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Introduction

In the following sections, we provide discussion and information to supplement the Feature Article. This material could not be included in the article itself due to space limitations of the printed version.

Mixing of Contaminants in Groundwater Monitoring Wells

Since the 1970s, monitoring wells have been the primary means of collecting samples of groundwater for chemical analysis. Monitoring wells are in many respects miniature versions of water supply wells, i.e. pipe with screened sections to allow water to enter and be extracted. In the 1970s and early 1980s, the screen lengths of monitoring wells were commonly 9 m (30 feet) or greater.

In the mid and late 1980s, however, a variety of practical and research efforts showed that many organic contaminant plumes are highly stratified, with concentrations of dissolved solutes varying by an order of magnitude or more over vertical distances of several feet (e.g. Mackay et al., 1986; Garabedian et al., 1991; LeBlanc et al., 1994). Thus it became apparent that water samples collected from conventional monitoring wells are actually composite samples drawn from the entire screened length of the well which understate the maximum concentrations of contaminants present in some horizons, and overstate concentrations in others. The effect of this compositing on contaminant concentrations is a function not only of the vertical contaminant distribution, but also the permeability of the sediments within the screened interval of the well, as well as other factors such as well construction, pumping rate, vertical flow in the well, and even the depth of the pump or pump intake (Robbins, 1989; Martin-Hayden et al., 1991; Robbins and Martin-Hayden, 1991; Gibs et al., 1993; Akindunni et al., 1995; Chiang et al., 1995; Conant
An additional dilution mechanism occurs if the monitoring wells partially penetrate (sample only a limited vertical interval of) an aquifer. Pumping of the well during purging and sampling causes flow lines to converge vertically into the well screens. The vertical convergence of flow causes water from above and below the well screens to be drawn into the well. Thus, if clean water occurs above and/or below the well screens, it will be drawn into the well during pumping, diluting the contaminants in the well (Akindunni et al., 1995; Chiang et al., 1995; Conant et al., 1995). For this and other reasons, a protocol for purging and sampling the wells at very low flow rates (i.e., micro-purging) evolved in the mid 1990s to minimize disturbance of the flow field in the immediate vicinity of the well (Puls and Barcelona, 1996). Furthermore, it is now standard practice to build monitoring wells with maximum screened lengths of 6 m (20 feet) or less in order to minimize the effects of compositing of the plume and especially dilution with clean water above and below the plume. Even with shorter well screens, however, researchers have shown that samples from conventional monitoring wells may underestimate the concentration of contaminants in the aquifer by an order of magnitude or more (Robbins, 1989; Martin-Hayden et al., 1991; Robbins and Martin-Hayden, 1991). And, unfortunately, even with all the research that has been done, it is difficult to quantify the amount of dilution that is occurring in monitoring wells because of the numerous mechanisms that control the process and the paucity of site-specific information to describe them.

**Conditions for Using a Simple Mass Balance**

Supplementary Figure 1 (the same as Figure 1 in the Feature Article) shows a plume of dissolved TCE being captured by a downgradient supply well. In that example, the well is being pumped at a constant rate of approximately 1000 L/m (264 gal/m) and TCE has been consistently detected in samples from the supply well at a concentration of 7 µg/L. The product of the concentration and extraction rate yields a $M_d$ value of approximately 10 g/d.

If the release site depicted in Supplementary Figure 1 is the only source of dissolved TCE within the capture zone of the supply wells, the $M_d$ of the TCE emanating from the source zone must equal the $M_d$ of TCE being extracted from the downgradient supply well if the following five conditions are satisfied:

1. The flow field is constant (in rate and direction)
2. The release rate of dissolved contaminants from the source zone is constant
3. Mass transfer processes within the saturated zone (e.g., sorption and/or diffusion into low permeability sediments) are at equilibrium
4. Mass transfer from the saturated zone (e.g. volatilization, transpiration) is negligible.
5. There is no loss of mass due to biotic or abiotic transformations *in situ*.

If these conditions were satisfied and if one were able to estimate the mass discharge emanating from the source zone (or migrating past any transect across the plume), then one could estimate
the maximum concentration of the contaminant that could occur in a downgradient supply well long before the plume reaches the well:

\[ C_{sw} = \frac{M_d}{Q_{sw}} \]

(Supplementary Equation 1 [Equation 1 in Feature Article])

Where:

- \( C_{sw} \) = maximum concentration of contaminant in water extracted from the supply well (mass/volume)
- \( M_d \) = discharge of contaminant mass from release site (mass/time)
- \( Q_{sw} \) = Pumping rate from supply well (volume/time)

What if Some or all of the Five Conditions Are Not Satisfied?

Few real plumes likely comply with the five conditions listed above. This does not mean that a mass balance approach cannot be useful. Rather, the departures from those conditions should be considered in the context of how they will affect the \( M_d \) of contaminants being drawn into the supply well. In general, most real sites will deviate from the five conditions in ways that result in an overestimation of the contaminant concentrations that will occur in a downgradient supply well. This, of course, is the reason reliance on natural attenuation offers promise for management of some contaminants. For example, if conditions 1 and 2 are satisfied but biodegradation is occurring and/or mass transfer is irreversible or not at equilibrium, the \( M_d \) measured near the source zone for the parent contaminants will overestimate the \( M_d \) for the parent contaminants eventually entering the supply well. Therefore, supply well contaminant concentrations calculated using Supplementary Equation 1 would be maximum values. If the maximum predicted value does not exceed levels of concern, and there are no transformation daughter products which pose health risk, then the source could be construed to have a relatively low priority for cleanup compared to other sources with more significant predicted impact.

If more detailed consideration of biodegradation and mass transfer processes (sorption, diffusion, transpiration and/or volatilization) is required, analytical or numerical models can provide quantitative estimates, for both parent and daughter contaminants, of \( M_d \) near the supply well for use in Supplementary Equation 1. Such models may also be formulated to simulate the contaminant concentrations in the extracted water, i.e. already accounting for in-well dilution (e.g. Johnson et al., 2000). Note that if the plume is fully captured by the well and the goal is to calculate the maximum concentration to be expected in the well, transverse dispersion can be ignored (or any reasonable parameter assumed) in the simulations because it does not alter the maximum mass discharge into the well. Longitudinal dispersion can be important if the emanation rate from the source changes significantly over time since it will serve to dampen the fluctuations, thus potentially reducing the maximum mass discharge reaching the well; the
importance of longitudinal dispersion clearly depends on the degree of dispersion, the rate of change of the emanation rate from the source, the distance from the source to the well, etc.

Transient changes to the groundwater flow field while a plume is being formed can affect the distribution of contaminant mass in the plume. The $M_d$ entering the supply well can be either higher or lower than the $M_d$ that would have occurred had the flow field remained constant throughout the entire time that the plume was forming. This interesting and potentially important issue can and should be examined via numerical simulations.

Short- and long-term fluctuations in the contaminant release rate from the source can cause variations in $M_d$ in the dissolved plume. Short-term fluctuations in the release rate arise from seasonal recharge, fluctuations in water level elevations, changes in groundwater velocity through the source area (e.g., by pumping of nearby supply wells), new releases, etc. Long-term changes in the release rate can result from, among other things, depletion of the source mass generating the plume. This may be especially significant in the case of MTBE which, because of its relatively high solubility, is expected to be preferentially dissolved from residual NAPL. For a single spill of MTBE-containing gasoline, the $M_d$ emanating from the source may decrease significantly over an initial time frame (months to years, depending on the situation), and thus measurement of $M_d$ just downgradient of the source after this initial time frame could underestimate the $M_d$ of MTBE already flowing in the more downgradient portions of the plume. If this were not recognized, one would under-predict the maximum concentration of MTBE that could be measured in water extracted by a downgradient supply well. Recent modeling studies illustrate that the mass emanation from source zones may depend rather strongly on site specific characteristics, notably the presence and properties of low permeability zones and their proximity to the NAPL (e.g. Durrant et al., 1999). Often, the information necessary to make reliable estimates of mass discharge via modeling may typically be lacking. Fortunately, however, contaminant discharge can often be assessed directly by field methods described below.

**Estimating the Mass Discharge of Contaminants Emanating from Point-Source Release Sites**

In North America, estimates of contaminant mass discharge have generally been made by collecting groundwater samples from closely-spaced monitoring wells installed in a transect across the plume. In Germany in recent years, estimates of contaminant mass discharge have also been made by drawing the contaminant plume into one or more pumping wells installed across the plume’s path and sampling the effluent from the well(s).

**Transects of Monitoring Wells Across the Plume**

Sampling transects can consist of closely-spaced single- or multi-level monitoring wells. Single-screened wells may be useful if plumes are thin or aquifer media and thus groundwater flow is very homogeneous. Sometimes, however, it is preferable to use transects of multi-level monitoring wells to capture important details of contaminant distribution. Ideally the transects are located orthogonal to groundwater flowlines; thus in a uniform flowfield, the transect would be a straight line, whereas in a converging or diverging flowfield the transect would be
curvilinear. Groundwater samples are collected from the monitoring points and analyzed for the contaminant of interest. To ensure that all of the contaminant mass leaving the site is accounted for, sampling points should extend a sufficient distance (both vertically and horizontally) so that the entire plume is bounded by points yielding non-detects (NDs). It is also necessary to estimate the groundwater specific discharge flowing through each hydrostratigraphic unit using Darcy’s law or via direct measurement of groundwater velocity. A cross section is drawn parallel to the transect, showing concentration contours and hydrostratigraphic units (see Supplementary Figure 2 herein, which is the same as Figure 3 in the Feature Article). Polygons are defined based on concentration contours and/or boundaries of hydrostratigraphic units. In the example in the figure, rectangles are the appropriate polygons because of the regularity of the monitoring grid and the relative uniformity of the geologic medium. The product of the average contaminant concentration, the area of the polygon, and the groundwater specific discharge yields the contaminant mass discharge flowing through the polygon ($M_{di}$). Summation of these values for all polygons yields an estimate of the total mass discharge ($M_d$) of the contaminant moving through the transect at the time of sampling. In mathematical terms, $M_d$ is calculated as follows:

$$M_d = \sum_{i}^{n} M_{di} = \sum_{i}^{n} C_i A_i q_i$$

(Supplementary Equation 2)

Where:
- $M_d =$ contaminant mass discharge (mass/time)
- $M_{di} =$ contaminant mass discharge through polygon $i$ (mass/time)
- $C_i =$ average contaminant concentration within area of polygon $i$ (mass/volume)
- $A_i =$ cross-sectional area of polygon $i$ (area)
- $q_i =$ specific discharge of groundwater in polygon $i$ (volume/area/time)

The polygon method was used to estimate the $M_d$ of cis 1,2 DCE flowing in a dissolved contaminant plume at Site 1, Alameda Point, California. Supplementary Figure 2a shows a monitoring transect across the dissolved plume, oriented perpendicular to the axis of the plume (looking at the figure, groundwater flows away from the reader into the page). Groundwater samples were collected from permanent seven-zone multi-level monitoring wells installed every 10 feet across the plume. Concentrations of cis 1,2 DCE measured during a December 1998 sampling event are shown in the figure (Einarson et al., 2000). The $M_d$ of cis 1,2 DCE flowing through the sampling transect was calculated by summing the mass of cis 1,2 DCE being discharged through evenly-spaced rectangular cells centered around each monitoring point. The concentration of cis 1,2 DCE in each cell was estimated by assigning the concentration of the solute measured in each monitoring point to the entire cell (Supplementary Figure 2b). The specific discharge of groundwater was then calculated using Darcy’s Law ($q = K_i$), then multiplied by the area of the cell ($A_i$) and the average cis 1,2 DCE concentration within the cell to yield the $M_{di}$ of each cell. The $M_{di}$ values were then summed, resulting in a total $M_d$ value of cis 1,2 DCE flowing through the sampling transect. At Alameda Point, calculation of $M_{di}$ is a relatively simple task because the dissolved plume occurs within one hydrogeologic unit. Given an average hydraulic conductivity value of $6.5 \times 10^{-3}$ cm/sec for the unit (Barker et al. 1999), a measured horizontal hydraulic gradient of 0.0029, and the distribution of dissolved cis 1,2 DCE shown in the figure, the calculated cis 1,2 DCE $M_d$ is approximately 31 g/d.
There are, of course, uncertainties associated with the calculation of contaminant $M_d$ 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 Theissen 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. This is especially true in highly stratified aquifers or where the distribution of residual NAPL in the source zone is spatially complex. Fortunately, transects of multi-level sampling points can often be economically installed using new direct-push sampling equipment and multi-level monitoring devices.

Short-Term Capture and Extraction of the Plume by Pumping

Another method of estimating contaminant mass discharge is based on short-term pumping of wells located in a transect across the contaminant plume. This technique, developed by researchers at the University of Tübingen, Germany (Teutsch et al. 1998; Schwarz et al. 1998; Holder et al. 1998; Bockelmann et al. 2000; Herfort et al. 1999; and Ptak et al. 1998), relies on capturing all of the contaminated groundwater flowing within the plume. An advantage of this method is that it does not require interpolation of contaminant concentrations between monitoring points as is the case with transects of monitoring wells. One or several extraction wells can be used for this purpose, the number depending on the known or presumed hydrogeologic properties of the media and distribution of contaminants. The wells are pumped until the entire mass discharge at the transect location is known or assumed to be extracted, at which point the contaminant concentrations are measured in the effluent from the wells. In this case, contaminant $M_d$ is calculated as follows:

$$M_d = \sum_{i=1}^{n} Q_i C_i$$  
(Supplementary Equation 3)

Where:
- $M_d =$ contaminant mass discharge (mass/time)
- $Q_i =$ extraction rate from well $i$ (volume/time)
- $C_i =$ contaminant concentration measured in effluent from well $i$ (mass/volume)

For this basic method to work, one must achieve steady-state capture of the contaminant mass discharge, a goal that may be difficult to achieve with certainty in heterogeneous media and/or where plumes arise from spatially complex sources. Also, the operation of the extraction wells necessarily alters the plume itself, both spatially and perhaps geochemically, which may have unanticipated or undesirable impacts. Furthermore, steady-state capture of a contaminant plume can generate a very large amount of contaminated water which would subsequently need to be treated or disposed of. For these and other reasons, Schwarz et al. (1998) have explored the application of this approach to estimating mass discharge via shorter duration non-steady-state extraction tests. However, such tests also would be confounded by heterogeneities in flow field and source characteristics.
Summary

In North America and Europe, there has been a considerable amount of effort directed at evaluating methods to estimated contaminant mass discharge in plumes. These efforts have yielded two reasonably well-studied methods. Given the power of $M_d$ as a predictor of the potential impact to supply wells from discrete spills, additional work is clearly needed to assess the applicability of these and other field methods for estimating contaminant mass discharge at contaminant release sites with a variety of source configurations and in a variety of hydrogeologic settings. Considerable insight can be gained by modeling, but comparisons of approaches at real sites would also be extremely valuable.

Simulated Examples of Dissolved Plumes Captured by a Supply Well

Three cases illustrating the mass balance approach to evaluating contaminant plumes are presented below. We will focus on MTBE plumes arising from fuel release sites. These are not examples of real sites, but rather simulated examples used to illustrate the principles discussed in the Feature Article. Cases 1 and 2 explore the dilution that occurs in wells pumped at relatively high extraction rates. Case 3 addresses the additive effect when several MTBE plumes are captured by a single supply well. The MTBE plumes are all approximately 60 m (~200 feet) wide, which is fairly typical for fuel release sites. In these simulations, we assume all five of the conditions listed earlier are satisfied.

For simplicity of illustration and simulation, we assume that the supply well either completely captures the plume or completely misses it. Numerical simulations of steady-state groundwater flow were performed to define two-dimensional capture zones. Contaminant transport simulations were not performed since (1) the source is assumed to be emanating MTBE at a steady rate (this may not be a realistic assumption at most MTBE sites, however; see discussion of MTBE source zones herein and in the Feature Article), (2) MTBE is assumed to be nondegradable and (3) transverse contaminant dispersion is irrelevant as long as the plume is completely captured or completely missed. Capture zone simulations were performed using Visual Modflow, V 8.2. The aquifer is unconfined, ~18 m (60 feet) thick, and the extraction well screen is open across the entire thickness of the aquifer (a “fully penetrating” well). We have assumed properties typical of sandy aquifers useful for water supply in the West or Midwest U.S. (hydraulic conductivity of 0.01 cm/sec, regional hydraulic gradient of 0.003, specific yield of 0.25, groundwater recharge of ~25 cm (10 inches) per year over the entire model domain). Tick marks show the distance that the contaminant plume travels in one year. Note that the leading edge of the contaminant plume, whose shape is affected by longitudinal dispersion and other factors, is not drawn quantitatively in the frames of Supplemental Figure 3.

Case 1: In this case, Site A began releasing MTBE-containing gasoline to groundwater in 1995 (Supplemental Figure 3a). We assume for illustration that dissolution of the NAPL results in a constant $M_d$ of 2 g/d of MTBE flowing into the aquifer, i.e. similar to the value estimated by Borden et al. (1997). Site A is located approximately 520 m (~1700 feet) directly upgradient from water supply well WS-1, which extracts groundwater at a steady rate of ~114 L/m (30 g/m). The simulation predicts that the contaminant plume will arrive at the supply well approximately
six years after the release. From Supplementary Equation 1 (or Figure 2 in Feature Article), the maximum MTBE concentration that could occur in the supply well is calculated to be approximately 12 µg/L. MTBE would not immediately be detected at concentrations this high in the supply well, however. A gradual increase in MTBE concentrations would be expected due to the effects of longitudinal dispersion in the leading edge of the plume.

Case 2: Case 2 is similar to Case 1, except that the supply well pumps steadily at the higher rate of ~757 L/m (200 g/m) (Supplementary Figure 3b). We assume again that the measured M_d near the source zone is 2 g/d. The MTBE plume arrives approximately two years earlier than in Case 1 due to the steeper hydraulic gradient toward the supply well. However, at the higher pumping rate of 757 L/m, the contaminated water extracted by the well is a much smaller fraction of the total water extracted. The additional groundwater is clean (i.e., devoid of MTBE), thereby causing dilution of the MTBE in the supply well. Using Supplemental Equation 1, the calculated maximum MTBE concentration is approximately 2 µg/L, i.e., on the order of the detection limit (DL) or practical quantitation level (PQL) of many analytical laboratories.

Case 3: In Case 3, we again assume a steady pumping rate of ~757 L/m (200 g/m). However, releases of MTBE have occurred from four sites (Sites A through D), all of which occurred in 1995 (Supplemental Figure 3c). Site B is closest to well WS-1, followed by Site A, C, and D. The MTBE M_d (measured in fictitious source zone transects) is highest at Site C (8.5 g/d) and lowest at Site B (0.5 g/d). MTBE M_d from Site D is not shown because that site is located outside of the capture zone of well WS-1. The MTBE plume from Site B arrives first, but has a low M_d and MTBE is blended to about 0.5 µg/L, likely below the PQL. The plume from Site A arrives next and the cumulative M_d from Sites A and B is predicted to result in a maximum MTBE concentration of 2.5 µg/L in the supply well. The plume from Site C does not arrive until about four years later, but has the most significant impact on the well due to its relatively high M_d. The measured M_d at Site C is 8.5 g/d which, when added to the M_d from Sites A and B, results in a total M_d of MTBE to the well of 11 g/d. From Supplemental Equation 1, this yields a predicted maximum concentration of MTBE in the supply well of 10.1 µg/L. An obvious implication of this example is that it is not necessarily the plume that first arrives at the supply well that causes the most severe impact. Furthermore, if the extraction rate were increased, it is conceivable that other plumes would be partially or completely captured (e.g. the Site D plume in this example). On the other hand, decreasing the extraction rate could conceivably reduce the number of plumes captured (plumes from Site B or C in this example).

The three scenarios described here are admittedly simplistic and assume that the five conditions discussed above are satisfied. Nonetheless, they illustrate an approach to site characterization that provides a quantitative way of assessing the threat posed by subsurface chemical releases to a downgradient water supply well that fully captures one or more dissolved plumes.

References


Technology Demonstration Facility (AATDF) for Environmental Technology, U. S. DoD and Rice University, 2 volumes.


Supplementary Figure 1. Schematic illustration of a dissolved plume of contaminants hydraulically “captured” by a downgradient supply well pumped continuously at a high rate. Depicted is a uniform sand aquifer (no fill) overlying a clay aquitard (hatched). Clean water on all sides of the plume is also extracted, diluting the concentration of dissolved contaminants in water pumped from well. (This figure is the same as Figure 1 in the Feature Article).
Supplementary Figure 2. Estimates of contaminant $M_d$ can be obtained by sampling a transect of multi-level monitoring points installed perpendicular to the axis of the dissolved plume: (a) contours of cis 1,2 DCE concentrations measured along the transect; (b) discrete concentration measurements are assigned to rectangular cells centered around each monitoring point. The mass discharge within each cell ($M_{di}$) is calculated by multiplying the concentration value by the flux of groundwater through the cell. Total contaminant $M_d$ is obtained by summing the individual $M_{di}$ values. See text for calculation. (This figure is the same as Figure 3 in the Feature Article).
Supplementary Figure 3. Simulations of MTBE distribution and capture zones for continuously pumped supply wells with approximate timelines showing MTBE concentrations in water pumped from the wells: (a) Case 1: well pumped at ~114 L/m (30 g/m) with only one plume captured; (b) Case 2: well pumped at ~757 L/m (200 g/m) with only one plume captured; (c) Case 3: well pumped at ~757 L/m (200 g/m), illustrating capture of three plumes, while a fourth plume migrates uncaptured. The maximum extracted concentrations are calculated using Supplementary Equation 1 from the pumping rate and the assumed mass discharge from the sites (listed in each frame). Note that the illustrated effects of longitudinal dispersion on the timelines are schematic, not quantitative.