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Definition, objectives, and evaluation of natural attenuation

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Abstract

Natural attenuation offers large benefits to owners and managers of contaminated sites, but often raises strong objections from those who live and work near a site and are asked to assume most of the long-term risks. Part of the controversy comes about because published definitions of natural attenuation do not identify a realistic end-point objective, and they also are ambiguous about the naturally occurring processes that can achieve the objective. According to guidance from the U.S. National Research Council (NRC 2000), destruction and strong immobilization are the naturally occurring processes that achieve a realistic objective: containing the contaminant relatively nears its source, thereby minimizing exposure risks. The strategy for obtaining solid evidence that the objective is being achieved requires measurements that establish a cause-and-effect relationship between contaminant loss and a destruction or strong-immobilization reaction. The cause-and-effect relationship is best documented with reaction footprints, which typically are concentration changes in reactants or products of the destruction or immobilization reaction. MTBE presents a contemporary example in which footprint evidence for biodegradation is especially crucial, since aerobic biodegradation of MTBE requires special conditions not present at all sites: a high availability of dissolved oxygen and bacteria expressing particular oxygenase enzymes.

Introduction

Classified as a remedy for the cleanup of sites contaminated with hazardous materials (USEPA 1999), natural attenuation is quite an unusual remedy. Its unique status comes about because natural attenuation relies only on un-enhanced natural processes. In other words, engineering measures – such as excavation, biostimulation, and pumping water and gas – are not part of natural attenuation. Instead of imposing conditions that remove or destroy the contaminant, natural attenuation requires proof that natural processes protect humans and other sensitive receptors from exposure to the hazardous contaminants (NRC 2000; MacDonald 2000; Rittmann & MacDonald 2000).

The potential benefits of natural attenuation are obvious. Engineered remedies usually are very expensive, and many last for years, despite severe engineering efforts (NRC 1994). In some cases, engineered remedies are disruptive to the landscape and those who live near the contaminated site. Thus, natural attenuation often reduces the costs of cleanup substantially, and it can keep life in the local community close to 'normal'.

Natural attenuation also is viewed with skepticism – even outright opposition – by some community activists and environmentalists (NRC 2000; MacDonald 2000; Rittmann & MacDonald 2000). These skeptics see natural attenuation as a 'do nothing' strategy that allows site owners and regulators to 'walk away' from a site, transferring all the risk to those who live and work nearby. Often, those directly affected by contamination want to see 'something' done actively and completed quickly.

The tension between those who value the benefits of natural attenuation versus those who fear its risks has made natural attenuation a controversial issue since the mid-1990s, when its use increased dramatically in the USA (NRC 2000; MacDonald 2000).

Adding to the controversy are two factors that have been less than clearly addressed over the years.

1. *The proper definition and objectives of natural attenuation*. What naturally occurring processes can be relied upon to protect humans and the environment? And, how do those processes eliminate significant exposures?
2. *The proper means to evaluate natural attenuation to ensure that it prevents exposures now and will continue to do so for as long as necessary*. What needs to be measured? How are the data to be interpreted? How long must monitoring continue?

In this introduction to the special issue on natural attenuation, I focus on these two factors, which provide context for understanding the more specific papers that follow. My presentation is based firmly on the 2000 report from the US National Research Council, Natural Attenuation for Groundwater Remediation (NRC 2000), which was prepared by a committee I chaired. The NRC study that produced Natural Attenuation for Groundwater Remediation was sponsored by 10 USA government and private agencies that realized that the science, technology, and policy of natural attenuation were not well elaborated, even though natural attenuation was being proposed and often approved at a rapidly increasing rate in the United States. NRC (2000) provided a state-of-the-art review of the science underlying natural attenuation and offered specific guidance on what are realistic objectives for natural attenuation. Furthermore, NRC (2000) provided a strategy for evaluating whether or not those objectives are being met in the field. The main messages of NRC (2000) have been reviewed in shorter articles, most notably MacDonald (2000), Rittmann & MacDonald (2000), and Bekins et al. (2001).

Here, I first address the definition and objectives of natural attenuation, which are intimately connected. Then, I review the approach needed to evaluate natural attenuation in light of its objectives. Finally, I present a contemporary example. In all cases, I base my message on NRC (2000), but I also extend that work beyond what the NRC report was able to include.

Definition and objectives

The definition of natural attenuation depends on the objectives that it can achieve. Different groups have provided a range of definitions for natural attenuation, and those definitions imply different objectives. Table 1 lists, in chronological order, five definitions used in the USA.

The five definitions show an evolution of end-point objectives for natural attenuation. Although the earliest definition (Wiedemeier et al. 1995) states no end-point objective, the later definitions become more specific: ‘contamination is reduced over time’ (US Army Science Board 1995), ‘reduction of mass or concentration over time’ (ASTM 1997), ‘achieve site-specific remediation objectives’ (USEPA 1999), and ‘protect human and environmental receptors from unacceptable exposures’ (Rittmann & MacDonald 2000, based on NRC 2000). The last definition recognizes that natural attenuation is, at its core, a containment strategy in which contaminants that are released from a source area are destroyed or immobilized within a relatively short distance from the source, thereby preventing exposures to human or sensitive environmental receptors.

Closely correlated to the definition of natural attenuation is the time frame in which it must work. The definition for the USEPA (1999) suggests a time-frame that is relatively short, commensurate with what might be achieved by an engineered remedy. On the other hand, the last definition (Rittmann & MacDonald 2000) implies a potentially longer time horizon when it states that the natural processes must ‘prevent harmful exposure for as long as the contaminant source exists’. The long-term view is the more realistic one in most cases, because sources often release contaminants for a long time that cannot be easily predicted. Examples of long-term sources include landfills, deposits of tars, residuals of hydrophobic solvents and fuels, and mine tailings (NRC 2000). To be consistent with natural attenuation being a containment strategy for long-term sources, its definition should underscore that it prevents exposures during the life of the source, but does not necessarily cleanup the source quickly.

Along with an end-point objective, the other essential feature of the definition is identifying the relevant processes that make natural attenuation work. The last definition in Table 1 differs importantly from the earlier definitions in this regard. The four earlier definitions list many naturally occurring processes that may act at a field site: e.g., ‘biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants’ (USEPA 1999). On the other hand, the latest definition distinguishes biodegradation and very strong immobilization as processes that render the contaminants harmless. Biodegradation

Table 1. Five definitions of natural attenuation in the USA

Agency (Source)	Definition
US Air Force (Wiedemeier et al. 1995)	A process resulting "from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Biodegradation is the most important destructive attenuation mechanisms. Nondestructive attenuation mechanisms include sorption, dispersion, dilution from recharge, and volatilization."
US Army (US Army Science Board 1995)	"The process by which contamination in groundwater, soils, and surface water is reduced over time … (via) natural processes such as advection, dispersion, diffusion, volatilization, abiotic and biotic transformation, sorption/desorption, ion exchange, complexation, and plant and animal uptake."
American Society for Testing and Materials (ASTM 1997)	"Reduction in mass or concentration of a compound in groundwater over time or distance from the source of constituents of concern due to naturally occurring physical, chemical, and biological processes, such as biodegradation, dispersion, dilution, adsorption, and volatilization."
Environmental Protection Agency (USEPA 1999)	"Reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by more active methods. The natural attenuation processes that are at work in such a remediation approach include a variety of physical, chemical, and biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These *in situ* processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants."
National Research Council, as summarized by Rittmann & MacDonald (2000)	"Natural attenuation relies on un-enhanced natural processes to protect human and environmental receptors from unacceptable exposures to groundwater contaminants. Many natural processes occur at contaminated sites. Some of these processes, particularly biodegradation and very strong immobilization, transform the contaminants to less harmful forms. Other natural processes dilute the contaminants or move them to other locations. Because natural attenuation is a legal remedy for waste-site cleanup, the presence of natural processes that may reduce contaminant concentration in the groundwater is not sufficient. Natural attenuation is an adequate remedy only when the natural processes are great enough to prevent harmful exposure for as long as the contaminant source persists."

can transform many organic and inorganic contaminants to innocuous chemical forms, such as CO_2, H_2O, Cl^-, and N_2 (NRC 2000). (Radioactive decay can achieve the same effect as biodegradation, depending on the daughter products. In principle, abiotic chemical reactions could transform a contaminant to a harmless product, but such reactions are rare.) A harmless material offers no exposure risk, even if it escapes the site and comes into contact with humans or environmental receptors. Very strong immobilization keeps the contaminant in or near the source zone, which prevents exposure by humans or sensitive environmental receptors.

The committee that wrote NRC (2000) thoroughly debated what processes to include as the foundation for natural attenuation. The unanimous conclusion was that destruction (mainly biodegradation and radioactive decay) and very strong immobilization (mainly precipitation and strong surface complexation) are the ones that can be proven and, therefore, accepted by the scientific and at-risk communities. The other processes often occur at a site and must be understood, but NRC (2000) clearly distinguishes between understanding the role of other processes and relying on them to prevent exposures. Because the 'technology' of natural attenuation is proving that natural processes prevent exposure risk, it essential that the processes responsible for natural attenuation actively eliminate exposure risk and can be positively demonstrated. Only destruction and strong immobilization can meet this criterion, and the definition based on NRC (2000) correctly distinguished those processes from others.

In summary, the definition of natural attenuation has evolved, and the evolution can lead to confusion. On the one hand, natural attenuation can refer to a set of microbiological, chemical, and transport processes that affect the fate of a contaminant, often resulting in reduced concentration over time and distance from a source. On the other hand, natural attenuation can refer to achieving the goal of protecting humans and sensitive environments from unacceptable exposure risk. The natural-attenuation processes occur whether or not natural attenuation successfully protects human and environmental receptors. Thus, it is possible to have natural-attenuation processes working without achieving the risk-reduction goal. The

NRC committee recognized this dichotomy and decided to emphasize the ultimate goal of achieving risk-reduction. It did so by giving special status to destruction and strong-immobilization processes, which have the potential to eliminate exposure risk and can be documented by the methods reviewed in the next section.

Monitoring and evaluation

The underpinning of natural attenuation is *knowledge* that naturally occurring processes destroy or strongly immobilize contaminants (or daughter products) fast enough so that exposures are negligible. Therefore, the 'technology' of natural attenuation is a monitoring and evaluation program that provides this knowledge. Observing that contaminant concentrations decrease over time or distance in groundwater samples is a valuable starting point for evaluation, but it is not enough. An adequate monitoring and evaluation program must establish a cause-and-effect link to the underlying destruction or immobilization reactions (NRC 2000; Rittmann & MacDonald 2000; MacDonald 2000).

Monitoring and evaluation involve three interrelated steps (NRC 2000; Rittmann & MacDonald 2000):

1. Develop a site conceptual model
2. Analyze site measurements to confirm loss of contaminants *and* establish a cause-and-effect relationship to a destruction or strong-immobilization reaction
3. Monitor the site over the long term to ensure that the natural-attenuation process continues to work

I elaborate on each of these steps.

All aspects of monitoring and evaluation flow from a *site conceptual model*. A conceptual model identifies the important features of the flow, transport, and reaction processes occurring at the site. Initially, a site conceptual model often is based on simplified assumptions, because detailed data are not immediately available. Therefore, the site conceptual model is not 'cast in stone' at the beginning of the program, but evolves and is improved as more information becomes available.

The key elements of a site conceptual model include (NRC 2000):

- the site's hydrogeology – the geometry and hydraulic properties of hydrogeologic units, as well as hydrologic boundaries
- hydraulic heads, which yield groundwater flow velocities
- a delineation of the source of contamination and the groundwater plume
- an identification of the known or likely destruction or immobilization processes that can contribute to natural attenuation.

Uncertainty is inevitable for most or all of these elements, particularly at the outset of the program. While uncertainty must be acknowledged, it is not justification for abandoning a site conceptual model. The knowledge-based technology of natural attenuation is impotent without knowledge about from where the contaminants come, where the water goes, and what reaction might act to reduce exposures. NRC (2000) provides guidance for dealing with uncertainty in a realistic and constructive manner.

Once the source zone and transport processes are delineated, it is possible to take samples from the site with the goals of *confirming the loss of contaminants and establishing a cause-and-effect relationship to a destruction or strong-immobilization reaction*. The key to establishing the cause-and-effect relationship is exploiting what NRC (2000) calls *reaction footprints*. Footprints typically are concentration changes in reactants or products of the destruction or immobilization reaction. Footprints occur because the natural-attenuation reaction consumes or produces other materials in established stoichiometric ratios to the loss of the contaminant. Quantitatively coupling the formation of footprints to the loss of contaminants is strong evidence that a natural-attenuation process is responsible for reductions in contaminant concentration. Loss of contaminant without the corresponding footprints suggests that the lower contaminant concentration may be an artifact. Artifacts can include missing the centerline of the plume in the horizontal or vertical directions, transfer of the contaminant to another location or phase, or losses during sampling. Measuring more than one footprint increases the certainty of the evaluation. Having several footprints is particularly valuable when one footprint has source or sink reactions other than the reaction with the contaminant.

Table 2 presents example reactions and their footprints. The first examples are for toluene (C_7H_8), a common component in gasoline. Toluene can be biodegraded aerobically and anaerobically (NRC 2000; Rittmann & McCarty 2001). When dissolved oxygen is available, the reaction will proceed aerobically, and the key footprints are loss of oxygen (9

Table 2. Examples of natural-attenuation reactions and their footprints

Contaminant	Reaction	Footprints
Toluene, C_7H_8 Aerobic biodegradation	$C_7H_8 + 3H_2O + 9O_2 = 7H_2CO_3$	• loss of 9 $molO_2/molC_7H_8$ • gain of 7 $molH_2CO_3/molC_7H_8$ • no change to alkalinity
Toluene, C_7H_8 Sulfate-reducing biodegradation	$C_7H_8 + 3H_2O + 4.5SO_4^{2-} + 9H^+ = 7H_2CO_3 + 4.5H_2S$	• loss of 4.5 $molSO_4^{2-}/molC_7H_8$ • gain of 7 $molH_2CO_3/molC_7H_8$ • gain of 9 $eqalkalinity/molC_7H_8$
MTBE*, $C_5H_{12}O$ Complete aerobic biodegradation	$C_5H_{12}O + 7.5O_2 = 5H_2CO_3 + H_2O$	• loss of 7.5 $molO_2/molC_5H_{12}O$ • gain of 5 $molH_2CO_3/molC_5H_{12}O$ • no change to alkalinity
TCE*, C_2Cl_3H Complete reductive dechlorination using H_2	$C_2Cl_3H + 3H_2 = C_2H_4 + 3H^+ + 3Cl^-$	• loss of 3 $molH_2/molC_2Cl_3H$ • gain of 1 $molC_2H_4/molC_2Cl_3H$ • gain of 3 $molCl^-/molC_2Cl_3H$ • loss of 3 eq $alkalinity/molC_2Cl_3H$ • no change in H_2CO_3
Uranium, UO_2^{2+} Reduction using H_2 and precipitation	$UO_2^{2+} + H_2 = UO_2(s) + 2H^+$	• loss of 1 $molH_2/molU$ • loss of 2 eq alkalinity/molU • no change in H_2CO_3

*MTBE = methyl-*tert*-butyl ether; TCE = trichloroethene.

$molO_2/molC_7H_8$) and the increase in inorganic carbon (7 $molH_2CO_3/molC_7H_8$). Because the oxygen supply usually is limited in the subsurface, toluene biodegradation in the interior of a plume usually proceeds anaerobically, such as by sulfate reduction shown in Table 2. Two footprints for toluene biodegradation via sulfate reduction are quite distinct from the aerobic footprints: the loss of sulfate (4.5 $molSO_4^{2-}/molC_7H_8$) and the increase in alkalinity (9 $eq/molC_7H_8$), shown by the consumption of acidic hydrogen (H^+). Plumes in the field normally have aerobic and several types of anaerobic reactions for toluene, which means that the overall footprints may be a composite of the different reactions, as is illustrated in NRC (2000).

The third example is for methyl-*tert*-butyl ether (MTBE), a widely used additive to gasoline. Because MTBE does not adsorb much to aquifer solids and is biodegraded under more restrictive conditions that are toluene, benzene, ethylbenzene, and xylenes (BTEX), MTBE plumes frequently extend well beyond BTEX plumes. However, MTBE can be aerobically biodegraded, and the footprints in Table 2 are for complete mineralization. As for toluene, the key footprints are loss of dissolved oxygen and release of inorganic carbon, but the ratios differ from those for toluene. MTBE is discussed in more detail in the contemporary example that follows.

The fourth example is reductive dechlorination of trichloroethene (TCE), a widely used cleaning solvent for metals, semi-conductors, and dry cleaning. In order to reduce TCE, an electron donor must be present and consumed. The electron donor indicated in Table 2 is hydrogen gas (H_2), which most often becomes available due to fermentation of organic matter. For example, fermentation of lactic acid ($C_3H_6O_3$) generates H_2 and acetic acid according to:

$$C_3H_6O_3 + 2H_2O = C_2H_4O_2 + 2H_2 + H_2CO_3$$

in which one mole of lactate generates 2 moles of H_2. The most critical footprint for the complete reductive dechlorination of TCE using H_2 is the loss of 3 $molH_2/molTCE$. If lactate were the ultimate source for H_2, 3 $molH_2/molTCE$ implies consumption of 1.5 $molC_3H_6O_2/molTCE$. Other potentially observable footprints are the formation of ethene (1 $molC_2H_4/molTCE$), gain of chloride ion (3 $molCl^-/molTCE$), and loss of alkalinity (3 eq/molTCE).

The last example in Table 2 differs from the others in that it leads to immobilization, not destruction of the contaminant. Uranium in the +6 oxidation state (UO_2^{2+}) is relatively mobile, but microbial reduction to the +4 oxidation state leads to a very low-solubility form that usually precipitates ($UO_{2(s)}$) (NRC 2000;

Banaszak et al. 1999). The crucial footprint for the reduction and precipitation of uranium is loss of an electron donor, shown as 1 moleH_2/molU here. In addition, the alkalinity declines by 2 eq/molU.

A monitoring program typically is divided into two phases. The first phase uses footprints to establish that the contaminant is being contained today and establishes the cause-and-effect relationship with the destruction or immobilization reaction. The second phase, long-term monitoring, is put in place to ensure that contaminant containment and the natural-attenuation reaction continues for as long as the contaminant is released from the source or persists in a plume. This long-term perspective is essential for two reasons.

The first reason is that many source areas are poorly delineated, releasing contamination at rates and over a duration that cannot be predicted in advance. Therefore, the natural attenuation reaction must continue for an indefinite time, and its ability to sustain containment must be verified for as long as containment is required.

The second reason is that important reactants for the destruction and immobilization reactions must have a supply rate that is *sustained* at a high enough rate to maintain containment. For example, biological oxidation of toluene requires that electron acceptors – e.g., O_2, NO_3^-, SO_4^{2-}, and Fe^{3+} – continue to be supplied at rates proportional to the rate at which toluene is released from the source. The source of Fe^{3+} is iron-oxide minerals, which can be exhausted. The supply rate of dissolved oxygen often is seriously limited by the oxygen's relatively low solubility is water. The reduction reactions, such as for TCE and uranium, require a continued source of H_2, which could come from co-contamination with organic materials or from natural organic matter, both of which can be depleted over time. Thus, the sustainability of the reactant supply must be monitored over the long term through footprints.

Although the concept of footprints is simple and directly establishes cause-and-effect, confounding factors can, in some cases, cloud their interpretation. I describe two types of confounding factors and how they can be overcome. The first confounding factor occurs when the contaminant of interest is in a mixture with other materials. A common example is MTBE present along with BTEX. Aerobic biodegradation of BTEX can mask the footprints of MTBE biodegradation, if they take place in the same place. On the other hand, MTBE biodegradation often takes place down-gradient of BTEX biodegradation, which eliminates the confounding effect if the two locations are monitored separately. This confounding factor is exacerbated when the target contaminant is in a relatively small concentration. An example is the release of Cl^- during TCE dechlorination. A high background concentration of Cl^- obscures the gain due to TCE dechlorination. However, confounding the chloride footprint does not necessarily confound other footprints.

The second type of confounding factor is another reaction that consumes or produces the footprint. A good example of this is release of inorganic carbon due to dissolution of calcareous aquifer solids:

$$2H^+ + CaCO_{3(s)} = Ca^{2+} + H_2CO_3$$

Adding inorganic carbon to the groundwater due to $CaCO_{3(s)}$ dissolution confounds the direct interpretation of the footprints of mineralization of an organic contaminant, such as 7 molH_2CO_3/molC_7H_8. On the other hand, the confounding effect can be overcome by realizing that the gain of H_2CO_3 from $CaCO_{3(s)}$ is accompanied by a gain of 1 molCa^{2+}/molH_2CO_3 and a gain of alkalinity of 2 eq/molH_2CO_3. Addition of Ca^{2+} is not associated with any biodegradation reaction for toluene, and the alkalinity footprint is unique for each type of biodegradation (NRC 2000). Therefore, the confounding effect of $CaCO_{3(s)}$ dissolution can be 'subtracted out' by taking into account the gains of Ca^{2+} and alkalinity.

Although a confounding factor may complicate the use of footprints, it is not an 'excuse' for abandoning footprints as the core for evaluating natural attenuation. The examples given in the preceding two paragraphs show that it often is possible to overcome a confounding factor by taking into account additional footprints. This underscores the value of monitoring several footprints, along with the contaminant. Furthermore, a range of supplemental measurements can be used to augment the typical footprints. Examples of supplemental measures are (NRC 1993, 2000; Rittmann & McCarty 2001; Rittmann et al. 1994):

- Aquifer solids can be removed and assayed for relevant degrading microorganisms. Traditional selective culturing or modern genome-based techniques can be used for detecting capable microorganisms (Smets et al. 2002).
- Aquifer solids can be removed and assayed for an immobilized contaminant, such as $UO_{2(s)}$ (Table 2) or a strongly sorbed organic.

- Carbon-13 stable-isotope analysis can be used a signature to determine the source of inorganic carbon, differentiating between $CaCO_{(3)}$ and toluene, for example.
- Microcosm studies can be performed with groundwater or aquifer solids to test if natural attenuation reaction are happening or could happen.

A contemporary example – MTBE

Perhaps the most timely groundwater contaminant for which natural attenuation is being considered in the United States is MTBE. NRC (2000) indicated that, although MTBE is 'generally resistant to biodegradation', bacteria containing certain oxygenase enzymes are able to initiate aerobic biodegradation. NRC (2000) advised that the 'natural attenuation potential (of MTBE) is unclear at this time'. Furthermore, NRC (2000) judged that the *likelihood of success* for natural attenuation of MTBE is *low*, due to a lack of firm understanding of its biodegradation and also due to the likely need for special conditions to allow aerobic biodegradation. The special conditions include significant dissolved oxygen and the presence of microorganisms containing and expressing the key oxygenase enzymes.

The contemporary interest in MTBE led me to receive two invitations to apply the NRC guidance on natural attenuation of MTBE. I accepted the invitations, carried out a critical review of MTBE biodegradation and natural attenuation as of about the end of 2001, and produced two critical reviews (Rittmann 2002a, b). The conclusions of those critical reviews can be summarized in the follow extract from Rittmann (2002b):

> Knowledge about the biodegradation of MTBE is growing rapidly and is likely to continue to grow. Based on laboratory and field experience so far, the most promising type of MTBE biodegradation is aerobic and involves initial monooxygenase reactions. This situation requires that the supply of dissolved oxygen be significant and that MTBE degraders expressing the monooxygenase enzymes be present in significant numbers. Having both requirements present is not a high probability circumstance for natural attenuation. Therefore, the original NRC (2000) judgment that the likelihood of success is low for natural attenuation of MTBE seems to remain valid.

It is very important to understand that a generic judgment that natural attenuation has a low likelihood of success for MTBE does not mean that natural attenuation cannot work for MTBE or that it should never be proposed. What it means is that that a significant effort will be needed to prove natural attenuation at a field site, because the conditions leading to aerobic biodegradation are not routinely present. In the words of Rittmann (2002b):

> If natural attenuation is proposed for an MTBE-contaminated site, footprints of the biodegradation reaction must be measured. In fact, the measurement of footprints takes on elevated importance for low-likelihood contaminants because of the higher level of effort needed to document biodegradation (NRC 2000).

Very recently, two evaluations of possible MTBE natural attenuation at field sites were reported in a special issue on MTBE in the *Journal of Environmental Engineering* (Wilson & Kolhatkar 2002; Gibbs et al. 2002). Neither of these studies made extensive use of the MTBE footprints in Table 2. I provide brief summaries of each study and discuss how footprints could enhance the power of their results.

Wilson & Kolhatkar (2002) assessed the 'rate of attenuation' of MTBE from the source area and within the plume for five sites throughout the U.S.A. They then compared the attenuation rate in the source area to the attenuation rate in the plume. In all five cases, the computed attenuation rate in the plume was significantly faster than the computed attenuation rate in the source area. From these results, Wilson & Kolhatkar (2002) concluded that, 'As these plumes progress through their life cycle, they should recede back toward their source'. As long as the current plume provides no exposure to any receptor (say via a water well or seepage to a stream), this conclusion is the same a saying that natural attenuation is containing the MTBE and preventing exposure risk.

The conclusion in Wilson & Kolhatkar (2002) is based solely on computed attenuation rates at different locations and by different methods. The first-order attenuation rates in the source areas were computed from changes in concentration *over time* from the most contaminated wells. On the other hand, the first-order attenuation rates for the plume were computed from changes in concentration *over distance* from different wells in the plume. The first-order rates in distance were then converted to first-order rates in time by multiplying the first-order rate in distance by the seepage velocity. First-order rates computed by either means include all processes that lower concentration at the location, including dispersion and dilution. Thus, these rates do not distinguish biodegradation, a destruction process, from other processes that affect local concentration, but do not contain the MTBE.

Basing the attenuation rates in the source and within the plume on different types of data adds a significant amount of uncertainty to the comparison, and that uncertainty is biased in favor of showing too high rates within the plume. The rates computed for the plume will be over- estimated if the measurements deviate from the plume centerline in the vertical or horizontal direction. Although Wilson & Kolhatkar (2002) made 'every effort to minimize these sources of error', they cannot be certain that the errors were insignificant. Furthermore, the error is one-sided, always over-estimating the rate in the plume.

Recognizing that MTBE biodegradation is likely to occur aerobically, Wilson & Kolhatkar (2002) point out that the two sites with the lowest attenuation rates in the plume are 'devoid of oxygen and nitrate, and there is little methane production'. They state that MTBE natural biodegradation is unlikely for these two sites, while dispersion is the likely reason for the higher attenuation rate. Thus, their limited use of biogeochemical footprints offers evidence that containment is not likely at two of the sites.

The analysis of the five sites could be strengthened significantly in two ways. First, the analysis should recognize the difference between a process that truly contains MTBE, i.e., biodegradation, and those that bring about reduced concentrations within the plume, but do not destroy the MTBE. Second, the analysis needs to include one or more footprints for MTBE biodegradation, such as are listed in Table 2 and reviewed in more detail by Rittmann (2002b). For example, consumption of oxygen and an increase in inorganic carbon commensurate with the loss of MTBE provide strong evidence that biodegradation occurred between two wells in the plume, not that the plume centerline by-passed the sampling wells.

Gibbs et al. (2002) studied the MTBE plume at a military base in Novato, California. The analysis was complicated by an engineered remediation that took place near the source area for part of the study period, but they had about two years of data after the engineered remediation was shut down. They had groundwater concentrations of MTBE in an extensive array down-gradient of the source area, and they used statistical means to estimate iso-concentration profiles over time. From the iso-concentration profiles, they computed the total mass of MTBE in the plume and the location of its center of mass.

From these results, Gibbs et al. (2002) concluded that the extent of the plume is 'relatively constant', although they saw 'some growth at the northeast corner', which is the far distal edge. The total mass of MTBE within the plume decreased by about 50% after the engineered remediation was shut down. The center of mass migrated back toward the source about 2% of the total plume length (c. 880 m) over the two years after shut down.

Gibbs et al. (2002) concluded that the advection rate of MTBE from the source area is roughly equal to the rate of aerobic biodegradation, which is responsible for the relative stability of the plume. They further state that the oxygen needed for aerobic biodegradation probably came from 'oxygen replentishment into groundwater during seasonal rain infiltration events'. The study did not report any other information on footprints of MTBE biodegradation. As with the study of Wilson & Kolhatkar (2002), the power of the interpretation by Gibbs et al. (2002) would be greatly increased by measurements of the loss of dissolved oxygen and an increase in inorganic carbon. The hypothesis that dissolved oxygen is supplied via rain infiltration is plausible in principle. An excellent footprint analysis to help verify the hypothesis would be to compare the rate of oxygen infiltration from rainwater to the observed rate of MTBE loss from the plume.

Conclusions

As a remedy for groundwater contamination, natural attenuation offers large benefits to site owners and managers, but often raises strong objections from those who live and work near a site and are asked to assume most of the long-term risks. Part of the controversy stems from the definition of natural attenuation, which has evolved since the mid-1990s. The definition must reflect a realistic end-point objective and identify the naturally occurring processes that can achieve the objective. NRC (2000) recognized that destruction (mainly biodegradation and radioactive decay) and strong immobilization are the naturally occurring processes that achieve the realistic objective of containing the contaminant relatively near its source, thereby minimizing exposure risks to humans and environmental receptors.

Decisions about when to accept natural attenuation must be based on a solid evidence that the contaminants are being contained and will continue to be contained by naturally occurring destruction or strong-immobilization reactions. According the NRC (2000), the strategy for obtaining solid evidence includes a site conceptual model, measurements to confirm loss of contaminants and establish as cause-and-effect relationship to destruction or strong-immobilization reactions, and long-term monitoring of the contaminant and footprints to ensure that the natural-attenuation processes continue to work. The key to documenting the cause-and-effect relationship between loss of contaminant and the destruction or immobilization reaction is measuring the footprints of the reaction. Footprints typically are concentration changes in reactants or products of the destruction or immobilization reactions, although other measurements can be used to help confirm the natural-attenuation reaction.

MTBE presents a contemporary example in which solid evidence for biodegradation is especially crucial, since aerobic biodegradation of MTBE requires special conditions not present at all sites: a high availability of dissolved oxygen and bacteria expressing particular oxygenase enzymes. Two very recent studies (Wilson & Kalhatkar 2002, Gibbs et al. 2002) provide field data that suggest that natural attenuation may be working. I describe how footprints could be used to eliminate the significant uncertainty still present in these studies.

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