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Article summaries

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Biobarrier formed by biostimulation

Researchers have used subsurface barriers to prevent the spread of contaminant plumes. Recently, researchers wanted to test the feasibility and the ecotoxic potential (potential of harmful effects to the environment) of a biobarrier. A biobarrier is formed with microorganisms and exopolymeric matter produced in an aquifer. "The indigenous microbial population of groundwater usually contains exopolysaccharide (EPS) producers, which could be stimulated to produce such compounds by injection of nutrients and electron acceptors" *(Ross and others, 1998)*. Specifically, researchers wanted to

- determine physicochemical conditions for the formation of biofilm (in terms of mircoorganism growth, biofilm density and thickness) on a ceramic substrate in groundwater, using an indigenous microbial population at 10ºC in darkness
- assess the ecotoxic potential of the biofilm and SMPs (soluble microbial products) produced

Key to biofilm development is the transport of mircoorganisms from the bulk to the porous or fractured media (in this study, the ceramic substrate). Biobarriers have been studied in the lab as

- a bioaugmentation with either a pure culture or a microbial consortium
- a biostimulation of the indigenous population

"Bioaugmentation can be achieved by injecting starved cells in a porous media followed by nutrient stimulation, resulting in production of a plugging biofilm. This approach has been studied on small-scale models (one-dimensional glass beads or sandstone cores) and larger-scale models (three-dimensional reservoirs and natural reservoir cores) using ultramicrobacteria (UMB) found from oil-well water isolates. Results showed that when the matrix was flooded with nutrients, injected UMBs penetrated and returned to their full vegetative size and their normal level of EPS production. The permeability of the matrix was reduced by at least 99 percent within 30 days."

"*Biostimulation* for lab-scale biobarrier development is achieved by stimulating indigenous bacteria to produce EPS, which eventually will clog the pore space. Flow-through experiments were developed for continuous recirculation of natural groundwater. Results showed that gravel and sand columns were biofouled up to 95 percent in about 90 days for gravel and 21 days for sand at room temperature. Another laboratory study used aquifer material contaminated by BTEX (benzene, toluene, ethylbenzene and xylenes) to measure the production of EPS and the effect on hydraulic conductivity in the presence of different electron acceptors and carbon sources. Column studies (0.5 m x 80 mm) showed that atmospheric O_2 resulted in the largest production of EPS while the presence of H_2O_2 limited the production of EPS. Hydraulic conductivity decreased from an initial value of 0.33 to 0.023 m/day after 390 hours" *(Ross and others, 1998)*.

Physicochemical conditions influencing microbial growth and biofilm development

Specific conditions researchers studied included

- type of carbon source and feeding rate
- type of aeration system
- enrichment with calcium chloride
- PCP addition

Type of carbon source and feeding rate. Those factors had the most significant effect on biomass growth, EPS production and biofilm development. For instance, when molasses provided the carbon source, biofilms developed were 70 percent thicker than those developed in saccharose-fed reactors. The molasses

- promoted the growth of the microbial population
- conditioned the ceramic surface before cell attachment; inorganic salts and amino acids in molasses could adsorb onto ceramic by ionic interactions; divalent ions in molasses could have promoted the irreversible cell adhesion onto the ceramic
- offered more interactions between cells, EPS and the surface with hydrogen, hydrophobic and ionic bonding

Saccharose, however, was probably not as effective in conditioning the ceramic surface and promoting cell attachment.

"A high carbon source feeding rate (20 $mg/m^2/min$) resulted in the production of 78 percent more suspended biomass than at a low rate (2 $mg/m^2/min$) on the average." Other effects of a high feeding rate include

- decrease in pH
- increased production of suspended EPS

Type of aeration system. "Type of aeration system used in the reactors influenced the dissolved oxygen concentration and water turbulence. On average, air sparging resulted in a biofilm 70 percent thicker than with agitation at 200 rpm. A closer analysis of the biofilm revealed that a biofilm was visible after 24 hours with agitated water (1.5 µm) as compared to 96 hours with air sparging (1.1 µm). In addition, the suspended biomass and EPS concentrations were not significantly affected by aeration type. Results indicate that the dissolved oxygen concentration was not a limiting factor in the reactor but did limit development of the biofilm. It is well known that transport controls the rate of initial deposition on the surface. A possible explanation for the longer lag period for biofilm development with air sparging is the increase in the hydrodynamic forces. A visual observation of the system under air sparging and agitation showed a difference in the force that generated a normal force to the ceramic. The desorption of cells weakly adsorbed to the ceramic could have been greater when the water velocity increased. Similarly, the overall thicker biofilm with air sparging could be explained in part by an increase in downsweep forces. After the conditioning and the irreversible adsorption of cells on the ceramic, greater drag and lift forces would improve the mass transfer from the bulk into the biofilm, leading to a thicker film" *(Ross and other, 1998)*. Researchers suggested that an increase in water turbulence led to a thicker biofilm because of

- a preferential attachment by certain species
- a physiological response to environmental stress
- the squeezing of loosely bound water from the film by the fluid pressure force

Oxygen concentration did not limit the growth of the indigenous microorganisms; the mixed microbial population from groundwater usually contains significant facultative aerobic bacteria.

"Enrichment with calcium chloride (100mg/L) contributed to an increase in the microbial population, which suggested that the number of microorganisms in the biofilm also increased. The concentration of calcium ions in the synthetic groundwater was probably not optimum for the development of the suspended biomass. An increase in the microbial population in biofilms is associated with a densification of the biofilm rather than an increase in thickness. The biofilm mass was not measured but it would not have been surprising that it had increased with the calcium enrichment due to a higher biomass content and EPS gelation."

"*PCP addition* (10 mg/L) to stimulate groundwater contamination affected microbial growth by decreasing the population on average by 22 percent. A decrease in PCP (pentachlorophenol) concentration from 10 mg/L down to zero was also observed in some cases, which indicated the presence of PCP degraders. Biodegradation of PCP either by a microbial consortium from a PCP-contaminated soil or a biofilm developed with pure culture bacteria has been reported at high concentrations such as 500 and 366 mg/L respectively, with lab-scale experiments. The 10 mg/L PCP addition did not influence significantly either EPS production or biofilm thickness over 192 hours. No assumptions of the biofilm fixed biomass viability can be made because of the resistance mechanisms for penetration of toxic substances such as PCP. Those mechanisms include EPS binding, chemical reaction with EPS, uptake of the PCP by cells, and catalytic detoxification of PCP in the biofilm" *(Ross and others, 1998).*

Conclusions

The stimulation of an indigenous microbial population to produce EPS and biofilms was effective in groundwater conditions, at 10ºC and in darkness. The biofilm created was resistant to PCP, indicating its potential as a barrier to contaminants. The presence of PCP did induce a response, and further work suggests that any ecotoxic potential should be taken into account. Researchers found that carbon source type and feeding rate significantly influenced the speed and magnitude of biofilm development, suggesting a large contribution of ionic, hydrophobic and hydrogen bonding interactions between the solid surface, microbial cells and EPS. Other compounds formed, such as soluble microbial products (SMPs), could possibly be adverse to the ecosystem if accumulated locally. Future investigation on biobarrier development should focus on

- fractured media hydrodynamics
- accumulation and/or biodegradation of contaminants in the biobarrier
- comprehension of the ecological significance of SMPs production in the groundwater environment

References

Ross, N., Deschenes, L., Bureau, J., Clement, B., Comeau, Y. and R. Samson, "Ecotoxicological Assessment and Effects of Physicochemical Factors on Biofilm Development in Groundwater Conditions," *Environmental Science and Technology*, Vol. 32, 1998, p. 1105-1111; 202-872-4600.

For definitions of some terms used in the article, the BioTech Dictionary, http://biotech.chem.indiana.edu/pages/dictionary.html, was accessed.

For more information on contaminant barriers, see the related articles and websites:

- Field testing of a permeable reactive zone, *UTTU*, Vol. 12, No. 5, 1998
- "Modeling of plume capture by continuous, low-permeability barriers," K. Garon, D. Schultz and R. Landis, *Ground Water Monitoring and Remediation*, Summer 1988; 614-898-7791
- Federal Remediation Technologies Roundtable: http://www.frtr.gov/
- Groundwater Remediation Technologies Analysis Center: http://www.gwrtac.org/
- Oregon Graduate Institute: http://cgr.ese.ogi.edu/iron
- SECOR: http://www.secor.com/index.htm
- Remediation Technologies Development Forum: http://www.rtdf.org

Economic value of groundwater

Several governmental organizations recently evaluated approaches to assess the future economic value of groundwater as well as the economic impact of contaminating and/or depleting groundwater resources. These organizations were the Committee on Valuing Groundwater, Water Science and Technology Board, Commission on Geosciences, Environment and Resources, and the National Research Council. This article is a summary of the report, often stated verbatim *(NAP, 1997)*.

Some groundwater supplies can be considered nonrenewable because of the long timeframe required to replenish them. Depletion of groundwater (including overdrafting and mining) in deep aquifers, for instance, is essentially irreversible. Groundwater is a unique and potentially exhaustible resource vital to future generations. Without planning and protection of groundwater, this resource may not be available to support future generations.

Fundamental to valuing a groundwater resource is recognizing and quantifying the resource's total economic value (TEV). Knowing the resource's TEV is crucial for determining the net benefits of policies and management actions. In this study, groundwater services were divided into two categories: extractive services and in-situ services. Each of these has an economic value, and these values can be summed to yield TEV as follows:

TEV = extractive value + in situ value

Extractive values are derived from the municipal, industrial, commercial and agricultural groundwater demands. The in situ services include the capacity of groundwater to

- buffer against periodic shortages in surface water supplies
- prevent or minimize land subsidence from groundwater withdrawals
- protect against sea water intrusion
- protect water quality by maintaining the capacity to dilute and assimilate groundwater contaminants
- facilitate habitat and ecological diversity
- provide discharge to support recreational activities

It is not always possible to develop scientific quantitative separations of the TEV components of groundwater. Delineation of what can and cannot be quantified can be useful both to decision makers for either development or remediation projects and to researchers seeking to advance conceptual and methodological approaches. Descriptive information or surrogate quantitative measures that are not monetized may be the only information that can be assembled on some TEV components. Even a partial or inexact measurement of TEV, however, can aid decision making by providing insight into how TEV changes, based on decisions rendered concerning a water resource.

In some circumstances the TEV is likely to be largely composed of *nonuse values*. This appears to be the most likely when groundwater has a strong connection to surface water and any decision would substantially alter these service flows. Focusing on use values alone could incorrectly measure changes in TEV and would ill serve decision making. Decison makers should approach valuation with a careful regard for measurement of TEV using direct techniques that can incorporate nonuse values.

While the valuation for a given groundwater resource may be complex, several simple principles may be applied to almost any valuation problem. These principles follow.

1. Because groundwater resources are finite, decison makers should take a long-term view in all decisions regarding valuation and use, proceeding very cautiously with any actions that would lead to an irreversible situation. Groundwater depletion, for instance, is often irreversible. Some aquifers do not recharge quickly. Moreover, overdrafting can sometimes lead to a collapse of the geologic formation, permanently reducing the aquifer's storage capacity.
2. Decision makers should be cautious regarding groundwater contamination. Restoration of contaminated aquifers, even when feasible, is resource-intensive and time-consuming. Restoration methods are uncertain and unlikely to improve significantly in the near future. As a result, it is almost always less expensive to prevent groundwater contamination than to clean it up.
3. Groundwater often makes significant contributions to valuable ecological services. For example, in the Southwest, many flowing streams have been eliminated by overpumping. Because the groundwater processes that affect ecosystems and base stream flow are not well understood, combined hydrologic/ecologic research should be pursued to clarify these connections and better define the extent to which changes in groundwater quality or quantity contribute to the change in ecologic values.
4. Groundwater management entities should consider appropriate policies such as pump taxes or quotas to ensure that the cost of using the water now rather than later is accurately accounted for by competing pumpers.

   Defining the best long-term management of groundwater requires balancing the needs of the present with those of the future. In theory, the balancing is done every day by markets as reflected in the discount rate. Many citizens, policy makers and scientists believe, however, that the discount rate does not adequately consider the value of goods or services for future generations.

Discounting is a procedure that adjusts for future values of a particular good by accounting for time preferences. Higher discount rates give less weight to future net benefits, encourage present use and deter present investments. The market rate of interest will also influence individual and corporate decisions regarding resource extraction. Public entities can choose the discount rate they prefer, and much has been written about these choices. The discount rate a water utility employs when valuing groundwater reflects perceptions of risk, returns, and possibly intergenerational equity. A high discount rate implicitly places a low value on the water's value to future generations. A low rate implies the opposite.

Valuation methods

Groundwater services are difficult to value because much of the information needed for valuation is not readily available. Market trades can provide data useful in valuation, but most services provided by groundwater are not traded on markets. Techniques, however, do exist for valuing nonmarket goods.

Economic value is not a fixed, inherent attribute of a good or service, but rather depends on time, circumstances and individual preferences. The economic value of a good or service can be inferred either from someone's willingness to pay (WTP) or willingness to accept compensation (WTA) for giving it up.

Several taxonomies have been developed to categorize the types of economic values associated with natural resources, such as groundwater systems. One taxonomy distinguishes between use values, which are determined by the contribution of a resource to current or future production and consumption, and nonuse values, which typically refer to aesthetic or contemplative values arising from goods and services.

Previous groundwater valuation studies have focused primarily on a small part of the known groundwater functions and services. Thus, the current empirical knowledge of groundwater values is quite limited and concentrated in a few areas, such as extractive values related to drinking water use.

Contingent valuation methods (CVM) have the potential for producing reliable estimates of groundwater use values in certain contexts. CVM allows analysts to focus precisely on the total value of a resource attribute; other approaches generally fail to capture total economic value. For instance, few if any studies to date meet the stringent conditions, as established by a panel of Nobel-Laureate economists, that are required to produce defensible estimates of nonuse values. More research to compare use values from CVM with those of other methods is needed to determine whether CVM will consistently yield reliable estimates.

Given the problems in using CVM to measure groundwater values, the authors of this study suggest that the EPA and other appropriate government agencies should encourage ways of enhancing the utility of CVM. For example, contingent ranking or behavior methods may be useful in improving the robustness of CVM estimates and may expand the potential for transferring existing CVM estimates to other empirical settings.

If data are available and critical assumptions are met, indirect valuation methods can produce reliable estimates of the use value of groundwater. Groundwater values obtained from both indirect and direct methods are dependent on the specific groundwater management context. Attempts to generalize about or transfer values from one context to another should be pursued with caution.

Uncertainty

The decision maker attempting to value groundwater faces significant uncertainties regarding hydrologic, institutional, economic, and human health aspects of groundwater management. One source of uncertainty lies with predicting the consequences of environmental policies and actions. A related set of challenges stems from the difficulty of assessing groundwater benefits in the future and the irreversible nature of some present groundwater management decisions and impacts. Economic uncertainties regarding nonmarket goods and services are even more substantial because there is no accurate documentation of monetary value when markets are absent.

The notion of risk contrasts with uncertainty. Risk characterizes situations about which there are a known set of probabilities. By contrast, uncertainty characterizes situations in which the probabilities are incompletely known or unknown. One method of accounting for risk involves addition of “risk premiums” to the discount rate. The size of the “risk premium” varies directly with the degree of risk. Risk is extremely important in analyzing the potential costs associated with degraded water quality.

Conclusions

Authors of this study *(NAP, 1997)* offer the following conclusions:

1. To obtain valid and reliable results, the valuation methods must match the context and the groundwater function or service of interest. To generalize about the validity and reliability of a specific valuation approach in the abstract is difficult.
2. The EPA and other appropriate federal agencies should develop and test valuation methods for addressing the use and nonuse values of groundwater, especially those concerned with the ecological services provided by groundwater.
3. Technical, economical and institutional uncertainties should be considered and their potential influence delineated in groundwater valuation studies.
4. If the data are available and critical assumptions are accurate, traditional valuation methods such as cost of illness, demand analysis, and production cost can be used for many groundwater management decisions that involve use values. Such methods offer defensible estimates of what are likely to be the major benefits of groundwater services.
5. The pervasiveness and magnitude of nonuse values for groundwater are uncertain. Little reliable evidence exists concerning the importance of groundwater’s nonuse values, therefore research is needed to document occurrence and size of these nonuse values.
6. Estimates of cleanup costs of hundreds of billions of dollars raise the question of whether all contaminated groundwater can and should be remediated to the strictest criteria—pristine conditions—or to only health-based standards. This raises another question of the long-term economic and resource impacts of permitting deterioration of groundwater quality. It is necessary to consider the observed tendency of subsurface contamination to become more intractable the longer it is left in place, so that long-term contamination may be virtually irreversible.
7. The cost-of-illness approach of valuing health losses from drinking contaminated groundwater has several limitations. First, it does not consider the actual disutility of those afflicted with illnesses. Second, it overlooks that individuals contracting illnesses from contaminants might undertake defensive actions and incur expenditures to protect themselves.

8. Decision makers should be cautious about groundwater contamination: restoration of contaminated aquifers, even when feasible, is resource intensive and time consuming. Restoration methods are uncertain and unlikely to improve significantly in the near future. **As a result, it is usually less expensive to prevent groundwater contamination than to clean up the water**.

Macroeconomic vs. microeconomic issues

(Editor's note)

The study summarized above describes some of the macroeconomic issues associated with groundwater valuation. The summary, however, does not address microeconomic issues, such as the economic responsibility applying to business and other individual economic entities that could potentially affect groundwater resources. Consider a profit-making business that produces goods and/or services and provides a positive value to society: because the market value of these goods and services is known, the monetary value that the business offers to society is readily calculated in economic terms. If the business, however, depletes and/or degrades a natural resource that society values (such as a groundwater aquifer), the reduction in the value of that resource is considered a *negative externality*. When taxes or use fees are imposed on the business to reimburse society for the resource's lost value, the *negative externality is internalized* and becomes a cost of doing business.

When negative externalities are not internalized, a business could produce goods/services that have a positive value to the society, a positive value that could be masked by the negative economic impacts to society's natural resources. In such a case, society would benefit economically if that business did not exist. In addition, the use of insurance to pay for costs of a business' catastrophic event, such as a contaminant release to an aquifer, should be considered.

Reference

National Academy Press, *Valuing Ground Water: Economic Concepts and Approaches,* 1997, 2101 Constitution Avenue N.W., Washington D.C. 20418; 1-800-824-6242; http://www.nap.edu.

For a related article, see "Ethics and Hydrogeology" by R.C. Heath in *Ground Water*, Vol. 36, No. 6, November-December 1998; jross@ngwa.org. There was a discussion of this article by the Groundwater Discussion Group, http://groundwater.com; Vol. 1092, Ethics.

Sensitivity analysis of parameters used for predicting hydrocarbon plume biodegradation

McNab and Dooher *(1998a)* recently developed a screening model to quantify the parameters that affect hydrocarbon plume biodegradation. Their approach used a Monte Carlo simulation and an analytical solution to the advective-dispersive solute transport equation. The equation also included a first-order degradation term. This model was coupled with mass balance constraints on electron acceptor use (e.g., geochemical data). Researchers then applied this model to an existing LUFT (leaking underground fuel tank) site. Comparisons were made between actual measured parameters and model predictions.

Transport models

Remediators often use transport models to assess the risk to potential downgradient receptors and to predict plume behavior and cleanup time. But even in simple models, uncertainty in parameters such as groundwater velocity, contaminant degradation rate, dispersivities and source characteristics can create cumulative uncertainties in the projected plume behavior. Because models are calibrated to existing or historical contaminant concentration data, they generate parameter uncertainty, which results in nonunique solutions. Statistical analysis of the data, however, can help to better define parameter uncertainty.

The transport model McNab and Dooher used applies to "solute transport in a homogenous infinite aquifer of constant thickness with a uniform fluid flow field assuming an instantaneous point source." As such, the model

- is a highly idealized conceptualization of solute transport
- is uniform first-order kinetic
- neglects the influences of microbial growth on substrate use rates
- does not account for variability in degradation rates associated with different biogeochemical redox regimes

The analytical solution, which accounts for retardation and a continuous source release, is as follows:

$$\mathbf{c}\,(\mathbf{x},\mathbf{y},\mathbf{z}) = \int_{\tau=0}^{\tau=t} \frac{\mathbf{dM}}{4\pi\phi\tau\mathbf{H}\sqrt{\mathbf{D}_l\,\mathbf{D}_t}} \exp\left[-\frac{\left(\mathbf{x}-\frac{\mathbf{v}}{\mathbf{R}}\tau\right)^2}{4\frac{\mathbf{D}_l}{\mathbf{R}}\tau} - \frac{\mathbf{y}^2}{4\frac{\mathbf{D}_t}{\mathbf{R}}\tau} - \lambda\tau\right] d\tau$$

c is concentration

where

dM is the mass introduced into the system per unit time

f is porosity

H is aquifer thickness

$\mathbf{D_1}$ and $\mathbf{D_t}$ are the longitudinal and transverse dispersion coefficients, respectively

v is groundwater velocity

R is the retardation coefficient

d is the first-order decay coefficient

x and **y** are the distances between the source location and the monitoring point in the longitudinal and transverse directions, respectively

τ is the elapsed time between source introduction and sampling

Geochemical aspects with respect to the transport model

Biodegrading hydrocarbons often change the local inorganic geochemistry through oxidation-reduction reactions, which are mediated by microorganisms. For example, electron acceptors such as oxygen, nitrate or sulfate may be locally depleted where hydrocarbons are oxidizing whereas chemically reduced species (e.g., sulfide, methane) or mineralization products (i.e., carbon dioxide) may accumulate. These reaction rates can provide constraints on relationships between model parameters such as degradation rates and source mass.

Using the transport equation above, McNab and Dooher (1998) calculated the quantity of hydrocarbon biodegraded, or change in hydrocarbon contamination. With toluene, C_7H_8, as a surrogate for all hydrocarbons present, the oxidation of Δc (change in concentration) must be balanced by the reduction of one or more electron acceptors: oxygen, manganese oxides, iron oxides, nitrate, or sulfates. These reactions (reduction of toluene) are listed in decreasing thermodynamic favorability:

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$$

$$C_7H_8 + 18MnO_2 + 36H^+ \rightarrow 7CO_2 + 18Mn_2^+ + 22H_2O$$

$$5C_7H_8 + 36NO_3^- + 36H^+ \rightarrow 35CO_2 + 18N_2 + 38H_2$$

$$C_7H_8 + 36Fe(OH)_3 + 72H^+ \rightarrow 7CO_2 + 36\,Fe^{2+} + 94H_2O$$

$$2C_7H_8 + 9SO_4^{2-} + 18H^+ \rightarrow 14CO_2 + 9H_2S + 8H_2O$$

$$2C_7H_8 + 10H_2O \rightarrow 14\,CO_2 + 9CH$$

“For iron and manganese, the electron acceptor species consists of solid phase mineral oxides. For modeling purposes, these may be represented as fictitious aqueous species based on observed concentrations of Fe^{2+} and Mn^{2+} within the hydrocarbon plume. Methane concentrations (CH_4) may be predicted using the last geochemical equation. Assuming that most of the carbon dioxide produced in the hydrocarbon mineralization reactions is converted to bicarbonate (HCO_2^-) under near-neutral pH conditions, location changes in carbon dioxide (bicarbonate) can be estimated using the geochemical equations.” This analysis has limitiations because it does not account for

- fraction of hydrocarbon that is converted into cell biomass
- significant retardation of hydrocarbons resulting from adsorption

Probabilistic modeling

Probabilistic modeling uses probability distributions of physical and chemical parameters, which represent the uncertainty in the data. Monte Carlo simulations are then run to produce predictions or forecasts. In the McNab and Dooher *(1998)* study, “each Monte Carlo simulation consisted of executing 1000 realizations with the prescribed parameter space at each monitoring well location and then tallying the forecast concentrations.” McNab and Dooher then compared the predicted with the measured concentration of each constituent.

Example at Fairfield, California

The Fairfield site at Travis Air Force Base has two gasoline stations with unknown quantities of releases between 1960 and the late 1980s. The site is characterized by

- unconsolidated Holocene and Pleistocene alluvial clays, silts, sands and gravels
- groundwater at 4 to 5 meters below surface under semiconfined conditions
- south-southeast groundwater flow direction at 10 to 15 m/yr

Monitoring well data indicate a dissolved BTEX plume extending about 100 meters downgradient of the gas station. Table 1 shows the differences in indicator concentrations between the plume interior and background, suggesting that sulfate reduction is an important biodegradation site mechanism; sulfate reduction accounts for more than 95 percent of the inferred electron acceptor use.

Indicator	Background (mg/L)	Plume interior (mg/L)
O_2	0.5	0.2
Fe(II)	0.03	2.8
Mn^{2+}	0.1	2.8
NO_3^-	4.9	0.95
SO_4^{2-}	876.	530.
CH_4	0.0045	0.16
HCO_3^-	393.	746.

Table 1. Median geochemical indicator concentrations in background wells (BTEX not detected) and plume interior wells (BTEX above detection limit) from McNab and Dooher, 1998a.

McNab and Dooher used predominantly measured site parameters (such as hydraulic conductivity, effective porosity, soil organic carbon) to model the BTEX plume. They then compared two modeled plumes with a plume generated from monitoring data obtained from August-September 1995. They found that “a general qualitative correlation exists between the field data and the simulated distributions for both realizations” for the sulfate and bicarbonate distributions. Similar correlations exist between other geochemical indicators. In their paper McNab and Dooher *(1998a)* give a more detailed discussion on the transport model parameter assumptions and statistical analysis procedures.

Sensitivity analyses

Investigators used rank correlation to determine parameter sensitivity. Rank correlation can address strongly nonlinear data trends and suppress the effects of outliers. "Rank correlation involves assigning ranks to both the dependent variable (the forecast or predicted) and the independent variable (the parameter) and performing a linear regression on the corresponding rank sets. The resulting correlation coefficients are then tallied for each forecast and normalized. This yields the relative contribution to variance of each parameter (e.g., hydraulic conductivity, source location, background concentration) to each forecast (concentrations of total BTEX and geochemical indicators at each well)."

Predicting BTEX and geochemical (sulfate and bicarbonate) parameters

For the Fairfield, California site, McNab and Dooher graphed parameter sensitivities for predicted (forecast) BTEX concentrations as a function of distance from the source area. Factors that predict BTEX concentration in the source area include

- degradation rate
- source location
- hydraulic conductivity

Further downgradient, BTEX predictions

- depend on groundwater velocity (as indicated by conductivity and gradient)
- are not as dependent on degradation rate as near the source area

For the geochemical indicators, the pattern of parameter sensitivity is more complex than for BTEX. With sulfate predictions, for instance:

- background concentration dominates concentration predictions both near the source area and far downgradient
- this pattern reflects a high variability and high concentrations of sulfate

For bicarbonate predictions, near the source area, concentrations are affected by

- groundwater velocity parameters
- source location
- bicarbonate concentration

This pattern indicates hydrocarbon mineralization in the source area. Downgradient, background concentrations of bicarbonate dominate any predictions of concentration.

Other findings include these:

- methane levels in the source are affected by the background sulfate concentration; sulfate must be used up before methanogenesis can occur
- predicted oxygen levels far downgradient of the plume are dominated by groundwater velocity, as are concentrations of nitrate, iron and manganese
- in this plume, because of the relatively low concentrations of nitrate, iron and manganese, it is likely these electron acceptors were used up entirely in the source area; thus, changes in concentration downgradient largely reflect "the migration rate of the anaerobic shadow emerging from the BTEX plume"
- geochemical indicators **do not** appear to be sensitive to BTEX degradation rate
- in the source area, background concentrations dominate predicted concentration
- downgradient, predicted concentrations are most affected by groundwater velocity, which determines how far geochemical indicators migrate

Approach applicability

Factors that may contribute to differences between predicted concentrations and field data include the following:

- physical heterogeneities in the flow field not adequately addressed by the transport model
- transport in the third dimension (including dilution effects associated with long well screens)
- complex source release history
- significant retardation effects
- spatially variable biodegradation rates
- use of BTEX concentrations (toluene as a surrogate) as a mass balance constraint on geochemical indicator concentrations
- lack of accounting for the non-BTEX components in gasoline that will also biodegrade and influence the local geochemistry

Potential for misinterpretation of degradation rates

In a related study McNab and Dooher *(1998b)* examined the 1995 Buscheck and Alcantar method for estimating contaminated biotransformation rates from source to risk receptor. The formula, given by McNab and Dooher, is an idealization that required, at its inception, further work to refine the formula. Difficulty arises "when dispersive processes (macroscale mechanical mixing and molecular diffusion) produce concentration distributions that, ideally, decline with distance from a continuous source as determined by an error function term (even in the absence of any solute degradation). In many instances, particularly when analyzing only a small number of data points (i.e., monitoring wells) **it is often possible to fit a straight line through log concentration vs. distance data with a high degree of correlation even when this transformation is insignificant or absent altogether**. Therefore, it is possible to derive estimated biotransformation rates that are entirely spurious."

Observed concentration profiles may vary from those predicted by models because of the following factors:

- steady-state conditions are assumed
- source strength fluctuates with time
- solutes disperse by non-Fickian means
- flow and transport is strongly heterogeneous
- wells are often placed off the plume centerline
- dilution effects occur due to screen length
- degradation and distribution rates are non-uniform

Thus, in-situ biotransformation rates may give misleading results if data is not applied in a “judicious manner.” Furthermore, “Monte Carlo analyses using simulated plumes suggest that this method may lead to significant overestimation of apparent transformation rates. Potential erroneous or even spurious transformation rates may arise because of the effects of dispersion in stable plumes as well as in plumes in the early stages of development before steady state is reached. In particular, the methods may yield incorrect results when only a small number of wells are used.”

References

McNab, W.W. Jr. and B.P Dooher, “Uncertainty Analyses of Fuel Hydrocarbon Biodegradation Signatures in Ground Water by Probabilistic Modeling,” *Ground Water*, 1998a, Vol. 36, No. 4, 1998; 800-332-2104; cgrubb@ngwa.org

McNab, W.W. Jr., and B.P Dooher, “A Critique of Steady-State Analytical Methods for Estimating Contaminant Degradation Rates,” preprint from *Ground Water*, 1998b; 800-332-2104; cgrubb@ngwa.org

UTTU thanks Brendan Dooher, Lawrence Livermore National Laboratory, for his help on the article.

Inspector’s guide for impressed current CP systems: checklist, part 3

This is a continuation of the articles that appeared in the July/August and September/October 1998 issues of *UTTU*. The topic covers components and materials brought to the site for installing impressed cathodic protection systems.

1. Was the required number of anode junction boxes delivered to the job site?

   ☐ Yes ☐ No Number of terminals _____________

2. Did the anode junction boxes have the required number of terminals?

   ☐ Yes ☐ No Number of terminals _____________

3. Were the specified shunts installed in the anode junction boxes?

   ☐ Yes ☐ No

4. Did the shunts delivered have the specified resistance(s) and was the actual resistance of each shunt within +/- 1% of that specified?

   ☐ Yes ☐ No

5. Was the required number of test stations delivered to the job site?

   ☐ Yes ☐ No

6. Did test stations have the required number of terminals?

   ☐ Yes ☐ No Number of terminals _____________

7. Were the test stations delivered the type required?

   ☐ Yes ☐ No Type(s) of test station ____________

8. Was the insulated cable for the test-station connections specified to be color-coded?

   ☐ Yes ☐ No

9. Were sufficient lengths of the color-coded, insulated conductors for the test-station connections delivered?

   ☐ Yes ☐ No

10. Copper-conductor size ___________________________

    Insulation thickness ______________________________

    Insulation type on cables _________________________

11. Did the conductor size, insulation thickness, and insulation type for the cables to the test-station connections satisfy requirements?

    ☐ Yes ☐ No

12. If the copper conductors for the test stations were to be exothermically welded to the structure, how were the conductors attached?

    ☐ Exothermically welded

    ☐ Welded

    ☐ Brazed

    ☐ Other _____________________________________

13. If the copper conductors for the test stations were to be exothermically welded to the structure, what was the mold-part number and the weld-metal-part number used?

    Mold-part number ________________________________

    Weld-metal-part number ___________________________

14. Were these parts in accordance with the manufacturer’s recommendations?

15. How was the copper conductor on the cable to the direct current power source connected?

    ☐ Exothermically welded

    ☐ Welded

    ☐ Brazed

    ☐ Other _____________________________________

16. If the copper conductor on the cable to the direct current power source was to be exothermically welded to the cathodically protected structure, what was the mold-part number and weld-metal-part number

    Mold-part number ______________________________

    Weld-metal-part number __________________________

17. Were the weld-metal-part number and the mold-part number in accordance with the manufacturer's recommendations?

    ☐ Yes ☐ No

18. Were the reference electrodes permanently installed?

    ☐ Yes ☐ No

19. Was the required number of these delivered to the job site, and did each have a potential within +/- 7 millivolts of a calibrated reference electrode of the same type?

    ☐ Yes ☐ No

20. What products were delivered to the job site for repairing coating damage on the structure(s) in the vicinity of the copper conductors attached?

    Coating products ______________________________

21. Were the coating damage repair products in accordance with specifications?

    ☐ Yes ☐ No

22. Were weld caps (i.e. backfill shields) required by the specifications attached to the structure(s) near the copper conductors?

    ☐ Yes ☐ No

23. Was a sufficient number of weld caps of the required type delivered to the job site?

    ☐ Yes ☐ No

24. If the anodes were to be installed in a deep-anode bed, was a sufficient number of the specified anode-centering devices delivered to the job site?

    ☐ Yes ☐ No

25. Were the anode-centering devices fabricated using a metallic material?

    ☐ Yes ☐ No

26. If the installation involved a deep-anode bed, was a sufficient length of the specified-diameter, properly perforated (i.e., perforated by drilling and not by punching the holes), non-metallic, vent tube delivered to the job site?

    ☐ Yes ☐ No

27. If the carbonaceous backfill was to be placed around the anodes during their installation (i.e., if the anodes were not prepackaged), was an adequate quantity of the specified backfill delivered to the job site?

    ☐ Yes ☐ No

28. Was the specified direct current power source delivered to the job site?

    ☐ Yes ☐ No

29. If the direct current power source delivered to the job site was a rectifier, who was the manufacturer and what was the manufacturer's model number?

    Manufacturer ________________________________

    Model number ________________________________

30. Did the model satisfy specifications?

    ☐ Yes ☐ No

31. Was there any evidence of damage to the direct current power source/rectifier delivered to the job site?

    ☐ Yes ☐ No

32. If the rectifier was an oil-immersed type, was an adequate quantity of the proper oil (e.g. NEMA Grade 100) available for filling the unit?

    ☐ Yes ☐ No

33. Was the direct current power source/rectifier altered or modified at the job site during installation?

    ☐ Yes ☐ No

34. Was adequate equipment available at the job site to successfully install the cathodic protection system? Was equipment available for augering/drilling holes for the anodes, preparing trenches for the insulated cables, bending galvanized-steel conduits, and (for deep anode beds) mixing and pumping the carbonaceous backfill?

    ☐ Yes ☐ No

Reference

Myers, J., "Acceptable Criteria for Impressed-Current-Type Cathodic Protection Systems: An Inspector's Guide/ Checklist for Components and Their Installation," 1996, J. Myers, 4198 Merlyn Drive, Franklin, Ohio 45005.

UTTU thanks Dr. Myers for sending us this article.

Information sources

Aquifer Hydraulics: A Comprehensive Guide to Hydrogeologic Data Analysis, 1998, is available from John Wiley & Sons for $95; call 800-CALL WILEY or see the website, http://www.wiley.com.

Field Applications of In-Situ Remediation Technologies: Chemical Oxidation (EPA 542-R-98-008) can be viewed or downloaded at http://clu-in.org/techpubs.htm; for hard copies call 800-490-9198, or 513-489-8190.

Geostatistics for Environmental and Geotechnical Applications, papers from an ASTM standards development group, is available from Dave Becker, U.S. Army Corps of Engineers, 12565 W. Center Road, Omaha, Nebraska 68144-3869.

Quality Assurance Guidance for Conducting Brownfields Site Assessments (EPA 540-R-98-038), viewed or downloaded at http://clu-in.org/techpubs.htm; for hard copies call 800-490-9198 or 513-489-8190.

Site Investigation, Remediation, and Closure: A Simplified Guide for Environmental and Real Estate Professionals is available from Government Institutes, 4 Research Place, Suite 200, Rockville, Maryland 20850; phone 301-921-2323 or fax 301-921-0373.

These hard-copy reports are available from diana.krop @em.doe.gov, and to be posted at http://em-50.doe.gov:

- *Innovative Technology Summary Report: Innovative Grouting and Retrieval* (DOE/EM-0380)
- *Innovative Technology Summary Report: Horizontal Wells* (DOE/EM-0378)
- *Innovative Technology Summary Report: Surface Acoustic Wave/Gas Chromatography Systems for Trace Vapor Analysis* (DOE/EM-0367)

Technical papers available from American Petroleum Institute (202-682-8375; http://www.api.org) include:

- *A Compilation of Field-Collected Cost and Treatment Effectiveness Data for the Removal of Dissolved Gasoline Components from Groundwater* (#4525)
- *Alcohol, Ethers and Gasoline-Alcohol and Ether Blends* (#1642)
- *Anecdotal Health-Related Complaint Data Pertaining to Possible Exposures to Methyl Tertiary Butyl Ether (MTBE): 1993 and 1994 Follow-up Surveys* (#4623)
- *A Study to Characterize Air Concentrations of Methyl Tertiary Butyl Ether (MTBE) at Service Stations in the Northeast* (#4619)
- *Chemical Fate and Impact of Oxygenates in Groundwater: Solubility of BTEX from Gasoline-Oxygenate Mixtures* (#4531)
- *Chinese Hamster Ovary (CHO.HGPRT) Mutation Assay of Tertiary Amyl Methyl Ether (TAME)* (TR 411)
- *Chromosome Aberrations in Chinese Hamster Ovary (CHO) Cells Exposed to Tertiary Amyl Methyl Ether (TAME)* (TR410)
- *Closed-Patch Repeated Insult Dermal Sensitization Study of TAME in Guinea Pigs* (TR 403)
- *Cost-Effective, Alternative Treatment Technologies for Reducing the Concentrations of Ethers and Alcohols in Groundwater* (#4497)
- *Delineation and Characterization of the Borden MTBE Plume* (#4668)
- *Effects of Fuel RVP and Fuel Blends on Emissions at Non-FTP Temperatures, Vols. 1 & 2* (#4533 and 4534)

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- *Effects of Oxygenated Fuels and Reformulated Diesel Fuels on Elastomers and Polymers in Pipeline/Terminal Components* (#1132)
- *Evaluation of Fuel Tank Flammability of Low RVP Gasolines* (#4646)
- *Field Evaluation of Biological and Non-biological Treatment Technologies to Remove MTBE/Oxygenates from Petroleum Product Terminal Wastewaters* (#4655)
- *Gasoline Vapor Exposure Assessment at Service Stations* (#4553)
- *Laboratory Evaluation of Candidate Liners for Secondary Containment of Petroleum Products* (#328)
- *Odor Threshold Studies Performed with Gasoline and Gasoline Combined with MTBE, ETBE and TAME* (#4592)
- *Petroleum Industry Data Characterizing Occupational Exposures to Methyl Tertiary Butyl Ether (MTBE): 1983-1993* (#4622)
- *Service Station Personnel Exposures to Oxygenated Fuel Components* (#4625)
- *Storage and Handling of Gasoline-Methanol/Cosolvent Blends at Distribution Terminals and Service Stations* (#1627)
- *Toxicity to Freshwater Alga, Selenastrum Capriccornuttum* (TR 402)
- *Transport and Fate of Dissolved Methanol, MTBE and Monoaromatic Hydrocarbons in a Shallow Sand Aquifer* (#4601)

The U.S.G.S. has published 20 circulars concerning water quality in 20 large river basins and aquifers in the United States. The circulars are free and can be obtained from the U.S.G.S. Branch of Information Services, Box 25286, Federal Center, Denver, Colorado 80225; phone 703-648-5716 or fax 303-202-4693.

Websites

American Standards Testing and Materials: to order documents, e-mail gzajdel@astm.org

ChemFinder: http://chemfinder.camsoft

Enviromine website and discussion group: http://www.enviromine.com

Ground penetrating radar site (being built) http://www.g-p-r.com

Hazardous Waste Clean-Up Information (CLU-IN) http://clu-in.org.

LowFlow/MicroPurge references and links: http://members.aol.com/telecorder/qed.html

National Climate Data Center: http://www.ncdc.noaa.gov/onlineprod/tfsod/climvis/main.html

Natural Attenuation Tool Kit: http://members.aol.com/jacrosby1/home.htm

Reaction walls: http://www.rmtinc.com

SoilVision Systems Ltd.: http://www.soilvision.com

U.S. EPA Robert S. Kerr Environmental Research Center, Center for Subsurface Modeling Support, groundwater and vadose zone models/manuals: http://www.epa.gov/ada/kerrlab.html

U.S. environmental and health and safety regulations: http://www.rcpinc.com

U.S.G.S. water resources information: http://h2o.er.usgs.gov

Many of these sites and other information came from the Groundwater Mailing List (http://groundwater.com), the Bioremediation Discussion Group (http://biogroup.gzea.com), TechDirect (http://clu-in.com/techdrct.htm) and The Newsletter of the Association of Groundwater Scientists & Engineers (mcdolb@ngwa.org).

UTTU thanks the moderators from these groups—Ken Bannister of Groundwater, Richard Schaffner of Biogroup and Jeff Heimerman from U.S. EPA's TechDirect and Michelle Crow-Dolby from National Ground Water Association.

Underground Tank Technology Update

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