

# Natural Attenuation Rate Clarifications: The Devil's in the Details

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## Abstract

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. Monitored natural attenuation (MNA) protocols 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 (COC's) to establish predominant biodegradation mechanisms. Modelers using the first-order decay expression typically use the rate coefficient as a calibration parameter and adjust it until the transport model results match field data. With this approach, uncertainties with a number of parameters (e.g., dispersion, sorption, biodegradation, etc.) are lumped together in a single calibration parameter. We examine the problems associated with the lumped parameter approach using two commonly used models, BIOSCREEN and Buscheck/Alcantar Analytical Solution in a variety of practical examples. The natural attenuation decay rate estimated using the lumped parameter approach is distinguished from a biodegradation rate established by isolating processes and examining biodegradation lines of evidence. The half-life determined from empirical data using the lumped parameter approach is often mistakenly interchanged with a biodegradation half-life when it is an all encompassing half-life based on the interaction of numerous processes. We isolate the processes as they are represented in the governing transport equation and provide a rationale approach at parameter estimation to avoid the potential pitfalls of the all-inclusive "attenuation rate".

We close by providing general guidelines on degradation rates and half-lives in the following categories: (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.

## Introduction

The purpose of this work is to demonstrate the importance of clarifying and isolating the processes involved in the detailed examination of groundwater natural attenuation processes. An abundance of recent publications, regulatory directives and remediation protocols involved quantification of natural attenuation processes. We highlight some of the details in recent work in the industry and comment on the take home messages that these works deliver. The take home message we wish to convey is quite simple-when rates and half-lives are put in tables, let's make sure they are accurate as to what they represent. A perfect example of a problem that exists is illustrated in the following sentence taken from a recent publication "A biodegradation rate derived from mass changes was calculated from changes in the total dissolved BTEX mass over time; this was used in a solute transport model to estimate the cleanup time" (Suarez and Rifai, 2002). This quote cuts to the heart of our paper. Let's be very careful with our interpretation of site data and be even more careful with what we call the results of our quantifications. Changes in dissolved phase mass calculated from chemical concentrations from monitoring wells are not only limited by the quality of the monitoring network they are taken from but do not represent any one singular process.

## **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 as 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.

## **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."

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 recognition 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.

## **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 downgradient 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 feet 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 significant contaminant 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?

## **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. The protocol assume 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, 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—a parameter that is often overlooked. So the biodegradation is being inferred, rather than directly confirmed.

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.

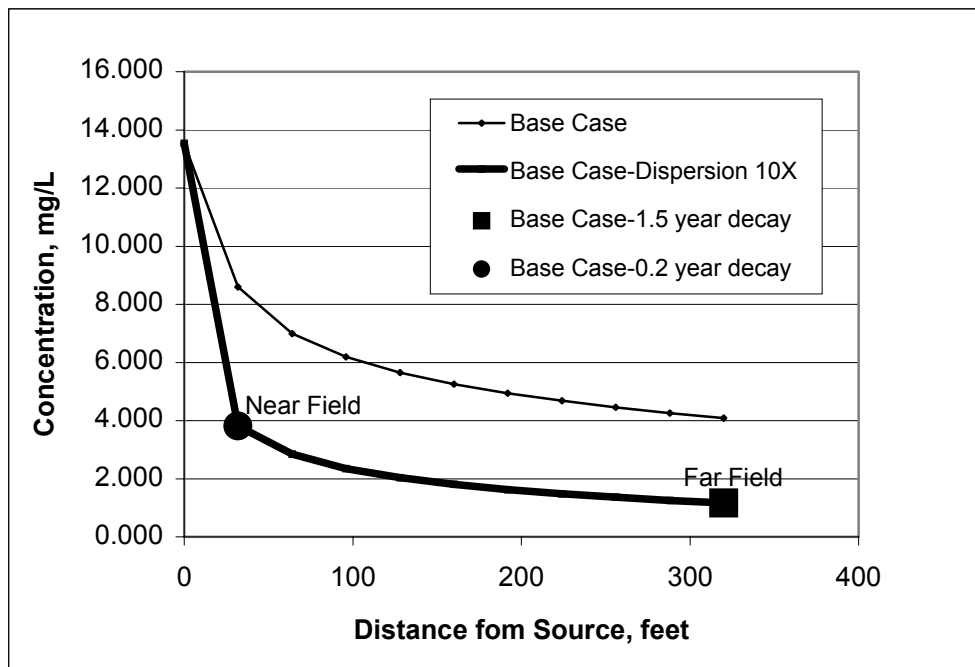
Continuing with our example, consider a situation where we are faced with applying a common model, BIOSCREEN, to estimate the NA at a site. We have a well at 30 feet downgradient (near-field) and one at 300 feet downgradient (far-field). We prepare to run the model by methodically estimating all the 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 year 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.

**Figure 1. Increased Dispersion and Decay Compared to Base Case**

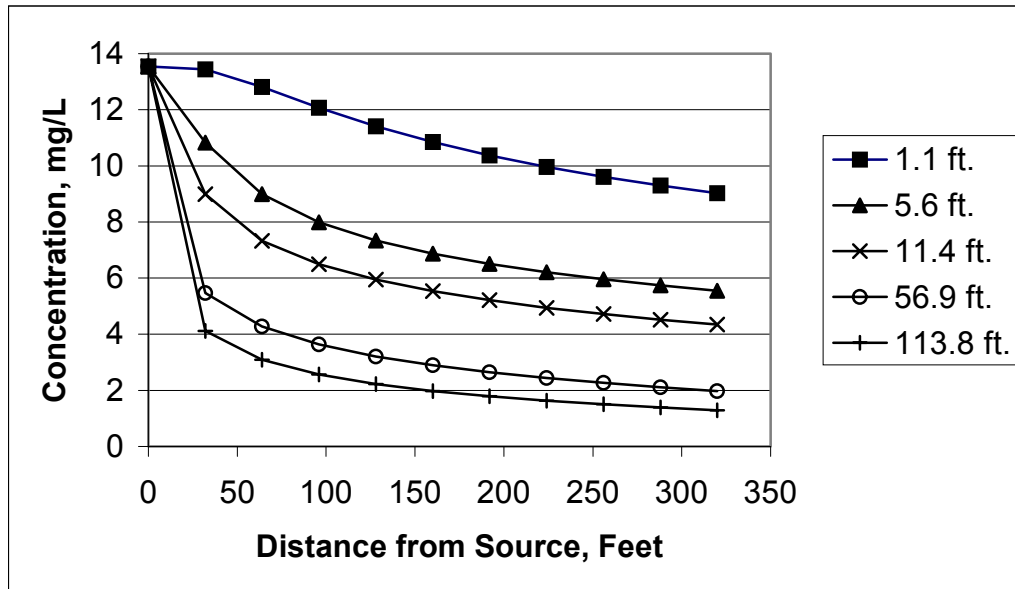


Unfortunately, the BIOSCREEN “Help” section encourages the mixing of processes as seen from the following passage: “Modelers using the first-order decay model typically use the first-order decay coefficient as a calibration parameter and adjust the decay coefficient until the model results match field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

## Buscheck and Alcantar Approach

Buscheck and Alcantar (1995) [BA] derived a steady-state solution to the advection-dispersion equation with first-order decay. Their approach assumes concentration of a constituent a certain distance downgradient from a continuous source can be translated a time away from the source by the groundwater velocity. This coordinate transformation, along with a line of best fit through an exponential line of best fit through the time versus concentration plot allows an estimate of the decay rate using the groundwater velocity, the linear retardation factor and the longitudinal dispersivity. Using the same parameters to generate the nonreactive profile in Figure 1 (groundwater velocity-0.37 feet/day, retardation factor-1.0 and longitudinal dispersivity of 11.38 feet), we determined the slope factor, after performing comparisons to previously published work using the BA method (Wiedemeier et al, 1998), and then calculated that a “decay half-life” of 2.29 years would be necessary to calibrate to the Base Case profile in Figure 1. Considering the profile in Figure 1 was generated from a nonreactive case, we found the necessity of any decay surprising. In order to explore the source of the discrepancy, several more nonreactive profiles were generated using BIOSCREEN at a range of different longitudinal dispersivities. Figure 2 is a plot of five profiles at five dispersivities. You will find the curve matching the dispersivity of 113.8 feet is the sample as the base case x 10 in Figure 1.

Figure 2. Concentration Profiles at Several Dispersivities.



The next step in the process was to determine the relationship of the BA decay half-life necessary to match all of the curves above. Figure 3 is a plot of the decay half-life versus dispersivity using the BA model to match a nonreactive case with different dispersivities. There is an intuitive trend in that more decay is necessary to match the higher dispersion values up to a dispersivity of 56 feet. At 85 and 133 feet dispersivities the trend reverses. Note we ran four additional dispersivity values than shown in Figure 2 in order to find the minimum decay half-life.

**Figure 3. Buscheck Alcantar Decay Half-Live Versus Dispersivity for a Nonreactive Case. The half-live at a dispersivity of 113.8 feet is 2.39 years (not shown on plot).**

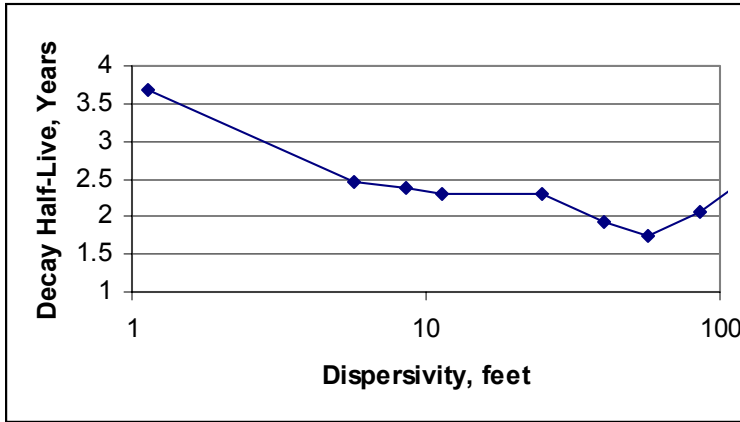
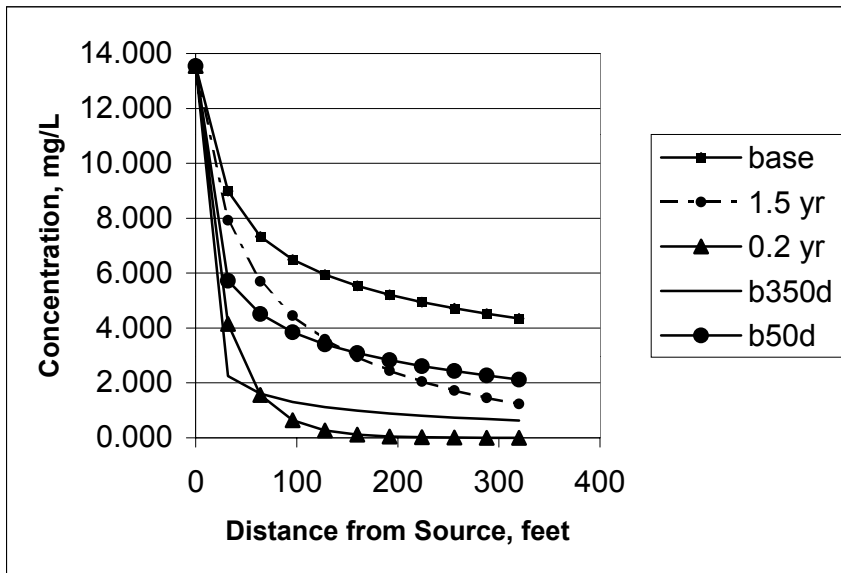


Figure 3 is a perfect example of some of the confusion that can arise by blindly using modeling approaches without being absolutely sure of what processes are being accounted for. There seems to be an issue with either the fundamental assumptions or the mathematical formulation associated with the BA approach.

**Decay or Dispersion? Examples.**

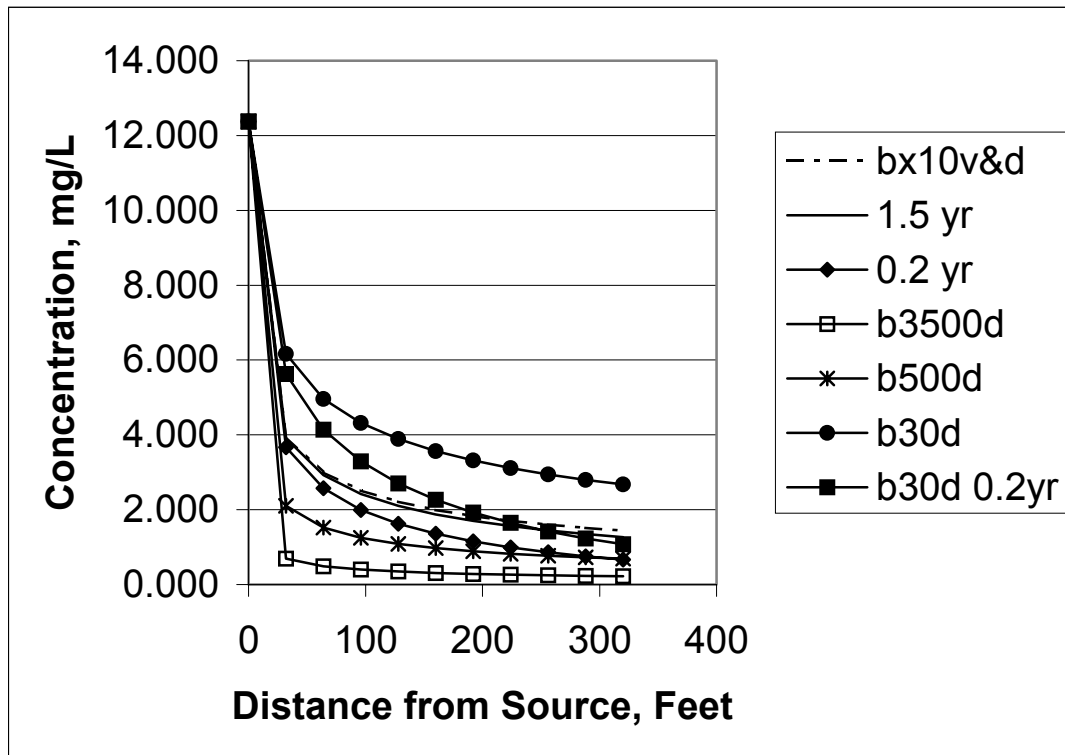
Complete profiles of the decay examples presented as “point-wise” results in Figure 1 were generated to determine if changes in dispersion might account for a majority of the system behavior depicted in these plots. Figure 4 shows a dispersivity value of 350 feet (approximately 31 times larger than the base case dispersivity) matches the overall profile of the 0.2 year decay half-life. Recall the simulation is a nonreactive case with a large amount of dispersions. It should be noted that the theory of dispersion is a scale dependent phenomenon and it is quite possible that what may seem unrealistically large might be possible. Especially when considering the large distances some plumes can travel, e.g. MTBE. Figure 4 also shows a 50-foot dispersivity (approximately 4 times larger than the base case dispersivity) does a decent job of mimicking the system as the profile generated using the 1.5 year decay half-life.

**Figure 4. Concentration Profiles of Decay and Dispersion About the Base Case.**



The final series of profiles were generated to demonstrate the effect of velocity on decay and dispersion. Figure 5 is a series of profiles generated about a new base case which consists of the previous base case with a groundwater velocity ten times higher or 3.7 feet/day. The new base case dispersivity was also increased by a factor of ten to 113.8 feet. The continuous source or first-type boundary is distributing ten times the mass into the system. Therefore, the 1.5 and 0.2 year decay half-lives show a much smaller effects on the concentration distribution as compared to the previous base case. The next two profiles show the effects of 31 and 4 times the new base case dispersivity. The new effect of the increased groundwater velocity and the larger dispersivities have a much larger impact on the plume dissipation because the two parameters are multiplicative, i.e. the new effect of hydrodynamic dispersion is much larger than in the previous case. The last two profiles illustrated the effects of a more moderate amount of dispersion (30 foot dispersivity) combined with a fairly significant decay half-life (0.2 years or 2.4 months). The new effect of the decay is much more pronounced on the higher velocity case with the smaller dispersivity (more on the order of the longitudinal scale of the profiles, 30 feet or approximately 10%).

**Figure 5. Profiles of Base Case with Ten Times Greater Groundwater Velocity with Varying Amounts of Dispersion and Decay.**



## Conclusions

The purpose of presenting summaries from the published literature and some work of our own is quite clear; let's be very careful with our oversimplified analysis and especially careful with what we are calling different processes. Consider something as simple as groundwater velocity. We have uncertainty in the hydraulic conductivity which is universally known and understood to varying degrees. Although we have less uncertainty with hydraulic gradient and effective porosity, the uncertainties multiply. Please keep in mind these general take home suggestions pertaining to degradation rates and half-lives in the following categories: (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.

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