

## Oxygenates

# Natural Attenuation: Is Dilution the Solution?

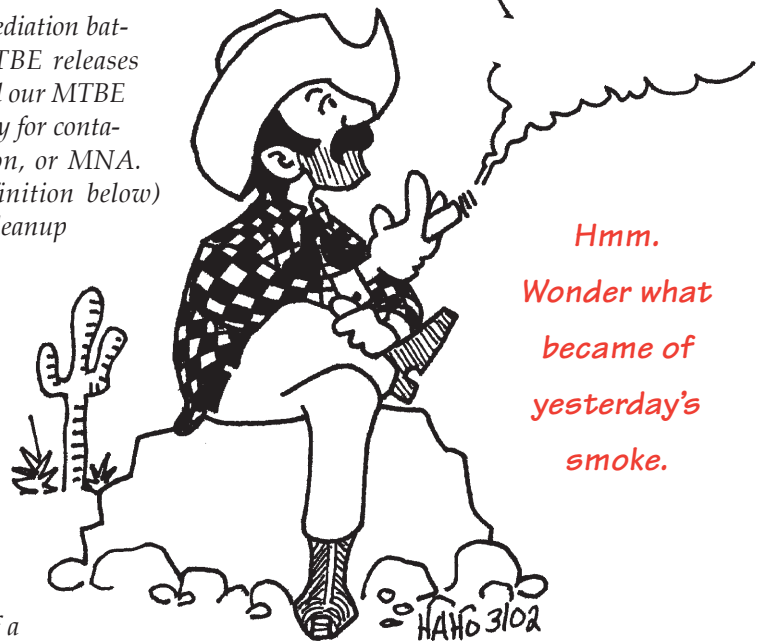
by Joseph E. Odenchantz, Mark D. Varljen, and Richard A. Vogl

Just as it was beginning to look like we were winning the remediation battle at groundwater contamination sites, the impact of MTBE releases reared its ugly head. In the midst of our remediation battle and our MTBE discoveries, we have seen the blossoming of a management strategy for contaminated groundwater known as monitored natural attenuation, or MNA. MNA refers to the reliance on natural attenuation (see definition below) processes within the context of a controlled and monitored site cleanup approach to achieve remedial objectives.

A close examination of the application of MNA, however, reveals some potential problem areas involving the misidentification of processes that govern contaminant plume behavior. These problems are often the result of the misapplication of simulation modeling techniques and/or consideration of unrepresentative data due to outdated or inappropriate monitoring well construction and sampling approaches. Dispersion on a grander scale has been advocated at municipal production wells as one approach to diluting the problem plume.

Such problems have become especially apparent at MTBE release sites, where the use of MNA could present the danger of a potential false sense of security. We may be encouraging "walk away" site closures when active remediation should really be implemented.

In this article we'll discuss potential pitfalls associated with MNA and explore the limitations of monitoring networks. Groundwater sampling techniques can promote misidentification of plume biogeochemical parameters and in some instances excessive dilution. We'll examine the location and construction of monitoring wells, seldom spelled out in state standards or guidelines. We'll conclude by highlighting the potentially false sense of security we may have when we mistake concentration dilution for concentration destruction at a LUST site or in a municipal production well.



### Destructive Processes?

The term "Natural Attenuation" (NA) has been defined as "naturally occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media" (Wiedemeier et al., 1999). This popular definition goes on to mention that the "in-situ" processes of NA include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants, meaning that natural attenuation is composed of numerous contributing factors of which biodegradation is only one.

In practice, unfortunately, the term "natural attenuation" is often used synonymously with such terms as intrinsic bioremediation, self remediation, natural restoration, passive

bioremediation, or intrinsic remediation. The negative result of this is that it is increasingly common to interchange "natural attenuation" with "remediation," when in fact they are not synonymous.

Natural attenuation occurs to some degree at every site; however, depending on site conditions, there can be definite limits to its effectiveness as an interim or long-term solution because natural attenuation does not necessarily imply that contaminants are removed. Furthermore, the site-specific conditions that often limit the effectiveness of natural attenuation as a contaminant removal/destruction process are rarely properly evaluated. It is vital that we distinguish between destructive processes and dilution. To do this it is first necessary to establish the types of biological processes that may be induced or monitored at a site.

### Intrinsic or Engineered?

Consider a "Biologically Active Zone," or BAZ, which occurs in close proximity to the contaminant source in the presence of electron donors in the mix of available electron acceptors. Contamination that escapes the BAZ escapes biological reaction and continues to move downgradient. Perhaps this is the reason why many of our chlorinated solvents plumes are so long (miles and kilometers long). For chlorinated solvents dissolved in water, biodegradation typically occurs within a BAZ, and the limiting factor is the availability of electron donors (primary substrates) for which a zone of increased biological activity can be established. In other words, there must be some growth of bacteria in order for biodegradation to occur, and growth requires the overlap of bacteria, electron donors, and acceptors.

Biodegradation can be either intrinsic or engineered. Intrinsic biodegradation processes refer to those which occur under indigenous aquifer conditions within the contaminant plume. Contaminant plumes vary in size and shape in accordance with each constituent, as does the intrinsic biodegradation rate of each of these compounds. Oxygen is often consumed near the source of a gasoline leak by the indigenous bacteria, using benzene as an electron-donor and oxygen as an electron-acceptor. In the far-field region of the plume, indigenous oligotrophic bacteria (those which survive on trace levels of substrates) may be stimulated by some gasoline constituents, causing biodegradation to occur at slow rates.

Engineered biodegradation refers to the adding of nutrients, bacteria, electron-acceptors (e.g., oxygen, nitrate, sulfate) and perhaps other electron-donors (e.g., molasses, lactate) primarily in the near source area to develop a healthy BAZ. Flow control or a circulation system to aid in the efficiency of the BAZ sometimes accompanies this in situ biodegradation.

In examining the potential biodegradation of a compound in the field, you should rely on other lines of evidence such as tracers, microcosm studies, lack of degraders, published biodegradation pathways, comparison of movement to the other constituents in the source, and changes of mass of the compound (National Academy of Sciences, 2000).

Regardless of the type of biodegradation process that may be occurring at a site, establishing lines of evidence on a compound-by-compound basis is necessary. An examination of the spatial variability of oxidation-reduction potential and dissolved hydrogen may provide us with some idea of the potential zones of dominant biodegradation regions; however, it does not necessarily tell us if there has been biodegradation of a particular compound.

For intrinsic biodegradation processes, how do we determine if decay rates are sufficiently large to cause a change in mass or if biodegradation is occurring at all? Unfortunately, these biodegradation processes are commonly misidentified, and decay rates are, therefore, incorrectly determined.

## Puff of Smoke

A recent study conducted at the Borden Aquifer, Borden Airfield, Ontario, Canada, focused on a 16-month university research project which was extended to 8 years after the initiation of the original project (Schirmer and Barker, 1998). Eight years after MTBE was instantaneously (for all practical purposes) injected into an aquifer, the researchers decided to "go find it."

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The researchers only found 3 percent of the injected mass and concluded that 97 percent had biodegraded—simply because they didn't find the mass. This is analogous to trying to find all the smoke from a puff of smoke released to the outdoor air 7 hours after its release (assume dispersion in air is 10,000 times that in water; 8 years is 70,080 hours). Finding all of this smoke is clearly something that we would not expect to be possible, yet when reviewing this work, few seem to consider that perhaps the researchers simply didn't find (or couldn't quantify) the dispersed contaminant.

The work was excellent with respect to quantifying the natural attenuation of a small instantaneous amount of MTBE; however, it did not document biodegradation. There was no definitive proof (such as the presence of metabolic byproducts) presented that suggests that biodegradation of MTBE occurred in groundwater. Unfortunately we are now seeing this assumption of intrinsic decay being carried forth in practice by both the consulting and regulatory communities. What was missed in the research was recogni-

tion that natural attenuation of MTBE can occur, under the right set of circumstances, in the absence of biodegradation processes.

So where do you draw the line between dispersion/dilution and biodegradation? You must first determine whether changes in concentration are changes in mass of the plume or if the plume has moved to places unknown in the aquifer.

## Decay, Dispersion, and Misnomers

Monitored natural attenuation protocols (OSWER Directive 9200.4-17P, 1999) generally involve the collection of biogeochemical data from groundwater monitoring wells at sites. The data are correlated in time and space with the various chemicals of concern (COCs) to establish predominant biodegradation mechanisms.

In evaluating the size, behavior, and mass of groundwater plumes, monitoring wells are sampled by a variety of techniques at fixed locations. This protocol assumes that the monitoring wells fully delineate the plume and that there is an adequate number of wells to calculate a plume mass every time the wells are sampled (unfortunately this is not often the case in practice).

Under this assumption, though, can we really give some kind of explanation of what the plume is doing (i.e., expanding, remaining stable, or shrinking) by examining the time history of concentration of a gasoline compound at a well? Of course this depends largely on where the well is located (i.e., source proximity), how it was constructed (e.g., type, screen length), and how it was sampled (i.e., low-flow, traditional purge, or no purge). If the concentration rises and drops over a 2-year period, does this mean that the plume is shrinking, that it has moved past the well, or that there is a change in flow direction?

This question cannot be answered unless we look at the conceptual model of the site, changes in concentration at other wells, and, perhaps, changes in other biogeochemical parameters—parameters that are often overlooked. So the biodegradation is being inferred, rather than directly confirmed.

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These considerations are intuitive, and most practicing professionals routinely use standard methods and state guidelines to work through these types of evaluations. When evaluating the dominant attenuation processes, obtaining representative data from monitoring wells is a critical first step in moving onto isolating NA processes. The importance of collecting representative sampling data (as influenced by well location, construction, and sampling protocols) cannot be underestimated. This will be discussed further in later sections of this article.

Assume for the moment, however, that we have not only an adequate number of wells to fully delineate our plume but that there are only nondestructive NA processes at work (i.e., advection, dispersion, sorption, and volatilization) and we can predict them perfectly using models (another assumption that is never really achieved in practice).

Now if sorption and volatilization were minimal, the mass of the plume would remain virtually constant if we calculated it each time from the concentration in the wells. We could go back and adjust any small changes in mass by our models of sorption and volatilization. This approach has been used at a variety of research sites where several transects of multilevel monitoring wells were placed perpendicular to the groundwater flow direction. If we had the typical monitoring wells at a service station site, however, and the same exercise was performed, it would be nearly impossible to make a reasonable estimate of the plume mass with time.

Continuing with our example, consider a situation where we are faced with applying a common model, BIOSCREEN, to estimate the NA at a site. We have a well at 30 feet downgradient (near-field) and one at 300 feet downgradient (far-field). We prepare to run the model by methodically estimating all the independent variables (i.e., source concentration, hydraulic conductivity/gradient, and longitudinal dispersivity). We run the model with no first-order decay and find both wells are off significantly.

In this particular case we do not have lines of evidence of biological degradation, so we will try to use a first-order “decay” coefficient to match the results found in the field. The near-field well matches with a first-order decay rate of 0.2 years and the far-field well matches with a rate of 1.5 years.

Without getting into the details of transport modeling, it might seem reasonable that there is more decay near the source than away from the source. Using the decay coefficient in this manner assumes decay is a lumped parameter in that it is not specific to a mechanism such as biodegradation. In this case it is used to account for loss of mass in a general sense. Perhaps the loss mechanism is not necessarily decay and there is more dispersion in the system than initially estimated. We ran the model with ten times the dispersion without first-order decay and found the model output matched the data from the wells as shown in Figure 1. This suggests that perhaps first-order decay in some sites is not occurring.

So the next time you see a degradation rate or half-life presented, (a) be sure you clarify what processes it encompasses, (b) establish exactly how it was determined, (c) make certain other processes, such as dispersion, were estimated correctly, and (d) if it is a first-order biodegradation

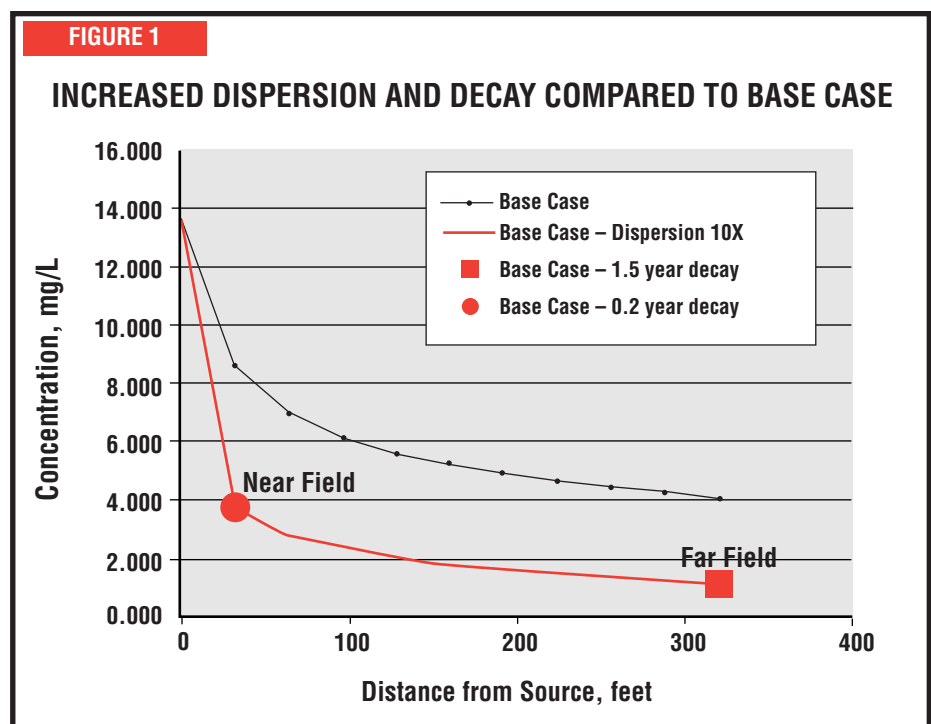
rate, examine the available lines of evidence to substantiate it.

Unfortunately, the BIOSCREEN “Help” section encourages the mixing of processes, as seen from the following passage: “Modelers using the first-order decay model typically use the first-order decay coefficient as a calibration parameter and adjust the decay coefficient until the model results match field data. With this approach, uncertainties in a number of parameters (e.g., dispersion, sorption, biodegradation) are lumped together in a single calibration parameter.”

Now that we have highlighted the potential ramifications of confusing dispersion and nondestructive decay with biodegradation processes, what about mixing at a larger scale? What if we assume that all the contaminant mass leaves from a site and enters a municipal groundwater production well? What happens then? First things first: How do you estimate the mass of a contaminant leaving a site?

### Mass Flux and Dilution

A recent paper by Einarson and Mackay (2001) presents a framework by which dissolved-phase mass of groundwater constituents mixes with water extracted from production wells. The mass-flux mixing approach takes the mass from a



groundwater plume and mixes it with the water from typically larger, deeper flows and formations.

The authors state: "They [the capture zones] are useful for illustrating contaminant dilution in continuously pumped supply wells." The capture zones are the regions of groundwater that are pumped into a production well as a function of time. According to the authors, when multiple plumes are heading toward a municipal well, "the larger pumping rates of many municipal supply wells may be sufficient to cause enough blending so that contaminant concentrations in extracted water remain relatively low."

Einarson and Mackay's paper seeks to establish the mass flux of contaminants leaving a site by using multilevel well fences on the down-gradient side of a plume in order to provide an accurate determination of flux leaving the site. In the example in the paper, seven locations spaced 11 feet apart each contained seven vertical probes spaced 2 feet apart; the first probe was located 1.5 feet below the water table (all distances approximate for they were scaled from diagrams in the original paper).

Each of the 49 probes sampled represented 22 square feet of aquifer perpendicular to the flow direction and the entire fence a 1,078-square foot section of the contaminant plume. Although this is an extensive monitoring array, the data seem to indicate that even this elaborate monitoring approach was not adequate. The sides and bottom of the transect contained contaminant in significant concentrations, implying that only a portion of the plume was sampled.

The example yielded a mass flux of 31 grams of a compound per day after multiplying by the calculated specific discharge (Darcy Velocity of 0.64 inch/day) and adding up each mass flux from the individual probe areas. If this mass flux were to enter a municipal supply well pumping 1,000,000 gallons per day (694.4 gallons per minute), the resulting concentration after mixing would be 8.2 ug/L. The average concentration at the fence was approximately 20,000 ug/L. The net effect is lowering the concentration by approximately 2,500 times once the water is pumped from the aquifer from the municipal supply well.

What does this imply? Have we now come to rely on end-user dilution to manage contaminant plumes? Furthermore, what does this say about our sampling results if monitoring wells are sampled with high-volume, high-flow purging and sampling techniques, or if the monitoring wells are located in areas that may underestimate the dimensions of the plume?

### The Sway of Sound Well Location, Construction, and Sampling

Most state standards or guidelines for implementing MNA do not address well construction and sampling procedures. Consider a LUST at a service station above a water table aquifer in a groundwater recharge area. Typical groundwater monitoring is conducted using wells with screens completed across the water table (presumably to measure LNAPL, even though they are far downgradient of the LUST, and no residual hydrocarbon was noted during drilling). Common sampling shortcomings may include the use of high-flow purging, including explosive vacuum truck purging (complete evacuation), bailing, failure to measure parameters with a closed flow-through cell, and passive or no-purge sampling.

These shortcomings can lead to an underestimation of the lateral extent of the dissolved contaminant plume (MTBE and BTEX) and misrepresentation of biogeochemical conditions (e.g., REDOX and other lines of evidence) in the following ways:

#### ■ Wells completed across the water table.

Water that is being sampled from a well completed across the water table will always have some direct contact with the atmosphere (increasing the likelihood of volatilization) through the well bore. Also, zones of artificially enhanced biodegradation (not representative of the aquifer) often occur in the immediate vicinity of the well due to increased atmospheric contact allowed by the well. Enhanced volatilization and biodegradation can occur right at the water table (due to atmospheric contact) but not at deeper levels in the aquifer, so the sample collected from the water table may not be represen-

tative of the dissolved plume; and in recharge areas a dissolved plume will likely move vertically downward and a well at the water table may completely miss the plume. In this situation, fresh water from precipitation recharge may also reduce concentrations of dissolved constituents right at the water table.

■ **High-flow purging.** This may cause dilution as described in the previous section. Also, volatilization losses may occur if excessive drawdown is caused, and water "cascades" into the well screen. Increased oxygenation may occur, eliminating the ability to accurately characterize REDOX conditions. If an electric pump is used, dissolved hydrogen determinations may be overestimated due to electrolysis.

■ **Sampling with a bailer.** Volatilization losses may occur due to agitation. Mixing of altered (due to atmospheric contact) water with water being sampled is inevitable. Accurate field parameter determination and proper sampling for dissolved gases (oxygen, hydrogen, methane) is impossible.

■ **Failure to measure parameters with a closed flow-through cell.** Both bias (high) and variability is introduced into dissolved oxygen determinations that have been collected by either pumping or decanting (from a bailer) into a cup and inserting a hand-held probe. Measurements of pH can be affected by off-gassing of CO<sub>2</sub>.

■ **Passive sampling or "no-purge."** These methods sample water in the well, not in the aquifer. While ambient flow may occur, and water in the well may be representative of the aquifer without purging, this must be verified by purging, because ambient flow (and hence "flushing") may occur to different degrees at different locations and may also vary seasonally at a given location. Furthermore, when passive sampling with diffusion-type samplers, the sampler itself may block any ambient flow.

In summary, we must keep in mind that many standard practices in groundwater monitoring are not giving us representative data that is

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useful for truly evaluating MNA. Solutions to this problem are to develop and enforce standards for well location, construction, and sampling protocols such that the data will be useful for the intended purpose.

When “standard” groundwater monitoring practices were first implemented years ago, no one was thinking that we would be “taking the pulse” of a site in the manner required for MNA evaluations. Our new information needs to exceed the abilities of the old practices to deliver the required information. New standards should encourage short-screened wells in three dimensions (only screened across the water table where NAPL monitoring is required) and low-flow purging and sampling with nonelectric positive displacement pumps.

### So, Do We Care?

It is all about liability and short-term versus long-term thinking. You might get approval for a “walk away” today based on some notion of NA; however, if it is not technically correct, it may be a long-term liability (for both regulators and the regulated community) regardless of current accepted technical practice. Both regulators and LUST owners are under pressure to get sites “off the list.” Both also stand to suffer some negative consequences if we have to revisit these sites and implement active remediation in the future because we find out that contaminant reduction processes were not what we’d thought they were.

One might initially think that in practice it doesn’t matter what is going on at a site—destruction versus dilution—as long as concentrations are reduced below a risk threshold. Maybe so, provided direct monitoring can prove this is happening. In practice, however, we are frequently closing sites and electing not to conduct active remediation, not because concentrations are already below a threshold, but rather because of some prediction that contaminant concentrations in groundwater will not exceed some risk-based threshold at some location downgradient some time in the future.

Seems to make sense. But what if for some reason (like the ones mentioned in this article) our predictions are not correct? What if we underestimate the plume mass in the first place, and we mistake concentration dilution (due to mixing or improper sampling) for concentration destruction (i.e., biodegradation)? What if we calculate a degradation rate and extrapolate that out? The model will paint a rosy picture, and we walk away from the site. In reality, those contaminants are still out there, spreading further while we sleep soundly with a false sense of security that they are being degraded.

This brings to mind a few more questions. What happens in an urban area where several of these diluted plumes commingle? What happens to the aquatic ecosystem that receives this contaminant mass discharge? We’re back to a question posed by the surface water pollution community 30 years ago. Is dilution the solution to pollution? In short, we think it can be, but only in certain circum-

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If we are to comfortably embrace MNA as an alternative to active remediation, we’d better be certain that (a) if concentrations are low, there will be no cumulative effects and (b) if we are relying on degradation to remove contaminants to achieve a risk-based concentration goal, we are very confident in our assessment of biodegradation. The

only way to do this is through better groundwater monitoring and biogeochemical evaluation practices that will result in the proper recognition of the natural attenuation processes that are actually occurring at a given site, their relationship to the concentration trends observed, and the use of these findings to accurately predict concentrations into the future. ■

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