

Predicting Impacts of Ground



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water

Contamination



A new framework for prioritizing environmental site cleanups considers the interaction of contaminant plumes with water supply wells.

Throughout the world, groundwater resources are faced with an unprecedented risk of contamination due to subsurface releases of organic chemicals. In the United States alone, releases of gasoline fuels containing MTBE (methyl *tert*-butyl ether) may have occurred at more than 250,000 sites, potentially threatening over 9000 large municipal water supply wells (1).

There is general agreement that, given the enormous amount of contamination, action is necessary, but the resources available for investigating and cleaning up such spills are extremely limited compared with the scope of the problem.

To tackle this problem effectively, a key but generally unanswered question must first be ad-

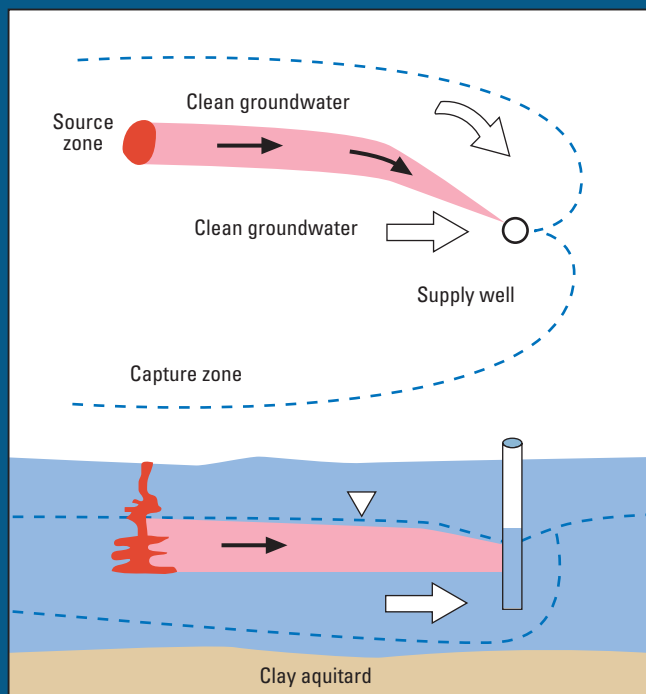
ressed: How significant are the releases in terms of their ability to impact downgradient water supply wells? Environmental scientists and regulators define the significance of an individual release in terms of the contaminant concentrations present in an impacted aquifer, but do not consider the release in terms of contaminant concentrations present in water pumped from supply wells that have been impacted by a contaminant plume. They have for decades considered this issue by focusing on processes affecting dissolved contaminant concentrations in migrating plumes in an impacted aquifer. But they have largely ignored another significant process—the blending of plumes with clean groundwater simultaneously captured and extracted by supply wells.

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FIGURE 1

Plume capture by a supply well

A dissolved plume of contaminants can be hydraulically captured by a downgradient supply well. The contaminant release shown is migrating within a uniform sand aquifer (no fill) overlying a clay aquitard. Clean water on all sides of the plume is also extracted, diluting the concentration of dissolved contaminants in the water pumped from the well.



We do not advocate reliance on in-well blending to maintain water supply standards but recognize that it must be considered in assessing potential impacts. The process does occur, and understanding it is fundamental to determining the risks posed by contaminant plumes drawn into water supply wells.

Fortunately, a framework can be constructed that considers the interactions of contaminant plumes with supply wells: one that incorporates the dilution of the dissolved contaminants caused by simultaneous extraction of clean groundwater.

Cherry and co-workers (2) note that the severity of the problem posed by a plume can be defined in terms of its total mass flux—the amount of contaminant mass migrating through cross sections of the aquifer orthogonal to groundwater flow. By expanding on this idea, it is possible to show that for contaminants from continuous point sources not transforming or transforming only to nontoxic products, a simple method can often estimate worst-case contaminant concentrations in supply wells long before plumes reach them.

The approach could be a powerful tool for risk management since, within any given groundwater resource, there are often numerous

contaminant release sites. The method provides a way to prioritize investigations and cleanup of release sites and focuses attention on those sites posing the greatest risks to water supply wells. Sites deemed less of a risk via such an analysis could be assigned a lower priority for action.

Nature of the problem

When released as nonaqueous-phase liquids (NAPL), large amounts of contaminants can be trapped in soils and remain there until they slowly dissolve into groundwater, a process that can continue for decades or even centuries (3). Over time, elongated contaminant plumes can form as the dissolved chemicals are carried downgradient along with flowing groundwater. If the plumes grow long enough, they can be drawn into downgradient supply wells or discharge to surface water.

In the past decade, it has been shown that natural attenuation alone can often be relied on to manage easily degraded contaminants such as the fuel hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX compounds) (4–6). But numerous contaminants, such as MTBE and some chlorinated solvents, do not degrade rapidly enough under typical subsurface conditions to allow plume management solely by natural attenuation.

Natural attenuation notwithstanding, if a contaminant's input to an aquifer exceeds its rate of transformation and mass transfer from flowing groundwater, a dissolved plume will continue to grow for as long as it takes to deplete the contaminants spilled at a release site, increasing risks to downgradient water supply wells. This problem is exacerbated if natural in situ transformations of released contaminants yield products or intermediates that are of public health concern. If the amounts spilled are large, plumes of very considerable length ultimately can be produced (7).

Plume capture mechanics

Figure 1 shows a plume of dissolved contaminants hydraulically captured by a downgradient supply well. In this example, the supply well is pumped continuously at a relatively high rate, say hundreds to thousands of liters per minute (L/m), that is, typical for larger water supply systems. If the hydraulic properties of the aquifer are known, one can calculate the portion of the groundwater in the aquifer that will eventually be extracted or “captured” by the well.

The figure shows both a plan view and cross-sectional projection of a hypothetical steady-state capture zone for such a well. When the extraction

rate is high, the well captures groundwater flowing in a much larger cross-sectional area of the aquifer than the area occupied by the contaminant plume alone. The capture zone of the well extends a significant distance beyond the edges of the plume. Thus, there is blending of the plume with clean water in the well, leading to significant dissolved contaminant dilution.

Note that the contaminant dilution caused by the hydraulic capture of an entire plume by a large supply well is different than the dilution caused by mixing of stratified contaminants in groundwater monitoring wells. Sample biases caused by mixing of contaminants in monitoring wells, especially those with relatively long screened intervals, has been the subject of considerable research over the past decade, as described in the supporting information found at the *ES&T* Web site (<http://pubs.acs.org/est>). The major difference is that supply wells often extract the entire plume, such as illustrated in Figure 1, rather than sampling a very small portion internal to the plume as is the goal of groundwater monitoring.

A mass balance approach

When a plume is migrating within the capture zone of a supply well, it is possible in some circumstances to estimate the impact using a mass balance approach long before the plume reaches the well.

To illustrate this concept, assume that a supply well, such as that shown in Figure 1, is already contaminated by a trichloroethylene (TCE) plume; that the well is extracting water at a rate of ~1000 L/m (264 gal/m), and that TCE has for some time been consistently detected in samples from the supply well at a concentration of ~7 µg/L. The product of the concentration of TCE in the water (mass/volume units) and extraction rate (volume/time units) yields the total mass flux or mass discharge (M_d) of TCE from the well (mass of TCE per unit time). In this example, the TCE M_d that is estimated for the 1000 L/m supply well is approximately 10 grams per day (g/d) over the time interval of interest.

If the release site depicted in Figure 1 is the only source of dissolved TCE within the capture zone of the supply well, 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 when the following five conditions are satisfied: the flow field is constant (in rate and direction); the release rate of dissolved

contaminants from the source zone is constant; mass transfer processes within the saturated zone (e.g., sorption and/or diffusion into low permeability sediments) are at equilibrium; mass transfer from the saturated zone (e.g., volatilization and transpiration) is negligible; and there is no loss of mass due to biotic or abiotic transformations in situ.

It follows, then, that if the mass discharge emanating from the source zone (or migrating past any transect across the plume) can be estimated, then one could predict the maximum concentration of the contaminant that could occur in a downgradient supply well long before the plume reaches the well using the following relationship;

$$C_{sw} = M_d/Q_{sw} \quad (1)$$

C_{sw} is the maximum concentration of contaminant in water extracted from the supply well (mass/volume), and Q_{sw} is the pumping rate from a supply well (volume/time), if M_d of TCE is 10 g/d during an initial assessment of the release site, then equation (1) predicts a maximum concentration of ~7 µg/L TCE when the plume is eventually drawn into the downgradient water supply well pumping at

1000 L/m.

If the extraction rate were higher, the plume would be diluted to a greater degree. For example, a 2000 L/min (~530 gal/m) or 3000 L/m (~790 gal/m) pumping rate would result in a maximum TCE concentration in the supply well of ~3.5 µg/L or ~2.3 µg/L, respectively. These simple calculations are well suited to graphical presentation, such as via the nomogram shown in Figure 2, which indicates concentrations of dissolved solutes in supply wells calculated from a range of M_d values and pumping rates. If these two parameters are known or can be estimated, then the approximate contaminant concentration can be read directly from the nomogram.

Unsatisfied conditions?

In reality, few real plumes satisfy the five conditions just discussed. This does not mean that a mass balance approach cannot be useful. Rather, the departures from the specified conditions should be considered in terms of how they affect the M_d of contaminants being drawn into a supply well. As discussed in more detail in the Supplemental Information, most real sites will generally deviate from the stated conditions in

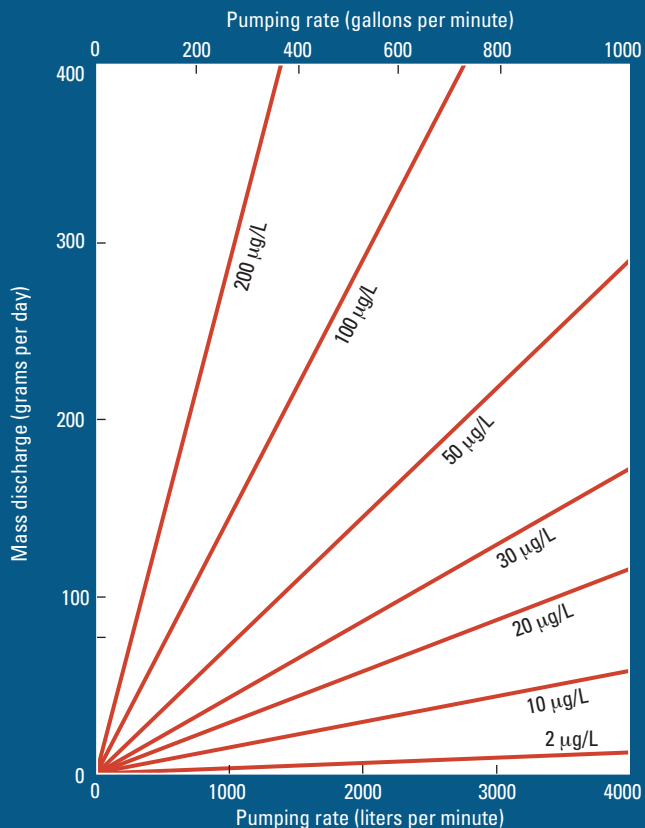


**We do not
advocate reliance
on in-well
blending to
maintain water
supply standards.**

FIGURE 2

Solute concentration nomogram

Concentrations of a dissolved solute in a continuously pumped well can be estimated if the pumping rate and contaminant mass discharge are known. It is assumed that the contaminant plume is fully captured by the well and that no mass is lost from the plume during transport from source to well. This simple figure does not account for various complexities; for example, mass discharge from the source may fluctuate seasonally and can change over time as a result of new spills or source depletion. Mass discharge can also be affected by variations in the pumping rates of supply wells located close to the contaminant source areas.



ways that result in an overestimation of contaminant concentrations occurring in a downgradient supply well.

An important exception is a contaminant source having an initially high M_d , which then decreases over time. This may be especially relevant in the case of MTBE, which, because of its relatively high solubility, is expected to preferentially dissolve from any residual NAPL trapped in soil beneath a release site. For a single spill of an MTBE gasoline blend, the M_d emanating from the source may decrease significantly over some time frame (months to years, depending on the situation). Therefore, measurement of M_d just downgradient of the source after this time frame could underestimate the M_d of MTBE already flowing in more downgradient portions of the plume. If this behavior is not recognized, the maximum concentration of MTBE that could be measured in water extracted by a downgradient

supply well could be underpredicted.

Site characterization

The approach outlined above is of little use if needed data are unavailable. Assessing water supply well contamination risks begins with a delineation of the hydraulic capture zone of the well. All release sites lying within the capture zone of a supply well pose a potential risk. Conversely, release sites that lie outside the capture zone pose no threat to a well as long as flow and pumping conditions remain the same (they could, however, pose a threat to another well further downgradient or to other receptors such as surface water bodies).

Efforts aimed at delineating the capture zones of municipal wells are under way in many U.S. states as a result of implementation of wellhead protection programs mandated by the 1986 Safe Drinking Water Act Amendments. However, defining the capture zones of these wells is not necessarily a simple task. The zones are three-dimensional, and they are controlled not only by pumping rate and hydraulic conductivity, but also numerous other parameters, including stratigraphy, well construction, interference with nearby supply wells, the presence of other artificial conduits (e.g., abandoned wells), and groundwater recharge. Judged against these complexities, the capture zones depicted in the preceding discussion and the Supplemental Information are simplistic. However, they are useful for illustrating contaminant dilution in continuously pumped supply wells and suggest important implications, which are discussed next.

Once the capture zone of a supply well is delineated, estimates of contaminant M_d emanating from release sites situated within the zone must be made. This can be done for all contaminants of public health concern by using data collected during environmental site assessments. We are aware of two methods that have been applied successfully for estimating contaminant M_d : snapshot sampling of transects of closely spaced single- or multilevel monitoring wells across the plume and short-term plume capture and extraction by pumping from one or more extraction wells. These methods are described in more detail in the Supporting Information. Figure 3 shows an example of the first approach. Estimation of M_d is not yet routinely performed during environmental assessments. So, although M_d has been estimated at several sites (see Table 1 (8–14)), few values of M_d can be found in the literature. The majority of these estimates have been derived using transects of monitoring wells to monitor plumes in North America; M_d has also been estimated for

several plumes in Germany using the second method.

The M_d values listed in Table 1 span a broad range. Clearly, because many factors in addition to contaminant type are important (e.g., time since initiation of release, subsurface distribution of residual NAPL, duration or constancy of release), more M_d values must be estimated within contaminant plumes before it will be possible to make generalizations about what values characterize the various types of subsurface chemical releases. Note that MTBE values are among the lowest reported in the table, but this may be a consequence of the monitoring having been performed relatively long after the MTBE release began. Perhaps the monitoring missed the earlier, higher mass discharge, which might be expected from some single-event contaminant releases.

Estimation of M_d is increasingly being performed to develop more accurate field estimates of degradation rates at sites where natural attenuation is an important component of groundwater remediation (15). At sites in the United States, two or more sampling transects are typically installed, allowing calculation of M_d at different distances along a dissolved plume. Under certain conditions, observed decreases in M_d with transport distance can be used to estimate apparent transformation half-lives of contaminants. M_d estimates have been shown to be valuable for evaluating natural attenuation, suggesting that they should also be useful for quantifying the probable impact of plumes on water supply wells.

Implications

When the focus is on contamination in water supply aquifers, the approach outlined in this article provides useful insights. In the Supporting Information, a set of simulations is provided showing how contaminant releases of varying magnitude might affect supply wells operating at different extraction rates.

As indicated in the Supporting Information, there may be instances in which contaminant plumes have been drawn into water supply wells but have not yet been detected because the concentrations are below current detection limits due to in-well blending with clean water. This is most likely when municipal wells are pumped at high extrac-

tion rates. This may explain why when contaminants are detected in supply wells, they occur at concentrations that are often hundreds or thousands of times lower than the concentrations measured in dissolved plumes. For example, concentrations of dissolved MTBE in contaminant plumes near source zones often exceed 100,000 $\mu\text{g/L}$. Yet, in a study of 793 municipal water supply wells in Maine, MTBE was detected in 16% of the wells, but at concentrations below 35 $\mu\text{g/L}$ in all cases (16).

Many water managers and regulators assume that detection of low contaminant concentrations in a supply well portends more serious contamination as the main body of the plume

FIGURE 3

Investigating contaminant M_d

Estimates of contaminant M_d can be obtained by sampling a transect of multilevel monitoring points (denoted PZ) 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_{dij}) is calculated by multiplying the concentration value by the flow of groundwater through the cell. Total contaminant M_d is obtained by summing the individual M_{dij} values. See supplementary material for details of this calculation.

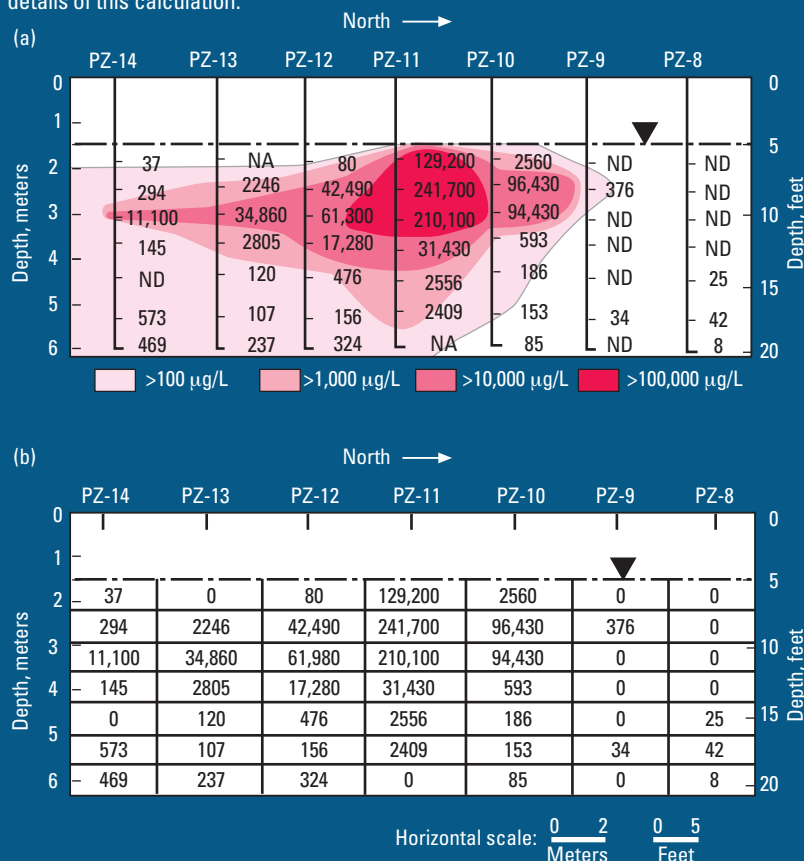


TABLE 1

Estimates of contaminant M_d

Mass discharge (M_d) varies widely by site and contaminant.

Site	Contaminant	M_d (g/d)	Estimation method	Comment	Reference
Sampson County, NC	MTBE	0.3–2	Transect of multilevel wells	M_d fluctuates seasonally. Range of values was measured along source zone transect.	(8)
Vandenberg AFB, CA	MTBE	1.2–7	Transect of multilevel wells	M_d fluctuates seasonally. Range of values from March 1999 to Jan. 2000 was estimated based on data from a transect 200 ft from source zone.	
Testfeld Süd, Germany	BTEX PAH ^a	1.8 29.5	Pumping of extraction wells	Measurements were made ~140 m downgradient from the source zone.	(9)
Landfill site, Heidelberg, Germany	TCE	2.51	Pumping of extraction wells	M_d was calculated using six wells pumped at a rate of 3.0 L/s for 14 d.	(10)
Unnamed	MTBE	4	Transect of multilevel wells	Concentrations in plume <50 µg/L. M_d increased by groundwater extraction near the source zone.	
Elizabeth City, NC	MTBE	76	Transect of multilevel wells	Estimate of discharge from source area in 1996	(11)
Site 1, Alameda Naval Air Station, CA	<i>cis</i> -1,2-DCE ^b	31	Transect of multilevel wells	December 1998 value was measured near source zone. Plume is undergoing natural biodegradation.	
Neckar Valley, Germany	PCE ^c	77	Pumping of extraction wells	Extraction wells were pumped at an average rate of 6.5 L/s for 4 to 6 d.	(12)
Port Hueneme, CA	MTBE	150	Transect of multilevel wells	Preliminary estimate of M_d near source area in Nov. 2000.	
Dover Air Force Base, DE	Total chlorinated organics	280	Transect of multilevel wells	M_d was estimated near source. Contaminant M_d decreases further downgradient because of in situ biodegradation.	(13)
St. Joseph, MI	Total ethenes	425	Transect of multilevel wells	Value from transect downgradient from source (Transect 1). Contaminant M_d decreased further downgradient because of in situ biodegradation and because reversible mass transfer was not at equilibrium.	(14)

^aPAH: polycyclic aromatic hydrocarbons; ^bDCE: dichloroethylene; ^cPCE: perchloroethylene.

is eventually drawn into the well. Our analysis suggests that, in some cases, the contamination will not get any worse: The main body of the plume has already arrived, resulting in concentrations just over the detection limit. This reasoning also suggests that, in other cases, contaminant plumes may already be affecting water supply wells but remain unnoticed unless the detection limit is lowered through better analytical methods.

Another common assumption often made by stakeholders is that large municipal supply wells are most at risk of significant contamination because they may capture multiple contaminant plumes due to their large capture zones. However, as previously discussed, contaminant concentrations in continuously pumped supply wells are inversely proportional to pumping rates. Even though more than one plume may be captured, the large pumping rates of many municipal supply wells may be sufficient to cause enough blending so that contaminant

concentrations in extracted water remain relatively low.

The same reasoning would suggest that, because small supply wells have smaller capture zones, they are less likely to capture dissolved plumes. However, when a dissolved plume does arrive at a small supply well, the impact can be more severe, because there is less dilution by blending. In the case of a small private supply well having an even lower pumping rate, the chance of capture may be lower still, but if the plume does impact the well, dilution may be minimal.

Thus, if an impact is defined by the concentration of contaminants in the extracted water, small private water wells may more often be at greater risk than large municipal systems pumping hundreds to thousands of liters a minute. Results from the Maine MTBE study appear to support this conclusion. MTBE was detected at concentrations greater than 35 µg/L in 10 of 951 small private wells but was below

35 µg/L in all of the tested larger public water supply wells (16).

Given the importance of contaminant M_d as an indicator of the severity of a particular subsurface contaminant release, it is prudent to expand our understanding of the factors controlling mass discharge. Much could be learned by thoughtful modeling; however, estimates from real sites must be developed, compiled and evaluated.

Because there are many potential MTBE release sources, it would be extremely valuable to gather reliable M_d values for gas stations, the most common type of release site, in various hydrogeologic settings. Such an effort could help define the range of expected MTBE M_d values, which would be very useful in first-approximation risk management analyses of groundwater resources known or suspected to be affected by a large number of gas stations for which site-specific data are not yet available.

For some aquifers affected by releases from multiple sites, estimating M_d from the sites may be a powerful and economical way to characterize the relative significance of particular releases and thus prioritize site remediation. This approach facilitates an understanding and discussion of the overall problem and clarifies otherwise perplexing observations.

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