

Caution Against Interpreting Gasoline Release Dates Based on BTEX Ratios in Ground Water

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Introduction

Numerous forensic techniques have been used (and misused) in the environmental profession to assess the age and liability of petroleum product releases. Such techniques often involve chemical analysis of ground water or free product sampled from the subsurface in conjunction with precise knowledge of historical usage and chemical compositions. The presence of gasoline additives can be particularly revealing, yielding valuable insight for forensic age dating. For example, tetraethyl lead was added to gasoline prior to 1985 (at 400 to 800 mg/L) to suppress pre-ignition and enhance the octane rating (Watts 1997). Therefore, the presence of organic lead in free product is indicative of a relatively old (pre-1985) release. Similarly, methyl-*tert*-butyl ether (MTBE) has been used as a gasoline oxygenate since 1979 (Steffan et al. 1997), and its national use increased rapidly in the early 1980s at 40% per year (Suflita and Mormile 1993). MTBE is not used in all current gasoline formulations, but this additive is used in amounts up to 15% by volume by many marketers. Thus, high MTBE concentrations in contaminated ground water suggest a relatively recent (post-1980) gasoline release to the subsurface. It should be kept in mind, however, that atmospheric deposition of MTBE that had been volatilized previously can be a non-point

source in urban areas (Pankow et al. 1997). Thus, traces of MTBE in ground water (<10 ppb) do not necessarily indicate recent gasoline contamination.

Forensic chemical analysis and examination of spatial concentration trends of ground water contaminants are bona fide components of liability assessment, but caution should be exercised to avoid stretching forensic inferences beyond scientific constraints. In this regard, there is a strain of folklore asserting that the age of a petroleum product release can be established in any situation by comparing aqueous concentration ratios such as benzene to xylenes (B/X) or benzene-plus-toluene to ethylbenzene-plus-xylenes ($[(B+T)/(E+X)]$). This provocative idea is based on the fact that benzene and toluene are more soluble than ethylbenzene and xylenes and, thus, are preferentially solubilized from the gasoline (Kaplan et al. 1997; Luhrs and Pyott 1992; Odermatt 1994). Thus, when solubilization is the sole fate and transport mechanism considered, B/X and $(B+T)/(E+X)$ ratios tend to decrease near the source as the time since the spill occurred increases. Such changes in BTEX ratios have been described empirically as a function of time. For example, Kaplan et al. (1997) proposed that the cumulative $(B+T)/(E+X)$ ratio, R_b , decreases exponentially with the time since a spill occurred (t) as follows:

“Traces of MTBE in ground water (<10 ppb) do not necessarily indicate recent gasoline contamination.”

$R_p = 6.0 \exp(-0.308 t)$. Solving for t for a given $(B+T)/(E+X)$ ratio is a tempting, simple approach to estimate the age of a release. However, inferring the age of a release based on BTEX ratios alone is a valid approach only in rare, well-constrained situations.

Establishing empirical relationships between BTEX ratios and age of release requires knowledge of the gasoline composition, volume of spill, and numerous physical, chemical, and biological processes affecting the fate of the BTEX species. The critical rate of change of the gasoline composition is affected by many site-specific variables, including soil texture and composition, microbial diversity, electron acceptor availability, size of release, ground water chemistry, and hydrodynamic characteristics. Unfortunately, site assessment work rarely provides sufficient sampling history and hydrogeochemical information to establish a scientific or empirical basis from which reliable estimations about release age can be drawn based on the BTEX ratios. Indeed, BTEX ratios from different sites cannot be expected to evolve on similar trends, and BTEX ratios found at one site will not necessarily correspond to another site of comparable release age. While the academic community recognizes this axiom, assertions are often made in litigation by environmental professionals who erroneously generalize correlations between BTEX ratios and the age of a release. Therefore, this paper aims to increase awareness that there is generally no clear etiology to permit reliable estimations of release age based only on BTEX ratios. To this end, the variable effect of several site-specific weathering processes on BTEX ratios are discussed with examples based on both modeling simulations and experimental data.

Weathering Processes Affecting BTEX Ratios

Several natural processes act on a fuel spill. These commonly are collected under the broad heading

of "weathering." The gasoline itself is subjected to leaching of contaminants to the aqueous phase and volatilization. Contaminants leached into the aqueous phase are subsequently transported with the ground water subject to dispersion, sorption, volatilization, and biodegradation. BTEX ratios are altered by all of these processes. The complexity of these interrelated processes results in BTEX ratios varying – sometimes in opposing directions – at different rates in both temporal and spatial dimensions. Because the aquifer properties that control the relative importance of these processes are site specific and often not well characterized (e.g., hydrodynamic heterogeneity, adsorptivity, electron acceptor pools, and microbial ecology), BTEX ratios could vary in an unpredictable manner. To demonstrate this concept, this section considers the theoretical basis of several weathering mechanisms and their effect on BTEX ratios.

Gasoline-Water Partitioning

Equilibrium partitioning between the fuel and aqueous phases determines the BTEX ratio in contaminated ground water in the immediate vicinity of the fuel spill. Assuming a certain volume of water and fuel are at thermodynamic equilibrium, aqueous phase concentrations and BTEX ratios can be estimated from a partitioning equation and a mass balance equation. Although there are many assumptions involved, Raoult's law is often used for defining the partitioning between petroleum products and water (Mackay et al. 1991):

$$C_i^w = C_{s_i}^w X_i^f \quad (1)$$

where C_i^w is the equilibrium aqueous phase concentration of species i , $C_{s_i}^w$ is the solubility of pure species i in water, and X_i^f is the mole fraction in the fuel. Alternatively, a more empirical partitioning coefficient approach has been used by Cline et al. (1991):

$$C_i^w = \frac{C_i^f}{K_i^{fw}} \quad (2)$$

Here, a partition coefficient (K_i^{fw}) is used instead of the solubility and the gasoline composition is quantified with a mass concentration for species i in the fuel phase (C_i^f).

A mass balance equation must be coupled with either one of these partition equations to relate the equilibrium concentrations to the amount and variable composition of the gasoline spilled. As a first approximation, it can be assumed that a volume of gasoline (V^f) is equilibrated with a series of n batches of water of volume V^w . Although there are no mechanisms for quantifying V^f , V^w , or n in the field, this modeling approach can be used to provide some idea of the impact of these system parameters on the BTEX ratios. Incorporating the partition coefficient (Equation 2) to relate the equilibrium concentrations of the two phases, the mass balance can be used to estimate the concentration of component i in the aqueous phase:

$$C_i^{w(n)} = \frac{C_i^{f(0)}}{K_i^{fw}} \left(1 + \frac{V^w}{V^f K_i^{fw}} \right)^{-n} \quad (3)$$

where $C_i^{w(n)}$ is the aqueous phase concentration after leaching with n batches of water and $C_i^{f(0)}$ is the initial concentration of species i in the fuel. Equation 3 assumes that the dissolution process does not significantly affect the total volume of gasoline ($V^f \approx V^{f(0)}$). This assumption is reasonable since the most soluble BTEX components generally comprise less than 20% of the total gasoline composition and only a small portion of this partitions into the aqueous phase.

Equation 3 illustrates that the aqueous phase concentrations and, hence, BTEX ratios depend on the initial composition of the gasoline, the relative volumes of water and gasoline equilibrated, and the total time of leaching — as represented by n . The importance of these three terms on the interpretation of B/X ratios near the source of fuel contamination is addressed later.

The composition of gasoline varies considerably with the octane rating, seasons of the year, geo-

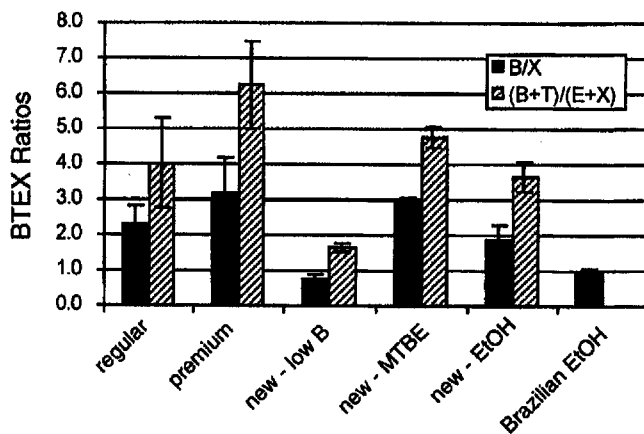


Figure 1. Variation in BTEX Ratios for Water Equilibrated with Different Gasolines. A wide range of B/X and (B+T)/(E+X) ratios have been measured in laboratory experiments where gasoline and water are equilibrated. The bars represent average ratios with one standard deviation indicated by the error bars. The dilution ratios (V^w/V^f) for these data ranged from 1 to 15. Data was obtained from Luhrs and Pyott 1992; API 1985; Fernandes 1997; Heermann and Powers 1998; and unpublished data from the University of Iowa Hygienic Laboratory.

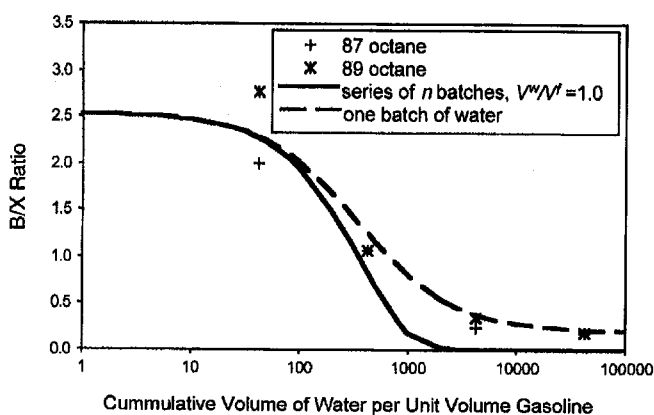


Figure 2. Effect of Dilution on B/X Ratios. The impact of the total volume of water equilibrated with one unit volume of gasoline on B/X ratios is depicted. The lines represent values estimated with Equation 3 for a series of batches of water each having the volume equal to the amount of fuel present (solid line), or for one batch of water of varying volumes (dashed line). Data from Luhrs and Pyott (1992) were generated in experiments with one batch of water ($n = 1$). The consistency between experimental and modeling data indicate that the model predictions of the decreasing B/X ratio under this type of experiment are excellent, even with variability in the initial composition of the gasoline.

graphic area, and period of manufacture. For example, premium gasolines with antiknock qualities generally have higher fractions of benzene since this species has a higher octane number (115) than other BTEX or alkane species (Speight 1991). In addition to changes in composition for performance objectives, the Clean Air Act Amendments passed in 1990 have also recently impacted gasoline compositions. One critical aspect of this law was the restriction of benzene concentrations in gasoline to 1.6% by volume (40 CFR 80.91). Gasolines formulated before

1990 generally had a higher benzene content (ca. 6% by volume) (API 1985; Johnson et al. 1990; Peterson 1995). Because the content of other BTEX compounds has not been similarly restricted, B/X and (B+T)/(E+X) ratios are generally lower for ground water equilibrated with a modern gasoline.

Figure 1 illustrates the range of B/X and (B+T)/(E+X) ratios obtained by equilibrating gasolines and water in laboratory experiments. B/X ratios generally ranged from 0.5 to 4.0 with a wide variety of values. The bar chart indicates some of the primary sources of

variation in the BTEX ratios. The higher ratios for premium gasolines and lower ratios for recent samples are apparent. A similar trend can be observed for (B+T)/(E+X), which also varied widely (from 1.5 to 7.5). Therefore, even by ignoring other weathering mechanisms that affect BTEX ratios, variation among fuel formulations may lead to erroneous interpretations of release age based solely on these ratios. For example, the empirical equation presented by Kaplan et al. (1997) is only valid for initial (B+T)/(E+X) ratios of 6.0. Data presented in Figure 1 illustrates that this could only be appropriate for a small percentage of the various gasoline formulations.

BTEX ratios are also affected by the relative volumes of water and fuel that are equilibrated. With greater volumes of water, leaching of the BTEX constituents can be significant enough to change the composition of the gasoline. For example, since benzene has a solubility approximately one order of magnitude greater than xylenes, it is preferentially leached from the fuel and B/X ratios decrease with increasing volumes of water. Data from Hinchee and Reisinger (1987) and Luhrs and Pyott (1992) show B/X ratios of 0.2 to 0.9 for water equilibrated with "weathered" gasolines. These values are significantly lower than the values presented in Figure 1 for regular and premium gasolines.

The impact of temporally variant gasoline composition as a function of leaching can be explored with Equation 3. Figure 2 illustrates that, as expected, B/X ratios decrease dramatically with increased volumes of water equilibrated with the gasoline. Model lines presented in this figure are representative of both a series of small batches of water equilibrated with the gasoline and the predicted behavior with just one batch of water. Average K^{fw} values reported by Cline et al. (1991) (i.e., $K^{fw} = 350$ for benzene and $K^{fw} = 4425$ for total xylenes) were used for these calculations with a gasoline comprised of 10% xylenes and 2% ben-

zene (by mass). The nature of these curves is similar. With relatively low cumulative volumes of water contacting the gasoline ($V^w < \sim 20 (V^f)$), there is little change in the composition of the gasoline and the B/X ratios remain relatively constant. With increasing volumes of water, the gasoline is either totally depleted of benzene with B/X ratios approaching zero in the case of a series of batch extractions, or the ratio approaches a constant value equal to the mass ratio of B/X in the gasoline for one extraction with a large volume of water. This case is indicative of nearly complete leaching of both benzene and xylene from the gasoline. In this case, aqueous concentrations are extremely low due to dilution, although B/X ratios remain constant.

Order of magnitude differences in B/X ratios may be due to the partitioning of species between gasoline and ground water. Therefore, excellent data, preferably from gasoline samples rather than from ground water samples, are required to quantify the gasoline composition and thereby incorporate the variance due to this factor. The preferential leaching of benzene and toluene from the spilled gasoline always results in decreased values of the B/X and $(B+T)/(E+X)$ ratios in the free product. Nevertheless, quantifying these decreases at a specific field site is difficult due to the lack of data necessary for applying partitioning and mass balance equations (e.g., V^w , V^f , and n).

Biodegradation

The ability of microorganisms to use BTEX compounds as food has been known since 1908, when Stormer isolated the bacterium *Bacillus hexavarbovorum* by virtue of its ability to grow on toluene and xylene as sole sources of carbon and energy (Gibson and Subramanian 1984). The ubiquitous distribution of soil bacteria capable of metabolizing aromatic compounds was first demonstrated in 1928 by Gray and Thornton, who reported that 146 out of 245 uncon-

taminated soil samples contained bacteria that degraded aromatic hydrocarbons (Gibson and Subramanian 1984). It is now widely accepted that BTEX biodegradation in aquifers is a common natural attenuation mechanism (e.g., Barker et al. 1987; Chiang et al. 1989; Hutchins et al. 1989; Lee et al. 1988; National Research Council 1993; Rifai et al. 1995; Raymond et al. 1976; Ward et al. 1989). In fact, both engineered and intrinsic BTEX bioremediation schemes are currently being used to clean up numerous contaminated sites throughout North America.

Microorganisms capable of degrading BTEX may be expected to be present in any soil-aquifer system. However, generalizing the degradability (and the rate of degradation) of a particular BTEX compound disregards an important ecological principle; that is, different sites, and different zones within a given site, are inhabited by different types and concentrations of microbial populations. Furthermore, different phenotypes can exhibit different substrate preference and removal rates. For example, some members of the consortium may prefer benzene over all other BTEX compounds (e.g., *Arthrobacter* HCB) while others may degrade toluene faster (e.g.,

Pseudomonas CFS-215) (Alvarez and Vogel 1991). Thus, differences in microbial consortia can result in differences in the rate and extent to which individual compounds degrade at different locations. Indeed, researchers have reported that toluene is degraded more readily than benzene in some aquifer systems (Karlson and Frankenberger 1989; Thomas et al. 1990; Wilson et al. 1989), while others have observed the opposite trend in other field studies (Davis et al. 1981; Werner 1985). Similarly, xylenes may be degraded faster than benzene and/or toluene at some sites (Barker et al. 1987; Reinhard et al. 1997). Hence, biodegradation may increase or decrease BTEX ratios, depending on which microbial phenotypes and electron acceptors are dominant. This concept can be illustrated with a simple mathematical model.

BTEX biodegradation rates in aquifers are often assumed to follow first-order kinetics, where the rate (dC/dt) is proportional to the contaminant concentration (C) (i.e., $dC/dt = -\lambda C$). To isolate the effect of biodegradation and eliminate confounding effects from other (transport-related) weathering mechanisms, it is convenient to consider a completely mixed batch system. Under these conditions,

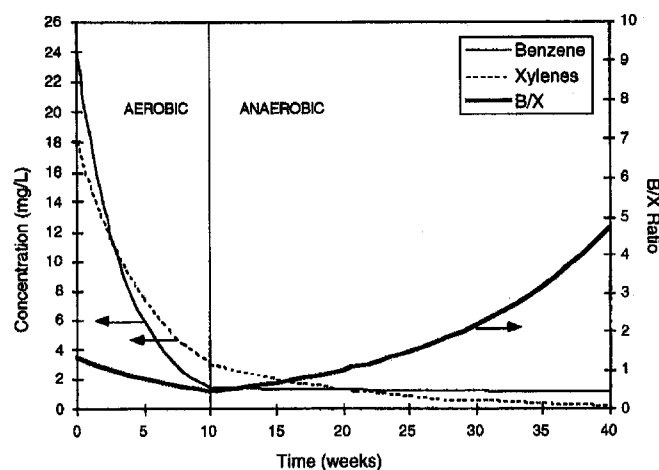


Figure 3. Effect of Aerobic and Anaerobic Biodegradation on B/X Ratios. Simulation depicts a hypothetical case where aerobic biodegradation depletes the available oxygen in 10 weeks, and anaerobic conditions prevail thereafter. Benzene and xylenes concentrations are assumed to decay exponentially (Equation 4), with the following first-order coefficients (day^{-1}): 0.04 for benzene under aerobic conditions, 0.001 for benzene under anaerobic conditions, 0.025 for xylenes under aerobic conditions, and 0.012 for xylenes under anaerobic conditions (Howard et al. 1991).

the above (first-order) rate expression can be integrated to yield:

$$\frac{C}{C_0} = e^{-\lambda t} \quad (4)$$

where

C = aqueous concentration of a given BTEX compound at time t (mg/L)

C_0 = initial concentration at $t = 0$ (mg/L)

λ = first-order decay coefficient for the compound of interest (system specific) (day^{-1}).

To illustrate that B/X ratios can vary in opposing directions even at a given spot, consider a typical scenario where subsurface microbial degradation of spilled hydrocarbons depletes the available dissolved oxygen, and anaerobic conditions develop after an arbitrary period of 10 weeks. Benzene typically degrades faster than xylenes initially, while aerobic conditions prevail. This is depicted in Figure 3, which simulates Equation 4 with first-order decay coefficients reported in the literature (i.e., $\lambda = 0.040 \text{ day}^{-1}$ for benzene, and $\lambda = 0.025 \text{ day}^{-1}$ for xylenes; Howard et al. 1991). The higher λ for benzene causes the B/X ratio to decrease with time under aerobic conditions (Figure 3). Nevertheless, the switch from aerobic to anaerobic conditions slows down the benzene degradation rate to a much greater extent than the other degradation rates. In this example, using typical values compiled by Howard et al. (1991), λ decreases by 98% to 0.001 day^{-1} for benzene, while it decreases only by 52% to 0.012 day^{-1} for xylenes. These coefficients reflect that benzene degrades slowly if at all under anaerobic conditions (Alvarez and Vogel 1995; Edwards and Grbić Galić 1992; Grbić-Galić and Vogel 1987; Kazumi et al. 1997; Lovely et al. 1989). The recalcitrance of benzene in anaerobic environments may be due to its chemical structure. Unlike toluene and xylenes, benzene lacks methyl substituents which have electrophilic character and facilitate microbial nucleophilic attack with water or acetyl-

CoA (Alvarez and Vogel 1995; Evans et al. 1992). Therefore, a switch from aerobic to anaerobic conditions tends to reverse a decreasing trend in B/X ratios to an increasing trend (Figure 3).

This example shows that biodegradation can have opposing effects on B/X ratios, depending on the prevailing redox conditions and the substrate preference of the dominant phenotypes. A similar argument could be made for (B+T)/(E+X) ratios. Thus, without detailed knowledge of pertinent biogeochemical parameters across a given site, one cannot rule out the possibility that such ratios can vary unpredictably and at unknown rates. In such cases, biodegradation alone can preclude reasonable inferences of release age based on declining B/X or (B+T)/(E+X) ratios.

Transport, Sorption, and Retardation

BTEX compounds have different tendencies to adsorb to aquifer material (Stuart et al. 1991). Adsorption causes individual BTEX compounds to migrate at different velocities through aquifers (Angle et al. 1992; Chen et al. 1992). This can result in a chromatographic separation, affecting their relative proportions at a given location and time (Odermatt 1994). Such effects can be illustrated using simple mathematical models. First, let us define some parameters.

The retardation factor (R_f), which represents the relative advective velocity of ground water to that of a dissolved contaminant, is defined for saturated flow as (Domenico and Schwartz 1997):

$$R_f = 1 + \frac{\rho_b K_p}{\epsilon} \quad (5)$$

where

ρ_b = bulk density of aquifer material (kg/L or g/cm^3)

K_p = partitioning coefficient between soil and water ($[\text{mg/kg}]/[\text{mg/L}]$ or L/kg or mL/g)

ϵ = porosity of the aquifer material.

For simplicity, this formula assumes linear local equilibrium. K_p is different for each BTEX compound, and increases with contaminant hydrophobicity and organic carbon content in the aquifer material (Karickhoff 1984). K_p can be estimated for each BTEX compound using the correlation (Schwarzenbach et al. 1993):

$$K_p = 0.1905 f_{oc} K_{ow}^{1.01} \quad (6)$$

where

f_{oc} = fraction of organic carbon

K_{ow} = octanol-water partition coefficient.

To illustrate the effect of retardation, consider an aquifer with the default parameters for the Iowa Risk-Based Corrective Action (RBCA) Tier-2 model (Iowa Administrative Bulletin 1996): $\epsilon = 0.3$; $\rho_b = 1.86 \text{ g/cm}^3$; and $f_{oc} = 0.01$. The K_{ow} values are $10^{2.12}$ for benzene, $10^{2.73}$ for toluene, and $10^{3.26}$ for *para*-xylene (Howard 1990). With these typical parameters, Equations 5 and 6 predict that the retardation factor is 2.64 for benzene, 7.75 for toluene, and 24.17 for *para*-xylene. This means that benzene would migrate 2.9 times faster than toluene and 9.2 times faster than *para*-xylene. Such differences in migration velocities would cause chromatographic separation of the BTEX, and thus changes in the BTEX ratios at different locations within a plume. These effects can be illustrated using a simple fate-and-transport model which is based on the solution to the one-dimensional advection-dispersion equation with retardation (Domenico and Schwartz 1997):

$$C = \frac{C_0}{2} \text{erfc} \left[\frac{R_f x - v_w t}{2\sqrt{\alpha_x v_w t R_f}} \right] \quad (7)$$

where

erfc = complementary error function = $1 - \text{erf}$

x = distance downgradient from the (constant) source (m)

α_x = longitudinal dispersivity (m)

v_w = ground water flow velocity (m/d); and all other terms as previously defined.

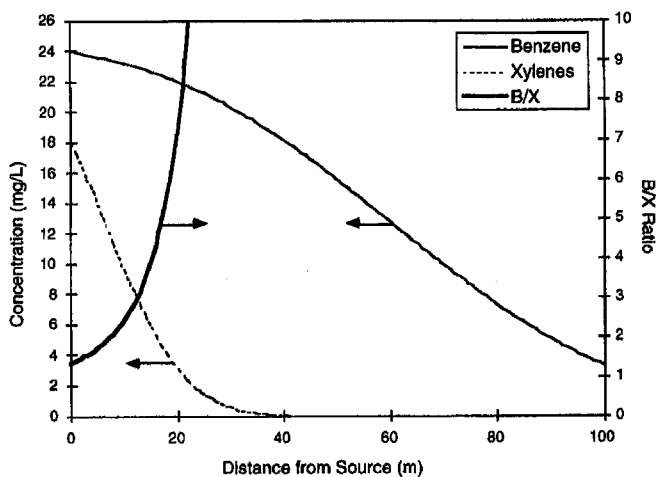


Figure 4. Effect of Retardation of B/X Ratios Downgradient from the Source. Benzene and xylenes concentration profiles were simulated with Equation 7 using the Iowa RBCA default parameters ($v_w = 0.044$ m/d, $R_f = 2.64$ for benzene, and $R_f = 24.17$ for xylenes). It was also assumed that $\alpha_x = 10$ m and $t = 10$ years.

This model, depicted in Figure 4, does not incorporate biodegradation so that the effect of retardation on BTEX transport can be isolated. The concentration profiles for benzene and xylenes along the principal flow direction were also simulated using Iowa RBCA default parameters: effective porosity (ϵ_{eff}) = 0.1; hydraulic gradient (i) = 0.01; and hydraulic conductivity (K) = 0.44 m/d. These parameters were used to calculate $v_w = K i / \epsilon_{eff} = 0.044$ m/d. Equation 7 simulations also used $\alpha_x = 10$ m and $t = 10$ years. Under this typical scenario, benzene would migrate further from the source area faster than xylenes. Its faster migration velocity would also increase its degree of dispersion, as indicated by a milder-sloped concentration front compared to xylenes (Figure 4). For a constant source, the faster migration and higher dispersion of benzene would increase B/X ratios just a few meters downgradient of the source (Figure 4). Therefore, regardless of the age of the release, retardation can have significant spatial effects on BTEX ratios. Interpretation of the situation at a site will likely be complicated by the distance of the sampling well from the source, spatial heterogeneities in soil f_{oc} and permeability, as well as incomplete knowledge of plume state (steady, advancing, or receding) and release(s) history.

Volatilization

BTEX loss from gasoline-contaminated ground water into air or air-filled pores is controlled by Henry's law. Compounds with higher Henry's constants (H) tend to volatilize more readily. However, Henry's constants for BTEX compounds are similar (i.e., H , in $\text{mol L}^{-1}_{air} / \text{mol L}^{-1}_{water}$, is 0.22 for benzene, 0.26 for toluene, 0.32 for ethylbenzene, and 0.29 for xylenes) (Howard 1990). Furthermore, volatilization has been reported to be a relatively minor removal mechanism for BTEX from contaminated aquifers (Chiang et al. 1989). Therefore, volatilization is not expected to exert a significant effect on aqueous-phase BTEX ratios, although the slightly lower Henry's constant for benzene suggests that benzene would volatilize to a lesser extent than xylenes. Thus, volatilization may be conducive to slightly increasing B/X ratios with release age.

Conclusions

Different weathering mechanisms can affect the relative proportion of BTEX compounds at different rates and sometimes in opposing directions. Benzene and toluene are more soluble than ethylbenzene and xylenes. Therefore, B/X and (B+T)/(B+X) ratios tend to decrease near the source

area with time (albeit, at site-specific and often unknown rates) by the action of dissolution, dilution, and transport. However, biodegradation could also increase such ratios in ground water near the source, especially when anaerobic conditions prevail (confounding the interpretation of decreasing BTEX ratios). This is so because benzene degrades slowly if at all under anaerobic conditions. Down-gradient from the source, BTEX ratios are predominantly influenced by adsorption-induced "chromatographic" separation (i.e., retardation) as BTEX compounds migrate at different velocities through the aquifer, and by differential biodegradation. Retardation tends to increase downgradient B/X and (B+T)/(B+X) ratios, while biodegradation can either increase or decrease such ratios, depending on the substrate preference of the prevailing phenotypes and the available electron acceptor pools.

The aquifer properties that control the rate and extent of different weathering mechanisms are site-specific. Therefore, one should not use the relative concentrations of individual BTEX compounds in ground water to determine the age of a petroleum product release reliably. Such attempts bear a burden of proof that is often beyond the limits of scientific constraints and require far more data than can be obtained given common technical and economic constraints.

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