (3.27 gallons per minute [gpm]). Dividing the mass discharge value of 15 kg/year by 6497 m<sup>3</sup>/year yields an average concentration ( $C_A$ ) of 2300 µg/L. Thus, the average concentration of PCE in the plume shown in Figure 1 is 2300 µg/L. This value could be used for regulatory decision making which, given its magnitude (460 times higher than the MCL for PCE), would likely warrant active remediation at most sites in the United States. Remediation would focus, however, on reducing the average plume concentration ( $C_A$ ) to the MCL rather than reducing PCE concentrations to the MCL everywhere in the subsurface (a goal that may not be achievable).

At many other sites, the average flow-weighted contaminant concentration could be at or below the MCL, even though there are local concentrations above MCLs in some low permeability units, and no active remediation may be necessary.

That average concentration value could also be used for risk evaluations because it would represent the maximum concentration of PCE in groundwater extracted from a hypothetical water supply well that fully extracts the dissolved plume at a rate of 3.27 gpm. Note that extraction of groundwater at a rate higher than 3.27 gpm would result in *lower* concentrations of PCE in the extracted water because clean water would simultaneously be extracted and blended in the well along with the dissolved plume. In this example, contaminant concentrations could be estimated for various in-well blending scenarios by mul-

tiplying the  $C_A$  value by the ratio of the natural groundwater discharge rate (3.27 gpm) to the hypothetical groundwater extraction rate. This latter calculation, expressed as  $C_A \times Q_p/Q_{well}$ , is simply  $M_d/Q_{well}$  (Equation 4).

Thus, for sites where both the contaminant mass discharge and flow rate of the dissolved plume are known or can be estimated, a spatially averaged, flow-weighted solute concentration ( $C_A$ ) can be calculated.

An important topic in this discussion is the accuracy of the parameters that factor into these calculations. As with all hydrogeological parameters, there are errors associated with measuring contaminant and groundwater fluxes. Errors are of two types: measurement errors and integration errors (Mackay et al. 2012). Examples of measurement errors include errors in the quantification of the target solute concentration in a groundwater sample or the Darcy flux of groundwater in a specific flow tube. Integration errors include the collection of samples or measurements at a scale that fails to include significant mass or groundwater flow passing through the vertical control plane.

Current methods for measuring contaminant mass discharge include synoptic sampling of groundwater along transects (e.g., the method described above and used by Guilbeault et al. 2005), passive flux meters (Hatfield et al. 2004), pumping methods (Bockelmann et al. 2003; Goltz et al. 2009), and estimates using numerical models (Nichols 2004). Mass discharge estimates that utilize mass removal data from pump-and-treat systems that fully capture the contaminant plume may be the most accurate (Einarson 2013). Groundwater fluxes can be measured using Darcy's law, single well borehole dilution tests (Freeze and Cherry 1979), passive flux meters (Hatfield et al. 2004), point velocity probes (Devlin et al. 2012), and conventional tracer tests.

Given the growing popularity of the mass discharge framework, there has been significant focus recently on quantification and reduction of errors in field methods used to calculate contaminant mass discharge (Li and Abriola 2009; Malcolm Pirnie 2011; Cai et al. 2011; Klammler et al. 2012;

Mackay et al. 2012; Chen et al. 2014; Brooks et al. 2015). Several new and novel methods of calculating mass and groundwater discharge have been developed in the last decade, and further advancements in field methods for quantifying mass and groundwater fluxes and discharge can be expected in the future. These efforts will only improve the accuracy of mass discharge and average contaminant concentration values in the future.

Measurement errors notwithstanding, spatially averaged, flow weighted concentration values are superior to individual solute concentration measurements for risk evaluations because they integrate the dissolved contamination in space and time. Consequently, they are a more meaningful and relevant concentration metric for regulatory decision making than the various disparate contaminant concentration values that are typically measured in samples collected from individual monitoring wells or direct push samplers at contaminated sites.

While contaminant mass discharge is likely still the most direct and relevant metric of the risk posed by a contaminated site to a downgradient groundwater receptor, spatially averaged, flow-weighted concentrations are better predictors of risk than individual concentration measurements and should be incorporated into regulatory statutes and orders that require concentration-based standards.

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