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SPECIAL ISSUE ON

Monitored Natural Attenuation

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Laboratory study of BTEX biodegradation

Investigators recently studied the aerobic and anaerobic biodegradation of BTEX in the laboratory (*Salanitro and others, 1997*). They created three laboratory microcosm systems using field samples of aquifer cores and/or groundwater. They wanted to demonstrate the potential for BTEX to biodegrade under the following conditions:

- aerobic
- chronic low DO (dissolved oxygen)
- anaerobic

Site characteristics

Table 1 shows the sites from which investigators obtained samples to perform this study. Using these samples, investigators created the following microcosms:

- groundwater
- soil-groundwater
- respirometer-coupled soil-groundwater

Groundwater microcosms. BTEX in these microcosms varied from 3 to 13 mg/L. Microcosms were inverted at room temperature and sampled for dissolved constituents (BTEX, Fe⁺², SO₄⁻², H₂S) and headspace gases (O₂, CO₂, N₂, H₂S, H₂ and CH₄). The groundwater microcosms described below were anaerobic, sterile and methanogenic.

Anaerobic groundwater was flushed with O₂-free helium; adding a commercial oxygen-consuming enzyme further decreased DO to about a 70 ml air headspace.

Sterile or microbially inhibited groundwater microcosms were prepared by autoclave sterilizing or adding sodium azide to inhibit respiration; in some cases investigators amended the microcosms with NO₃⁻ (nitrate ion), SO₄⁻² (sulfate ion) or amorphous Fe(OH)₃ (ferric hydroxide) to enhance the NR (nitrate-reducing), SR (sulfate-reducing) and IR (iron-reducing) conditions.

Methanogenic groundwater microcosms were those which had no added EAs (electron acceptors).

Soil-groundwater microcosms consisted of 50 g of aquifer core material and 80 to 90 ml groundwater. BTEX

compounds were added to achieve a concentration of 5 to 10 mg/L total hydrocarbon. The microcosms were incubated at room temperature and sampled for two months for dissolved species and headspace gases.

Aerobic slurries were flushed with sterile air to a DO of 6 mg/L. Headspace volume was about 20 ml.

Investigators prepared **anaerobic microcosms** similarly to the groundwater ones, but used O₂-free helium gas, Oxyrase enzymes and resazurin indicator. NO₃⁻ and SO₄⁻² were added to establish NR, SR and IR conditions.

Respirometer-coupled soil-groundwater microcosms were created to determine the effects of constant low DO (chronic) on BTEX biodegradation. (System setup is detailed in *Salanitro and others, 1997*.) Soil slurries, which consisted of 50 g aquifer soil and 550 ml groundwater, were flushed with various mixtures of O₂ and N₂ until the desired DO was attained. To obtain low DO (e.g., 0.1 to 0.2 mg/L), investigators added 0.5 to 2 ml Oxyrase preparation because it was difficult to achieve low DO levels with ordinary O₂-free N₂ or He gas flushing. After equilibrium with the appropriate O₂/N₂ mixtures, BTEX were added to the slurries in concentrations of 3 to 6 mg/L. "As DO is consumed by microbial oxidation, pressure in the headspace decreases and the pressure transducer valve opens, allowing O₂ gas to enter the microcosm and maintain atmospheric pressure within the vessel." Investigators recorded the volume of O₂ released over two weekends. In addition, CO₂ did not contribute to any increase in headspace gases.

Sample analyses

Investigators analyzed the microcosms for the following:

- BTEX-degrader populations (concentrated, filtered, numbers estimated)
- BTEX: (purge-and-trap chromatographic methods; PID detection)
- dissolved NO₃⁻ and SO₄⁻² (ion chromatography and inorganic carbon)
- total dissolved iron (Fe⁺²) and total iron (two Hach spectrophotometric chemical analyses)
- N₂, H₂, H₂S, and CH₄ (gas chromatography)

"Minimum first-order or pseudo-first-order BTEX biodegradation rates were estimated from curves (average of duplicate microcosms) using the equation $r = \ln(C_o/C_t)/t_o - t_t$ where the BTEX concentrations C_o and C_t were those determined at sample points t_o and t_t, respectively. In some

Site location	Contaminant	Aquifer conditions	Microcosm type	Condition
Sparks Terminal (NV)	Fuels, solvents	Aerobic	Groundwater	Aerobic
Phoenix Terminal (AZ)	Fuels	Aerobic, anoxic or anaerobic ¹	Groundwater	Aerobic, anaerobic
Aloha (OR)	Gasoline	Aerobic, anoxic or anaerobic	Soil/groundwater	Aerobic, anaerobic
Blue Lake (MI)	Natural gas, light liquids	Aerobic	Soil/groundwater	Aerobic

¹ Uncertainty regarding the actual redox status of these aquifers

Table 1. Some characteristics of soil and groundwater sites used in study (from *Salanitro and others, 1997*).

microcosms, there were insufficient sample points because of rapid biodegradation for estimating the true first-order decay. These were assumed to approximate a first-order degradation rate" (*Salanitro and others, 1997*).

Groundwater microcosms: Sparks Terminal

Results from the Sparks Terminal microcosm indicated that

- aerobic groundwater BTEX degradation rates differed at the site, ranging from 0.02/d to 0.39/d; researchers did not attribute differences to anything specific
- anaerobic microcosms prepared with low DO and negative electrode potentials, but no added EA, had low rates (≤ 0.01 /d) of BTEX degradation and 21-day lag periods; only toluene was appreciably metabolized (0.09/d) to non-detectable levels within eight weeks
- sterile aerobic and anaerobic microcosms showed little or no loss (< 0.01 /d) of BTEX
- larger-than-expected consumed amounts of O_2 suggest that most O_2 uptake may result from the metabolism of unidentified non-BTEX compounds in groundwater
- small amounts of CO_2 , CH_4 , H_2 and H_2S were formed in all anaerobic well water microcosms
- the measured DO (0.05 to 0.5 mg/L) and electrode potentials (-300 to -400 mV) in the anaerobic microcosms were within the expected range for bacterial sulfidogenesis and methanogenesis; these potentials along with the small amounts of CO_2 , CH_4 , H_2 and H_2S are not indicative of the anaerobic oxidation of BTEX; for instance, some CH_4 may have been formed from the reduction of soluble carbon or the oxidation of naturally occurring volatile acids, like formate and acetate
- in anaerobic microcosms, 70 to 100 percent of the SO_4^{-2} was reduced by sulfate-reducing bacteria (SRB); the dissolved HS^- that formed did not correlate well with the amount of sulfate reduced, and toluene degraded in one microcosm (MW-9); other data (calculated CH_4 and level of dissolved CO_3^{-2}) indicated that it is not possible to assign an EA process (sulfidogenesis and/or methanogenesis) to the apparent degradation of toluene in the groundwater of MW-9; also "formation of H_2S , CH_4 and H_2 in the microcosms of MW-1 and MW-3 well water in which no hydrocarbon was biodegraded indicates that the formation of these reduced gases may be common in groundwater which is made anaerobic (low DO and negative electrode potential)" (*Salanitro and others, 1997*).

Groundwater microcosms: Phoenix Terminal

Results from this study indicate that

- aerobic BTX-degraders were present in concentrations of 10 to $>10^8$ /L; higher levels (10^3 to 10^5 /L) were observed in the presumed anaerobic portion of the aquifer
- anaerobe populations were also low (≤ 50 to 500/L) in one Phoenix Terminal well that had a higher DO (0.8 to 3 mg/L)
- in the NR (nitrate-reducing) medium, BTX-degraders were low (< 50 to 500/L); however, denitrifying microbes were

present in five out of seven water samples

- two microcosms that had high denitrifier populations did not degrade hydrocarbons, indicated by low BTX biodegradation losses
- investigators detected high numbers of IR microbes in five of seven water well samples, but most showed low BTX metabolism
- sulfate-reducing bacteria were present in five of seven samples, but associated BTX-degraders were only ≤ 50 to 500/L
- CH_4 -producing organisms were present in low numbers (< 50 to 500/L) in all samples; these samples also had low numbers of BTX-degraders (≤ 10 /L) growing in the methanogenic medium

Data indicate that microbes in the Phoenix Terminal water samples taken from the plume's anaerobic zones did not contain high numbers of anaerobic BTX-degraders; thus, the EA-reducing activity (for NO_3^- , Fe^{+3} and SO_4^{-2}) was greater than the BTX-degrading activity. "Zones of plume which have shown apparent SR and NR also have high counts of bacteria. Similarly, well SP-W-5, which is in a presumed IR zone in the aquifer, had both high IR and SR bacteria ($\leq 5 \times 10^6$ /L) but low (50 to 500/L) associated BTX-degrading microbes. These observations indicate that groundwater samples may or may not reflect the anaerobic BTX-degradative activity in an aquifer" (*Salanitro and others, 1997*).

Researchers also prepared groundwater microcosms using groundwater from an "aerobic" and a presumed "anaerobic" source located near a hydrocarbon source. When they incubated these samples under aerobic conditions, all BTEX compounds degraded rapidly to low levels; under reducing conditions, however, biodegradation rates decreased.

"Aerobic BTEX degraders were always present at much higher numbers than comparable anaerobic degraders, and this correlates with the higher degradation rates when O_2 is the terminal EA. Also, the reduction of anaerobic EA (e.g., formation of CH_4 , H_2S , N_2 and Fe^{+2}) in the BTEX-degrader assay or the groundwater microcosms test—in the absence (or low rate) of significant BTEX metabolism—indicates that these processes may not be coupled. This suggests, furthermore, that anaerobic bacteria in aquifers may be well adapted to reduce EA using electron donors other than BTEX (e.g., short-chain acids, partially oxidized petroleum hydrocarbons, or cell-stored organic polymers)" (*Salanitro and others, 1997*).

Soil-groundwater microcosms: Aloha and Blue Lake sites

Soil-groundwater microcosm studies of BTX compounds under aerobic and anaerobic conditions have indicated:

- for two soil core samples, aerobic biodegradation rates were 0.11/d and 0.26/d respectively; biodegradation occurred without a lag phase
- aerobic biodegradation exceeded anaerobic biodegradation
- B and/or TX degraded when anaerobic slurries were amended with NO_3^-

- hydrocarbons were not appreciably metabolized in slurries supplemented with $\text{Fe}(\text{OH})_3$
- "It is not clear whether the high rate of Fe^{+3} reduction in these anaerobic soils was associated with the degradation of BTX in microcosms with NO_3^- , SO_4^{2-} or no EA"
- levels of Fe^{+2} in the anaerobic slurries suggested that Fe^{+3} was the predominant EA, except in the Fe^{+3} -amended slurries
- BTX was degraded in a SO_4^{2-} -amended microcosm of an aquifer core; toluene and m-xylene degraded without a lag phase, while benzene was metabolized after 42 days; soluble SO_4^{2-} was not reduced to $\text{H}_2\text{S}/\text{HS}^-$
- in anaerobic microcosms with no added EA, BTX degradation rate was 0.04/d to 0.20/d with lag times of 0 to 42 days

According to Salanitro and others (1997), "The results of these anaerobic soil-groundwater microcosms and the role of EA coupled to the biodegradation of BTX are not entirely obvious. Both NO_3^- and Fe^{+3} were reduced, and SO_4^{2-} reduction and reduced gas (CH_4 , H_2S and H_2) formation were not apparent. The rapid metabolism of BTX in microcosms with added NO_3^- , SO_4^{2-} or no EA and the concomitant formation of high soil-bound Fe^{+2} suggest that Fe^{+3} may be the predominant anaerobic EA in the natural attenuation of BTEX in Aloha aquifer sediments. This high Fe-reducing activity may also be coupled to hydrocarbon oxidation with some other soil component(s) such as co-EA." Recent experiments have reported that soil humic compounds function as intermediary EA to degrade organic compounds; here, cultures of Fe-reducing soil bacteria use Fe^{+3} as the terminal EA. "In this respect, it is interesting to note that in microcosms we prepared with well water (e.g. Phoenix Terminal study), significant Fe^{+3} reduction occurred, but this did not correlate with the anaerobic metabolism of hydrocarbon. This suggests that a soil fraction (e.g., humics) may be required in BTEX oxidation."

Respirometer-coupled microcosms

Investigators also monitored aromatic hydrocarbons in soil-groundwater microcosms that were kept at different but constant low DO levels in a pressure transducer-controlled respirometer. BTEX degraded at rates ranging from 0.3 to 0.7/d. Results of these experiments "suggest that microbial hydrocarbon metabolism can occur at much lower DO levels (0.2 to 2 mg/L) when the O_2 source is continuously replenished. These data also indicate that BTX degradation is not kinetically limited by numbers of hydrocarbon-degraders in soils and groundwater or availability of microbial growth nutrients (NH_3 , PO_4^{3-}). . . The biodegradation of BTX in the O_2 -controlled soil respirometer experiments suggests an analogy to aquifers that have low or chronically low levels of DO (i.e., ≤ 1 to 2 mg/L). **These plumes may exhibit significant and sustained hydrocarbon bioattenuation because O_2 is continuously supplied at some rate controlled by the aquifer hydrogeology, groundwater infiltration, advection, and capillary fringe diffusion rates. Many of these plumes**

would appear to be stable and nonmigrating and therefore display significant aerobic bioattenuation potential" (Salanitro and others, 1997).

Conclusions

Salanitro and others (1997) conclude that ". . . contaminant mass removal and the assignment of EA of anaerobic attenuation (e.g. by showing loss of NO_3^- or SO_4^{2-} , formation of Fe^{+2} or CH_4 within monitoring wells along a longitudinal groundwater flowpath of a BTEX plume) are confounded by the continual advective and diffusive influx of O_2 through water table fluctuations, rainfall events and vadose zone capillary fringe."

Results from microcosm studies indicate the following:

- "aerobic biodegradation of BTEX appears to dominate the microbial attenuation process at four sites" where hydrocarbons are extensively degraded at high ($\geq 0.1/\text{d}$) first-order decay rates
- "aerobic metabolism in aquifer sediments is rapid at low DO concentrations (0.2 to 2 mg/L) when the O_2 source is not limiting"
- "chronic low DO simulations suggest that at sites in which low DO is measured within the plume, soluble hydrocarbons would degrade as rapidly as in groundwater with higher DO (e.g. >2 mg/L) if there is a continuous diffusion of O_2 "
- "the equilibrium of low DO plumes would be controlled by abiotic and microbial-consuming processes"
- O_2 diffusion-limited aquifers may not be anaerobic (reducing and at low redox potential) but represent stable, slowly degrading plumes; the disposition of these plumes would also be governed by the presence and size of a residual hydrocarbon source and the rate of mass efflux from the source into the soluble plume"
- BTEX degradation rates are rapid under aerobic conditions
- respirometry-coupled microcosms operating with constant low DO levels (≤ 2 ppm) degrade BTEX at rates similar to those with higher O_2 levels
- reduction in EA and the formation of corresponding reduced species does not correlate well with apparent anaerobic BTEX degradation
- "microbial EA reduction is common in groundwater and soil that are adjusted to low DO and electrode potentials"
- ". . . hydrocarbons degraded in all microcosms amended with NO_3^- , Fe^{+3} , SO_4^{2-} or no EA; NO_3^- was denitrified and reduced gases (H_2 , CH_4 and H_2S) were not formed, but large amounts (10 times higher than predicted by stoichiometry) of soil-associated Fe^{+2} formed;" the role of Fe^{+3} or other EAs at this site is unclear

Salanitro and others (1997) suggest that investigators study "field verification of O_2 mass transport mechanisms in chronic low DO groundwater." They also need to evaluate "reduced EA in monitoring wells and the formation of reduced gases (e.g. soluble or vadose zone gaseous species) as bioindicators of anaerobic BTX attenuation."

Reference

Salanitro, J.P., Wisniewski, H.L., Byers, D.L., Neville, C.C. and R.A. Schroder, "Use of Aerobic and Anaerobic Microcosms to Assess BTEX Biodegradation in Aquifers," *Ground Water Monitoring and Remediation*, Summer 1997; <http://www.h2o-ngwa.org>; 614-898-7791.

UTTU thanks Dr. Salanitro, Shell Oil, for his help on this article.



Field and laboratory studies of nitrate-enhanced bioremediation

Researchers recently investigated bioremediation conditions in a naturally reducing wetland that typically lacks oxygen (Schreiber and others, 1997). Aerobic biodegradation efficiently degrades BTEX, but adding oxygen to reducing wetlands could be impractical because of its low solubility and limited capacity to oxidize dissolved iron (and precipitate iron) and natural organic carbon. When oxygen is not present, microorganisms may use electron acceptors (EA) such as nitrate, iron, manganese, sulfate or carbon dioxide to bioremediate a site. Because of nitrate's low cost and high water solubility, investigators have in the past used nitrate to enhance bioremediation.

The actual rates at which nitrate-enhanced bioremediation occurs in the laboratory vs. the field can vary widely, however. One laboratory study indicated rates were 26 times that of field-derived rates. Differences between laboratory and field rates may be due to

- temperature
- pH fluctuations
- inhibition or competition by other electron acceptors
- nitrate utilization by plants

Schreiber and others (1997) used a tracer experiment to compare nitrate utilization rates in the field with laboratory studies. The field study took place in west central Wisconsin. Site characteristics included the following:

- area underlain by sandstone bedrock covered with sandy alluvium
- a water table about 10 ft (3.1 m) below ground surface
- the sand aquifer at least 30 ft (9.1 m) above weathered bedrock
- hydraulic conductivity of the alluvium measuring about 30ft/day (9.1m/d)
- water table gradients of 0.01 to 0.02
- contamination from two LUSTs, with the BTEX plume extending over 350 ft (100 m) through a wetlands discharging into a creek
- maximum BTEX concentrations exceeded 10 ppm

BTEX concentrations tended to flux significantly, so investigators used parameters other than BTEX concentrations to assess the success of intrinsic bioremediation. For instance, they found that benzene-to-toluene ratios increased along the contaminant plume, indicating that toluene was degrading more quickly than benzene. They measured these and other values using "multi-level samplers installed along two transects, one in an uncontaminated area, and another in the contaminant plume." Redox-sensitive species, also indicative of intrinsic bioremediation, which investigators measured, included

- dissolved oxygen
- nitrate
- sulfate
- dissolved iron

Within the contaminant plume investigators found

- depletion of DO and nitrate
- lower sulfate concentrations
- high dissolved iron concentrations

Experiment and results

Investigators used bromide (conservative) and nitrate (reactive) tracers to "estimate flowpaths and advective velocities and to determine if nitrate would be utilized by the native microbes to enhance BTEX degradation." They installed 70 multilevel samplers (with 10 sampling intervals, from 3 to 12 ft below ground surface) to follow the tracer.

Investigators estimated advective velocities "by dividing the distance between two wells along the tracer path by the time it took for the peak concentration of bromide to travel between the two wells. In general, advective velocities were consistent for each depth along the flowpath but varied between the depths. For example, advective velocities averaged 0.87 ft/d at the 7-ft depth, while at the 9-ft depth, velocities averaged 0.97 ft/d."

"In the contaminant plume, nitrate was depleted with respect to bromide while below the contaminant plume, nitrate remained. Due to dilution and dispersion, however, nitrate concentrations below the contaminant plume were significantly less than 10 mg/L in a multilevel sampler at the stream (creek)."

Investigators found that the nitrate tracers were not retarded relative to bromide; therefore, investigators used "the ratio of the normalized nitrate concentration to the normalized bromide concentration . . . to assess if nitrate utilization is occurring and to quantify the rate constants of utilization."

Microcosm experiment

The laboratory microcosm experiment revealed that

- CO₂ was produced in all microcosms
- CO₂ production occurred more rapidly in microcosms containing nitrate, suggesting that nitrate (as an electron acceptor, EA) encouraged microbial growth
- addition of nitrate had a greater effect on uncontaminated samples at first

- CO₂ production was greater in microcosms containing both nitrate and toluene than in those containing nitrate but no toluene; toluene here is acting as the carbon and energy source; possibly toluene-degrading organisms had been established in aquifer materials
- nitrate was rapidly consumed in microcosms with and without toluene, suggesting denitrifiers were previously established in contaminated and uncontaminated samples
- accumulation of NO₂ in the presence of toluene was significantly higher than without toluene, suggesting that denitrification may involve different microbial populations depending on absence or presence of toluene
- nitrate utilization rates from microcosms are higher than the field rates; in uncontaminated sediments, "which approximates the area under the contaminant plume, the first-order rate constant is 0.048/d; in contaminated sediments that approximate the plume, first-order rate constant is 0.060/d"
- there was no nitrate utilization lag time in the microcosms
- toluene degradation occurred more rapidly when nitrate was present

Differences in field and microcosm situations

Researchers found these differences:

- in the field tracer experiment, nitrate was utilized after a lag time of 8 days with a rate constant of 0.031/d
- in the microcosm experiment, nitrate had no lag time; rate constants of nitrate utilization ranged from 0.048/d (uncontaminated sediments) to 0.060/d (contaminated sediments)

Reference

Schreiber, M.E., Bahr, J.M., Zwolinski, M., Shi, Y., Hickey, W.J. and K.A. Brownell, "Field and Laboratory Studies of BTEX Bioremediation Under Denitrifying Conditions," from *In-Situ and On-Site Bioremediation*, editors Alleman and Leeson, Vol. 5, 1997, Battelle Press.

Call for Instructors

The American Society for Testing and Materials (ASTM) is accepting resumes from candidates interested in teaching an ASTM course. The 1½- to 2-day course will be based on ASTM's proposed *Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites*. Initially, the course will be targeted to the regulatory community, but it will later encompass a broader audience. Applicants should send resumes, (five pages maximum) to Scott Murphy, ASTM Headquarters, 100 Barr Harbor Drive, W. Conshohocken, Pennsylvania 19428-2959. Applications must be received by ASTM no later than March 20, 1998. Interview candidates will be contacted no later than March 27, 1998.



Four critical considerations in assessing contaminated groundwater plumes

Implications for site-specific MNA/RBCA assessments at petroleum-contaminated sites

State and federal agencies are increasingly relying on risk based corrective action (RBCA) and/or monitored natural attenuation (MNA) for cleanup of petroleum-contaminated sites. ASTM (Association for Testing and Materials) released a RBCA protocol two years ago and recently finalized a remediation by natural attenuation protocol. The U.S. EPA has recently published a directive on MNA.

Historically, groundwater contaminant plumes from petroleum release sites were usually remediated at the source and/or downgradient locations with either pump-and-treat or in-situ air sparging. These active remediation methods offer safety factors; for instance, if an undersized pump-and-treat system fails to contain a plume, the plume would have lower downgradient concentrations than under MNA alone because the pump-and-treat system reverses the groundwater gradient downgradient of the extraction well(s).

RBCA and MNA incorporate no such safety factors that reduce contaminant concentration; these strategies rely solely on accurate and high quality hydrogeological site characterizations to demonstrate adequate public protection. Thus, most MNA proponents firmly endorse quality site characterizations. "In general, the level of site characterization necessary to support a comprehensive evaluation of natural attenuation is more detailed than needed to support active remediation" (*U.S. EPA, 1997*).

This article focuses on four issues that, if disregarded, can result in a RBCA or MNA assessment that may fail to accurately predict the plume location at a given time. These issues are

- hydraulic conductivity and groundwater velocity estimates
- diving plumes
- water sample interpretation and sentinel well placement
- inability to accurately predict or model plume behavior

Hydraulic conductivity and groundwater velocity estimates

One of the more critical factors in a RBCA or MNA assessment is an accurate determination of the rate that groundwater flows through and away from a contaminated source area. Calculations to determine plume travel times are based on estimates for hydraulic conductivity, effective porosity, horizontal groundwater gradient and retardation. Assuming that groundwater flow is through primary porosity and not secondary porosity, the parameter with the greatest potential for error is hydraulic conductivity. Thus, accurate

hydraulic conductivity estimates are often the most critical parameter for estimating plume travel rate.

Recently, Lawrence Livermore Laboratory studied files of petroleum release sites in California (Rice, et al, 1995), and the University of Texas Bureau of Economic Geology evaluated sites in Texas (University of Texas, 1997). Rice and others (1995) found that "it was often necessary to estimate LUFT site hydrogeologic parameters such as hydraulic conductivity because [data were] either not available or not entered into the historical LUFT case data set." The Texas study indicated that hydraulic conductivity was measured at only 137 of 605 sites. Both studies suggested that hydraulic conductivity tests are often not conducted even though **hydraulic conductivity is one of the most critical parameters in a RBCA or MNA assessment.**

Hydraulic conductivity considerations for a site undergoing a RBCA or MNA analysis include the following:

- is it cost-effective to measure hydraulic conductivity? Slug and bail-down tests are relatively inexpensive to conduct compared to pumping tests; the potential cost of "guesstimating" instead of measuring hydraulic conductivity can be significant if the "guesstimate" is in error
- when slug or bail-down tests are used, do they provide enough accuracy to represent the site's hydraulic conductivity? Many potential errors may occur when hydrologists conduct these tests (more detail below)
- what is the impact of an error? At a site with high groundwater velocity, estimate accuracy is critical because the risk of a rapidly expanding plume impacting a receptor is greater; however, if groundwater velocity is only a few feet per year, the impact of an error is small
- when slug or bail-down tests are used, how many wells should be tested? Due to the number of potential errors in test results and the low cost of each slug or bail-down test, many tests are usually conducted
- when a number of test results are available, which value(s) should be used: the highest value, arithmetic mean, or geometric mean?

Slug or bail-down tests are the most common methods used. Comparison of hydraulic conductivity results from slug/bail-down tests and pumping tests at the same site indicate that slug/bail-down test results often underestimate

hydraulic conductivity. Many hydrogeologists consider a measurement error of less than one half of an order of magnitude to be relatively small for slug or bail-down tests.

Errors in slug or bail-down test data result from

- smeared borehole walls that reduce the measured hydraulic conductivity; this is more common when monitoring wells are under—or poorly—developed
- test results that reflect only the hydraulic conductivity of the soil adjacent to the well screen; if most or all of the wells at a site are water table wells with less than 10 feet of screen within the aquifer, the test results reflect only a geologic horizon that is less than 10 feet thick; hydraulic conductivity may vary significantly at different depths (see Figure 1)
- considerable variation in hydraulic conductivity that exists within the screened interval of a monitoring well; the test result is an overall average of the hydraulic conductivity within that interval, and conductivity can vary within that interval (see Figures 1 and 2)
- procedure errors, such as slug injection into a water table well, which violate test procedures (Bouwer, 1989)
- in highly permeable soils, a filter pack in the well that may be less permeable than the native soils; here the measured value will be less than the true aquifer hydraulic conductivity

Figure 1 shows that high permeability zones often conduct most of the groundwater flow, but these zones generally constitute a minority of the total aquifer thickness. Figure 2 shows the results of hydraulic conductivity tests conducted in very small discreet intervals within three borings at another site. Although this hydrogeological unit is nearly uniform in composition, the hydraulic conductivity varies considerably with depth. Since a slug or bail-down test measures **average hydraulic conductivity** over the well's entire screened interval, and not the hydraulic conductivity of these high permeability zones, groundwater velocity estimates based on slug tests are often understated.

Furthermore, averaging high and low values from different wells to obtain an arithmetic or geometric mean may give an overall site average; however, that average will not reflect groundwater flow velocity within the most conductive portions of the aquifer.

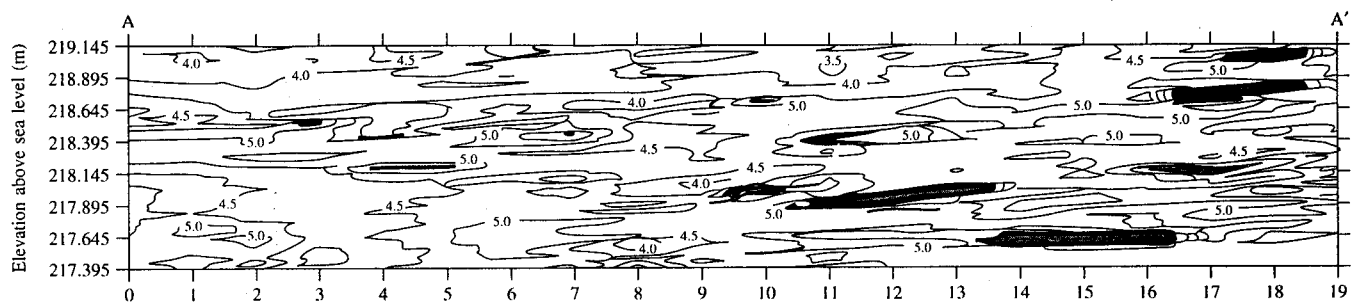


Figure 1. Distribution of the hydraulic conductivity along a cross section through a glacial drift aquifer. Hydraulic conductivity is expressed as a negative log value. (If $K = 5 \times 10^{-2}$ cm/sec, then $-\log K$ is 1.3.) Sample locations are every 5 cm vertically and every 1 m horizontally. Hydraulic conductivity was less than 10^{-3} cm/sec in the stippled zones. Source: E.A. Sudicky, *Water Resources Research* 22, No. 13 (1986). © 1986 American Geophysical Union.

When groundwater velocity is unusually high, even a small error in percentage terms could result in groundwater velocity estimate error of **tens to possibly hundreds of feet per year**. Test results are often only reproducible within an order of magnitude, thus inaccurate test results should not be unexpected. For this reason, when hydraulic conductivity values are relatively high, the importance of an accurate hydraulic conductivity estimate is much more critical to the RBCA or MNA assessment.

Because test results could be erroneous, conducting a slug/bail-down test in every well at a site may be appropriate so that a sensitivity analysis can be conducted, unless there are an exceptionally large number of wells.

Where the potential for a serious impact to a receptor exists, a slug or bail-down test may not give sufficiently accurate data for RBCA or MNA assessments. A pumping test may be warranted to derive a more accurate value for hydraulic conductivity. Although a pumping test can be quite expensive, the cost may be quite inexpensive compared to the cost of active remediation.

Another option that may be warranted at sites with significant hydrogeologic heterogeneities is to measure hydraulic conductivity at discrete depths (see Figure 2, Bjerg and others, 1992; Hinsby and others, 1992; and Wilson and others, 1997).

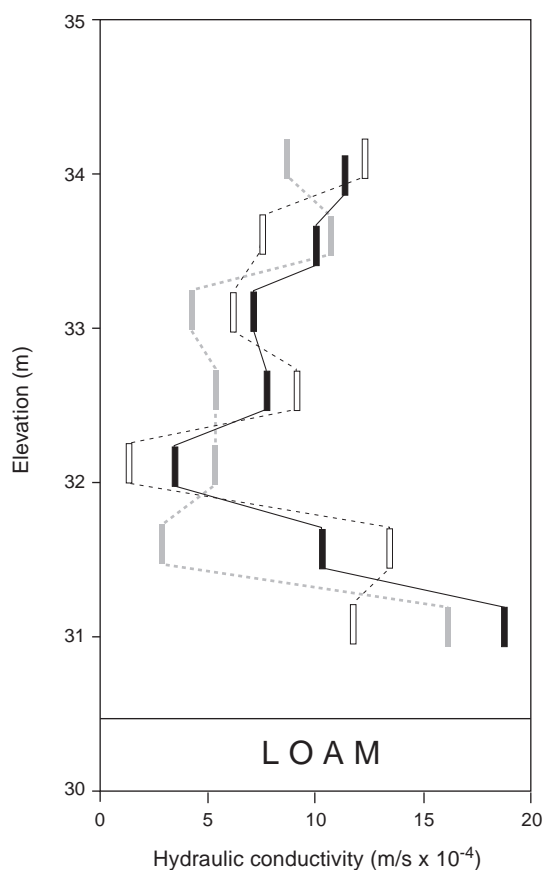


Figure 2. Vertical profiles showing the hydraulic conductivity at three adjacent locations with a horizontal distance of 0.7 m. © 1986 American Geophysical Union.

Diving plumes

Most investigators of petroleum-contaminated sites rely heavily on water table wells for characterizing groundwater conditions. For example, the Lawrence Livermore Laboratory report states that "... most sites in the LUFT database have monitoring wells completed at only one geologic horizon; most of the analytical data is 2-D" (Rice and others, 1995). Because contaminants enter the aquifer at the water table within the source area, presumably a water table well screened here will yield the highest contaminant levels for that site. Relying on water table wells further downgradient from the source area, however, could allow a plume to dive partially or completely below water table well screens and go undetected.

Recently-infiltrated water could depress a downgradient plume. Cross sections in Figures 3, 4 and 5 show regional groundwater flow from an upgradient recharge area to a downgradient groundwater discharge zone under three different hydrogeological scenarios. Figure 3 demonstrates how infiltration causes groundwater from the water table to dive at a shallow angle as it proceeds downgradient where horizontal permeability is 10 times greater than vertical permeability. A water table aquifer underlain by a layer 10 times more permeable than the upper layer causes groundwater to flow downward from the water table at a much steeper angle until the plume reaches the high permeability layer, then the plume flattens out and travels through that deeper layer (Figure 4). In a water table aquifer underlain by a more permeable layer (three orders of magnitude) where the upgradient recharge area has a strong downward gradient, groundwater flow will be directed almost straight downward, toward the high permeability layer (Figure 5).

A plume will almost always dive when a downward gradient is present. Thus investigators should evaluate sites for the likelihood of vertical gradients and significant infiltration. For example, high quality pavement can greatly restrict infiltration, whereas cracked pavement or an unpaved ground surface can promote high infiltration.

When investigators do not know if there is a deeper layer with higher permeability (see Figures 4 or 5), or if both a downward vertical gradient and high infiltration rates exist, a deeper boring may be warranted to assess hydrogeological conditions. Boring results may indicate

- discovery of a highly conductive layer; it may then be prudent to install a downgradient monitoring well screen in that layer so that contaminants, natural attenuation parameters and hydraulic conductivity can be measured
- no high permeability layers exist at depth; this provides increased confidence that a steeply diving plume does not exist and that a plume would dive at a shallow angle, if at all; a plume centerline depth can be estimated as explained further below
- existence of a relatively impervious layer below the water table aquifer; here data demonstrate that a plume is unlikely to dive to significant depths because that impervious layer limits downward flow; this helps the investigator to define a sentinel well screen's maximum depth (discussed next page)

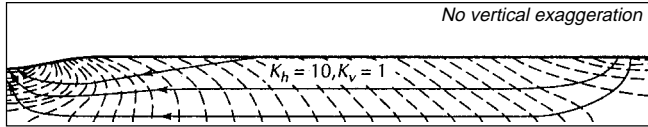


Figure 3. Flow in an anisotropic aquifer with the horizontal hydraulic conductivity ten times the vertical. Source: R.A. Freeze and P.A. Witherspoon, *Water Resources Research*, No. 3, (1967). ©1967 American Geophysical Union.

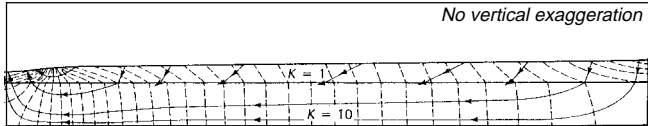


Figure 4. Regional groundwater flow in layered aquifers. The greater proportion of the flow occurs in the layer with higher hydraulic conductivity. Source: R.A. Freeze and P.A. Witherspoon, *Water Resources Research*, No. 3, (1967). ©1967 American Geophysical Union.

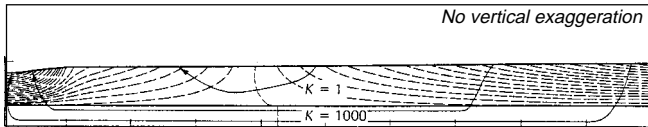


Figure 5. Aquifer confined by a flat-lying confining layer. Source: R.A. Freeze and P.A. Witherspoon, *Water Resources Research*, No. 3, (1967). ©1967 American Geophysical Union.

If investigators know that a highly conductive layer exists at a known depth, a downgradient monitoring well may be installed there without first drilling the boring.

Investigators can use several factors to estimate the depth of a plume centerline. The product of the infiltration rate and the period of time that infiltration has occurred, divided by porosity, give the expected plume centerline depth below the water table. Figure 6 shows example calculations to estimate plume centerline depth within a single hydro-geologic unit, given estimates for these parameters and estimated ground water velocity.

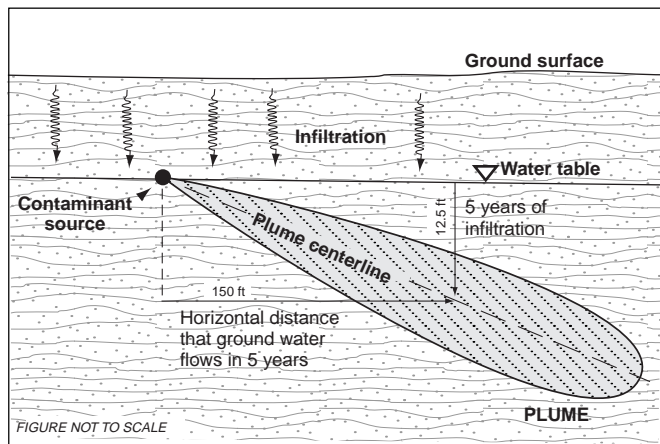


Figure 6. Shallow diving plume from a point source. The assumptions for this example are as follows: 1) Contaminants emanate from a single point source. 2) No retardation. 3) The variables used for this example are infiltration rate = 1.0 ft/yr, porosity = 40 percent, ground water average linear velocity = 30 ft/yr, and time is 5 years. Based on the above, at 5 years the plume has traveled 150 feet [30 ft/yr x 5 yrs = 150 ft] and infiltration constitutes the upper 12.5 feet of the aquifer [5 yrs x 1 ft/yr / 0.4 = 12.5 ft].

Not all sites have diving plumes, due to the following:

- if the release is very recent, there may not have been sufficient time for adequate infiltration to occur to cause the plume to dive to a significant degree; in most areas it will take several years of infiltration to depress the plume centerline below water table well screens
- sites with very high natural biodegradation rates may promote plume biodegradation before significant infiltration can occur
- sites in very dry areas have very little precipitation, thus little infiltration
- impervious ground surface seals such as pavement promote surface runoff and inhibit infiltration

Infiltration rates are difficult to measure with accuracy; thus, a qualitative assessment of the site's ground surface may be the best way to assess a plume's potential for diving. For example, a sandy ground surface that has minimal moisture-holding capacity has little runoff, evaporation and transpiration. Precipitation will generally infiltrate into the groundwater. Pavement, however, greatly reduces infiltration by channeling precipitation toward storm sewers. On the other hand, if pavement only channels runoff toward an unpaved ground surface, very high infiltration rates could occur at the pavement edges. In addition, a highly disrupted pavement surface may allow as much infiltration to occur through the cracks as an unpaved surface.

Some sites appear to have a non-diving plume in water table wells at a significant distance from the source area. In some cases, the plume may dive, but vertical dispersion allows contaminants to spread away from the plume centerline. When these dispersion effects are greater than infiltration, contaminants would be expected to be present at the water table. Figure 7 shows two examples of diving plumes, one with high vertical dispersion and one with

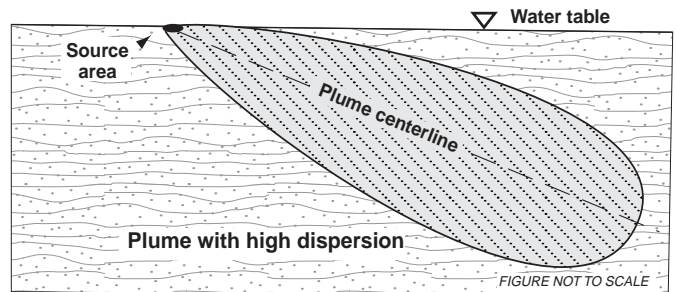
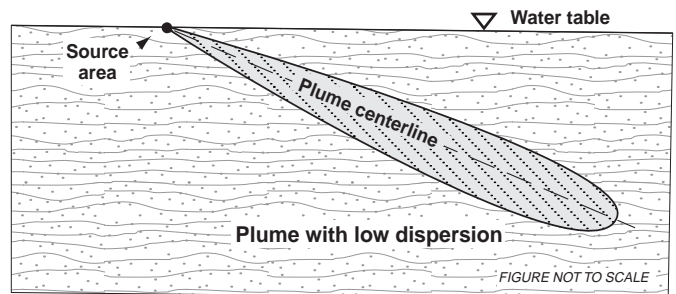


Figure 7. The effects of dispersion on diving plumes can be seen in the cross section of two plumes, one with low vertical dispersion and one with high vertical dispersion.

minimal vertical dispersion. When vertical dispersion is high enough to counteract infiltration, the plume may be detectable in water table wells, but well samples taken here would likely show lower contaminant concentrations than those within the plume centerline.

There are unusual situations where no vertical gradient exists, but a diving plume exists. When the potential for a high infiltration rate exists, but only minimal vertical gradient is measured, any plume would be likely to dive at a very shallow angle.

To identify contaminant concentrations at various depths, investigators may use direct push sampling tools, screened augers, or other methods as proposed by Robbins (1997). This data can help investigators establish the exact depth of a plume centerline for installing monitoring wells.

Water sample interpretation and sentinel well placement

A site's monitoring well samples generally provide very good information on plume location and travel direction, but as discussed above, the depth of the plume centerline may not be clearly defined. RBCA and MNA both rely on sentinel wells as early warning signals of plume migration. Because the sentinel well screen must be located at a depth to which the plume would migrate if the plume expands, sentinel well screen depth is critical; screen length, too, is critical: very short screens that provide "point" measurements are best.

Figure 8 portrays a cross section of a plume at a shallow angle with minimal vertical dispersion. There is a source area monitoring well, MW-1, and four downgradient water table wells numbered MW-2 through MW-5. Well samples suggest that the plume degrades quickly as it travels away from the source. MW-1 and MW-2 indicate high levels of contamination. The well screens for MW-3 and MW-4 are located in both contaminated and uncontaminated zones, thus samples are diluted with cleaner water from above the plume. The well screen for MW-5 does not intersect the plume; thus sample results suggest the plume does not exist here.

Figure 8 also includes a graph of contaminant concentration vs. distance for the monitoring well data and plume centerline concentrations. If decisions on sentinel well location and depth are based solely on monitoring well data, then MW-5 would be depicted as an excellent sentinel well.

Furthermore, as contaminants are flushed out of the source area, their concentrations decrease over time. Contaminant concentrations (see Figure 8 wells MW-1 through MW-4) would be expected to display a decreasing trend over time, suggesting a shrinking plume. MW-5 would continue to detect no contamination, suggesting a shrinking plume and indicating that MNA is an appropriate remedy for this site. This conclusion could be in error: in reality, no wells exist to sample contaminant concentrations at or near the plume's leading edge.

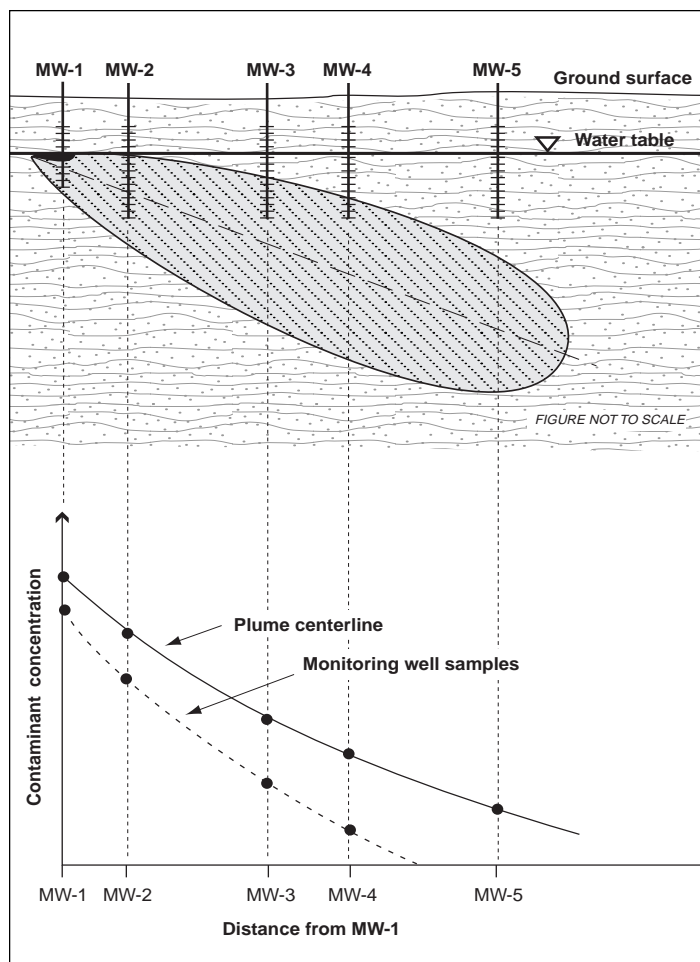


Figure 8. Cross section of a plume with conventional water table monitoring wells for sampling. Graph shows distance versus concentration for the plume centerline and for the monitoring well sample results.

Selecting the depth for a sentinel well screen may be no simple task if infiltration causes a plume to dive (see Figures 3-8). Investigators often do not know if the plume centerline is below the screen, centered within the screen interval, or above it; they know only that wells are screened within a contaminated zone. Therefore, even though wells may suggest plume location, exact location in the vertical dimension may not be known. Sentinel wells are downgradient from other wells, and estimating the proper depth to place a sentinel well screen is more uncertain.

Tools used to sample water at different, discrete depths can be used to investigate a diving plume. With this information, plume depth further downgradient can be predicted so that a sentinel well screen depth can be estimated. Because oxygen is consumed in the biodegradation reaction, almost all petroleum-contaminated sites have a plume core that is highly anaerobic. Therefore a well sample that displays characteristics of both aerobic and anaerobic zones suggests that

- the well screen is very long and/or
- the screen is not centered on the plume centerline but located well above or below the plume centerline

To determine if a sample contains a mixture of water from both aerobic and anaerobic zones, investigators may measure the following natural attenuation parameters:

- dissolved oxygen: if less than 2 mg/L, conditions are assumed to be anaerobic
- methane: a daughter product of the biodegradation reaction, if present at significant levels, represents highly anaerobic conditions

Dissolved methane and dissolved oxygen should not occur in the same water sample at significant levels because they are mutually exclusive. Therefore, if dissolved oxygen is above 2 mg/L and dissolved methane is present at several mg/L or more, investigators can conclude that the sampled water is a mixture of waters from both aerobic and anaerobic zones. Such a sample result would be expected as shown in Figure 8, well MW-3.

Natural attenuation parameters that investigators should analyze for include nitrate, dissolved iron (Fe^{+2}), sulfate and redox potential. Some investigators also analyze for pH, dissolved manganese, dissolved methane and total petroleum hydrocarbons. Investigators can measure many of these parameters in the field by using field instruments, Hach kits, and/or CHEMetrics test kits.

Dissolved methane is usually not analyzed, because few laboratories offer that analysis. Thus, the investigator may need to rely on contaminant data instead. For instance, if dissolved oxygen is present at 5 mg/L in the same water sample as moderate levels of petroleum contaminants, that suggests the water sample is a mixture of both an uncontaminated aerobic zone and an anaerobic contaminated zone. On the other hand, if a water sample contains almost no dissolved oxygen compared to background conditions, that is evidence that the sample is not diluted with "clean" aerobic water. Table 2 shows sample results from three wells at a site, an upgradient well that displays background conditions and two near-source area wells. One of the near-source area wells is nearly anaerobic; the other has elevated dissolved oxygen, suggesting that the sample is a mixture of "clean" aerobic water and contaminated water.

Dissolved methane data is superior to contaminant data because methane is produced only after other terminal electron acceptors (nitrate, iron, sulfate, etc.) are nearly exhausted. Because the zone of high dissolved methane concentration is separated from the aerobic zone by other biodegradation zones, the presence of both dissolved methane and oxygen at significant levels in the same water sample clearly shows that the well screen intersects multiple zones.

Discrete zone sampling tools may be used to determine with certainty the exact depth of the plume centerline. Assessing samples for mixtures of both aerobic and anaerobic characteristics does not establish the plume's exact depth; it only creates more uncertainty. For this reason, discrete sampling at various depths is the best way to use sample data to assess plume depth. Evaluating a sample for mixed zone characteristics, however, may be a useful test to determine when a well screen partially intersects a clean aerobic zone.

Monitoring well sample results that portray mixed and non-mixed groundwater samples

Analytical parameter	Well		
	MW-1	MW-3	MW-10
Dissolved Oxygen (mg/L)	8.97	1.15	4.53
Benzene ($\mu\text{g/L}$)	ND ¹	310	260
Ethylbenzene ($\mu\text{g/L}$)	ND	92	82
Toluene ($\mu\text{g/L}$)	ND	480	54
Xylenes ($\mu\text{g/L}$)	ND	680	280
GRO ² ($\mu\text{g/L}$)	ND	2,900	1,400

¹ Non-detect
² Gasoline-range organics

Table 2. Dissolved oxygen and petroleum-based contaminants from monitoring wells. In this example, MW-1 is upgradient from the source area and represents background conditions. MW-3 and MW-10 are both near the source area and are contaminated. Samples from MW-3 represent anaerobic conditions caused by biodegradation of petroleum contaminants that consume oxygen. MW-10 would be expected to be anaerobic, but the dissolved oxygen level indicates aerobic conditions. This suggests that petroleum-contaminated anaerobic water may be diluted with uncontaminated aerobic water within the well's screened interval.

Inability to accurately model or predict plume behavior

Proper use of RBCA and MNA relies on accurate predictions of plume concentrations and behavior over time and distance. In most cases this involves use of models. According to U.S. EPA (1997), "Demonstrating the efficacy of [MNA] likely will require analytical or numerical simulation of complex attenuation processes." Most simplistic groundwater models used for RBCA or MNA analyses are based on several assumptions, which can include these:

- Darcy's law is valid
- groundwater flow is through primary porosity, not secondary porosity
- a single isotropic geologic unit exists
- contaminant transport is through advective processes only; diffusion is commonly neglected
- infiltration does not recharge the aquifer

Complex models, often based on more complex assumptions, may allow aquifer recharge through infiltration. A model's predictions on future plume configurations must not significantly violate the model's assumptions, or results may not accurately predict potential risk. For example, utility trenches in the saturated zone that are backfilled with high permeability soils act as one-dimensional conduits for groundwater flow, which in almost all cases precludes the use of the simplistic models commonly employed for RBCA or MNA assessments. Applying these models at sites with flow through secondary porosity would also violate model assumptions.

Every model is different: no single model is best for all conditions. The evolution of inexpensive, powerful computers coupled with the development of inexpensive,

user-friendly modeling software allow models to be used with greater frequency and by more individuals. That is both an advantage and a disadvantage. These powerful tools can quickly predict how a plume will behave in the future, given site parameters. If the modelers are inexperienced, however, they may not realize that the site is more complex than the model can compensate for, or that key parameters were not estimated accurately.

One important tool used to evaluate model results is a sensitivity analysis on key parameters. According to ASTM (1995), "[A] sensitivity analysis is a quantitative method of determining the effect of parameter variation on model results. Two purposes of a sensitivity analysis are

- to quantify the uncertainty in the calibrated model caused by uncertainty in the estimates of parameters, stresses and boundary conditions
- to identify the model inputs that have the most influence on model calibration and predictions"

Every model relies on numeric inputs. When different values for a specific parameter are input into a model, model results vary. Any parameter not known with certainty should have several values input so that the model output can be assessed to determine model sensitivity to that parameter. With little effort, the modeler will then learn which parameters have little effect on model output and which parameters must be accurately known.

Parameters that most affect the model output warrant a sensitivity analysis. For example, all RBCA and MNA models require that hydraulic conductivity be input so that groundwater velocity can be calculated. Small variations in slug or bail-down test results (from different wells) suggest the presence of minor geologic heterogeneities, which is quite normal. A sensitivity analysis that inputs each measured hydraulic conductivity value will affect the model output only minimally. There are, however, sites where hydraulic conductivity varies by a wider margin. A sensitivity analysis on all hydraulic conductivity test results will yield much greater variation in model output. In this situation, the model output that provides the worst case scenario should be used to allow decisions that will ultimately provide the greatest level of public protection.

If site soils vary widely in composition, as indicated by soil boring logs, or if significant variation in site hydraulic conductivity exists, the modeler might conclude that the site does not consist of a single, uniform hydrogeological unit. The modeler should also conclude that a key model assumption has been violated, and therefore that the model may be unable to accurately predict contaminant transport. The model cannot safely predict future plume configuration for a RBCA or MNA assessment. This conclusion should be stated rather than relying on unreliable model results.

Several key parameters other than hydraulic conductivity (such as dispersion in all three dimensions), may or may not warrant a separate sensitivity analysis. Modelers should test any new model for sensitivity to all input parameters; only

then will the modeler learn which parameters must be accurately known to provide accurate model results.

Also, modelers should consider the level of uncertainty in model results. According to U.S. EPA (1997), "Where monitored natural attenuation's ability to meet ... expectations is uncertain and based predominantly on predictive analysis, decision makers should incorporate contingency measures into the remedy."

Conclusions

Over the past decade, the objective of a site characterization has changed dramatically, as follows:

- prior to promulgation of federal requirements for UST removal, many contaminated sites were discovered because those sites impacted the public; most of those early investigations focused almost entirely on determining the degree and extent of contamination with little regard to the next step in the cleanup process
- as more sites were discovered and remedial technologies developed, the objective of a site investigation evolved into determining the data necessary to design a remedy; different remedies had different data needs; thus, site investigations became more complex because (1) more data collection during the investigation phase was necessary and (2) the investigation was tailored to the most likely remedy for the site; poor investigations usually led to higher costs but usually did not impact the public because active remedies that offered safety factors were usually employed
- as the focus shifts away from site cleanup to site evaluation, data collection and interpretation for contaminant fate and transport processes are much more critical; the site characterization is now expected to gather data to evaluate risks of an unremediated plume and to determine the potential for a public impact; at many RBCA and/or MNA sites, site characterization and modeling will be the only mechanisms used to make decisions to protect public health

The environmental investigation and remediation field has evolved, and at each step, the complexity and importance of the site investigation has grown. This article has outlined a few issues that are expected to be much more important in the future than they were in the past.

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The view from U.S. EPA: MNA directive

On December 1, 1997, the U.S. EPA issued an interim final directive on the use of monitored natural attenuation (MNA) at Superfund, RCRA Corrective Action and UST sites. The directive does not substitute for EPA's statutes or regulations, nor is it a regulation itself. It does, however, provide guidance to EPA and state regulators, to the public and to the regulated community on how EPA intends to exercise its discretion in implementing national policy on the use of MNA. This directive does not provide detailed technical guidance on MNA remedies; however, such guidance documents, available from many sources, are listed at the directive's end. Following is a summary of the directive's key points (*EPA, 1997*).

Definition of MNA

MNA refers to the reliance on carefully monitored natural attenuation processes, within the context of a carefully controlled and monitored site cleanup approach, to achieve site-specific remedial objectives within a reasonable time frame. These natural attenuation processes, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in soil or groundwater. These processes include biodegradation, dispersion, dilution, sorption, volatilization, chemical or biological stabilization, transformation and destruction. Once an enhancer of any type is introduced in the process, the remedy is no longer considered "natural attenuation." **EPA prefers processes that degrade contaminants, and sites that have a low potential for plume generation and migration.**

Natural attenuation processes usually occur at all sites to varying degrees. These processes reduce the potential risk that contaminants pose by

- converting contaminants to a less toxic form through destructive processes such as biodegradation or abiotic transformation
- reducing exposure levels by lowering concentration levels, also through destructive processes, or by dilution or dispersion
- reducing contaminant mobility and bioavailability by sorption to soil or rock matrix

Other terms associated with natural attenuation, but not strictly synonymous, include intrinsic remediation, intrinsic bioremediation, passive bioremediation, natural recovery and natural assimilation.

Technology selection

EPA does not consider MNA to be a "presumptive" or "default" remedy—it is merely one option that should be evaluated with other applicable remedies. EPA advocates

using the most appropriate technology for a given site. EPA does not view MNA as a "no action" or "walk-away" approach, but rather as an alternative means of achieving remediation objectives. As with any remedial alternative, MNA should be used only where it

- meets all relevant remedy selection criteria
- will be fully protective of human health and the environment
- meets site remediation objectives within a reasonable time frame

In most cases, MNA may be appropriate as one component of the total remedy, either in conjunction with active remediation or as a follow-up measure. MNA should be used very cautiously as the sole remedy at contaminated sites.

As with other remedial methods, selection of MNA should be supported by detailed site-specific information that demonstrates its efficacy. EPA also expects evaluation of source control measures for all sites. In addition, the progress of MNA toward a site's remedial objectives should be carefully monitored and compared with expectations. Where MNA's ability to meet these expectations is uncertain and based predominantly on predictive analyses, decision makers should incorporate contingency measures into the remedy.

Concerns about petroleum contaminants

Natural attenuation processes, particularly biological degradation, are best documented at petroleum fuel spill sites. When microbial activity is sufficiently rapid, the dissolved benzene, toluene, ethyl benzene and xylene (BTEX) contaminant plume may stabilize, and contaminant concentrations may eventually decrease to levels below regulatory standards. Following degradation of a dissolved BTEX plume, a residue of heavier petroleum hydrocarbons with lower solubility and volatility will typically remain behind in the source area. Although this residual may not migrate far, it may still threaten human health/the environment by direct contact or by leaching contaminants to groundwater.

For these reasons, MNA alone is generally not sufficient to remediate even a petroleum release site.

Implementation of source control measures in conjunction with MNA is almost always necessary.

Furthermore, other chemicals that are more resistant to biological/degradation processes (e.g., methyl tertiary-butyl ether (MTBE)) may also be present in petroleum fuels.

Advantages and disadvantages of MNA

Potential advantages of MNA include

- generation of smaller volumes of remedial wastes
- reduced potential for cross-media contaminant transfer associated with ex-situ treatment and therefore reduced risk of human exposure
- less intrusive than other remedial approaches because fewer surface structures are required
- application to all/part of a site
- lower remediation costs than those associated with active remediation

Potential disadvantages include

- longer time frames to achieve remedial objectives, compared to active remediation
- potentially more complex and costly site characterization
- toxicity of transformation products potentially exceeding that of the parent compound
- long-term monitoring
- institutional controls to ensure long-term protectiveness
- possibility of contaminant migration and/or cross-media transfer
- hydrologic and geochemical conditions amenable to natural attenuation are likely to change over time and could result in renewed mobility of contaminants
- more extensive education and outreach efforts may be required for public to accept MNA

Effectiveness of MNA and site characterization

MNA is an appropriate remediation method only where its use will be protective of human health and the environment and it can achieve remedial objectives within a reasonable time frame as compared to other alternatives. Effectiveness of MNA should be demonstrated through

- sound technical analysis providing confidence in natural attenuation's ability to achieve remedial objectives
- performance monitoring
- backup or contingency remedies where appropriate

In addition, using MNA as a cleanup remedy does not imply that active remediation is infeasible or technically impracticable. The decision to use MNA for a dissolved plume should be distinct from the recognition that restoration of a plume portion may be technically impracticable; that is, MNA should not be viewed as a direct or presumptive outcome of a technically impracticable determination.

Decisions to use MNA as a remedy/remedy component should be thoroughly supported with site-specific characterization data and analysis. The level of site characterization necessary to support a comprehensive evaluation of natural attenuation is generally more detailed than that needed to support active remediation. Such site characterizations will generally require a quantitative understanding of

- source mass
- groundwater flow
- contaminant phase distribution and partitioning between soil, groundwater and soil gas
- rates of biological and non-biological transformation
- how above factors vary with time

MNA will generally not be appropriate where site complexities preclude adequate monitoring. In complex situations where it is technically feasible to monitor natural attenuation's progress, site characterization and long-term monitoring costs could be higher than costs of other remedial alternatives. **Under such circumstances, natural attenuation would not necessarily be the low-cost alternative.**

A related concern is how other remedial activities impact natural attenuation. For example, capping contaminated soil could alter the contaminant leached as well as its fate and transport.

Once the site is characterized and a conceptual model has been developed, investigators can evaluate natural attenuation's efficiency based on the following "evidence":

- historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time
- hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of active natural attenuation processes
- field or microcosm studies that can demonstrate the existence of a particular natural attenuation process, usually biological degradation, and ability of the process to degrade contaminants

More supporting information may be required at sites

- with contaminants that do not readily degrade through biological processes
- with contaminants that transform into more toxic and/or mobile forms than the parent contaminant
- where monitoring has been performed for only a relatively short time

MNA is appropriate as a remedial approach only where it is capable of achieving a site's remedial objectives within a reasonable time frame compared to other methods, and where it meets applicable remedy selection criteria. EPA expects that **MNA will be more appropriate when used in conjunction with active remediation measures (e.g. source control), or as a follow-up to previous active remedial measures. MNA should not be used where significant contaminant migration or unacceptable impacts to receptors exist.** Therefore, sites where

plumes are shrinking in size would be the most appropriate candidates for the MNA approach.

Reasonable remedial time frames

Defining a reasonable remedial time frame is a complex, site-specific decision that depends on

- classification of the affected resource (e.g., drinking water, agricultural water) and its value
- when the affected aquifer is needed as a water supply
- uncertainties regarding contaminant mass and predictive analyses
- reliability of monitoring and institutional controls over time
- public acceptance of the extended time for remediation
- provisions by the responsible party for funding of monitoring and performance evaluation; performance monitoring should continue as long as contaminants remain above required cleanup levels

Performance monitoring and contingency remedies

Performance monitoring is of even greater importance for monitored natural attenuation than for other remedies. A site's performance monitoring plan should specify location, frequency and type of samples and measurements to be taken. The plan should also

- demonstrate that natural attenuation is occurring to expectations
- identify potentially toxic transformation products resulting from biodegradation
- determine if a plume is expanding
- ensure no impact to downgradient receptors
- detect new contaminant releases that could impact MNA's effectiveness



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- demonstrate the efficacy of in-place institutional controls
- detect changes in environmental conditions (e.g. hydrogeologic, geochemical, microbiological) that may reduce efficacy of any natural attenuation process
- verify attainment of cleanup objectives

Performance monitoring should continue as long as contaminants remain above required cleanup levels. Typically, monitoring is continued for a specified period (e.g., one to three years) to ensure that contaminant concentrations remain stable and below cleanup goals.

A contingency remedy is a cleanup technology or approach that serves as a "backup" if the "selected" remedy fails to achieve cleanup goals. It may be a variation of the original remedy or a totally different remedy. The following criteria might trigger implementation of a contingency remedy:

- soil or groundwater contaminant concentrations exhibiting an increasing trend at certain locations
- near-source wells exhibiting large concentration increases, indicating a new/renewed release
- contaminants found in sentry/sentinel wells located outside of the original plume boundary, indicating renewed contaminant migration
- rates of decreasing contaminant concentration insufficient to meet remediation objectives
- changes in land and/or groundwater use that will adversely affect the protectiveness of the MNA remedy

Summary

Use of monitored natural attenuation does not signify a change in EPA's remediation objectives; MNA should be selected where it will be fully protective of human health and the environment. EPA does not view MNA to be a "no action" remedy, but rather considers it to be a means of addressing contamination under a limited set of site

circumstances where its use meets statutory and regulatory requirements. MNA is not a **presumptive or default** remediation alternative, but rather should be evaluated and compared to other viable remediation methods (including innovative technologies) during the study phases leading to the selection of a remedy. The decision to implement MNA should include a comprehensive site characterization, risk assessment (where appropriate) and source control measures. MNA should not be used where such an approach would result in significant contaminant migration or unacceptable impacts to receptors and other environmental resources. In addition, the progress of natural attenuation toward a site's remediation objectives should be carefully monitored and compared with expectations to ensure that it will meet site remediation objectives within a time frame that is reasonable compared to other methods' time frames. Where MNA's ability to meet these expectations is uncertain and based predominantly on predictive analyses, decision-makers should incorporate contingency measures into the remedy.

EPA is confident that monitored natural attenuation will be, at many sites, a reasonable and protective component of a broader remedial strategy; MNA is not, however, an appropriate remedy for ALL sites. This directive should help promote consistency in the proposition, evaluation and approval of MNA remedies.

Reference

U.S. EPA, OUST, "The Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Sites," directive 9200.4-17, 1997. For questions on the guidance, call the RCRA Hotline 800-424-9346 or 703-412-9810. To view or download a copy of the document on the Internet, see <http://www.epa.gov/swrust1/directiv/d9200417.htm>.

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