

## Adjusting Bioremediation Expectations to the Reality of Bioavailability

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### ABSTRACT

Bioremediation of hydrocarbons in groundwater systems has been conducted with great success at a multitude of sites. In most cases, hydrocarbon concentrations in groundwater can be brought near or below drinking water standards. This is not hard to believe since these are biodegradable contaminants that are solubilized and available for biodegradation. Attaining these low levels in soils has been a challenge in the bioremediation industry. The true issue, bioavailability, has been clouded by vendors' eagerness to cite other limitations such as biomass or nutrients. Bioremediation of most hydrocarbon contamination is limited most by the extent of sorption of contaminants to the soil particles. Therefore contaminant properties, soil type and mixing are the primary governing factors with respect to bioremediation. This paper will illustrate the issue of bioavailability of hydrocarbons in soil, focusing on the achievable endpoints and regulatory issues.

### INTRODUCTION

Biodegradation of petroleum fuels has been documented under both laboratory and field conditions (1,2). Many different matrices including groundwater, ocean water, sediment, soil and even gravel support bacterial populations capable of mineralizing various hydrocarbons into carbon dioxide and water. It is generally accepted that biodegradation can gradually mitigate most light end petroleum hydrocarbons to an extent that biodegradation can be used to "clean" contaminated soil and groundwater.

The challenge in applying accelerated biodegradation techniques is not the ability to stimulate bacteria to degrade hydrocarbons; it is judging how low the hydrocarbon concentration can go. This judgment is based more on physical/chemical properties of the soil and contaminants (and their interactions) which together are referred to as "bioavailability". The following text describes the current models regarding bioavailability and how the issue is incorporated into the practice of bioremediation.

### REASONS FOR BIOAVAILABILITY CONSIDERATION

**Cost** - The issue of bioavailability is met with mixed opinions. Some bioremediation vendors see it as an opportunity to produce and sell "elixir" products that might alleviate the limitation and further lower cleanup endpoints. Specific surfactants, bacterial blends and nutrient packages have all been offered to address the limitation of bioavailability. In cases where side by side testing with and without the product can be compared, the product does not provide a significant benefit that would justify the added cost (3). In more cases, comparable data from a test without addition of the product are not available. When site owners are uncertain of the principles of biostimulation (the practice of using indigenous bacteria), they tend to choose these products as a tangible enhancement to their system. Subsequent results are disappointing.

**Contaminant Detection** - Among the array of contaminants addressed with bioremediation, hydrocarbons present one of the most difficult analytical challenges. Most hydrocarbon contamination in soil and groundwater is derived from fuel, which is composed of several hundred compounds. Analytically, these compounds are typically measured using a method that groups these compounds into a single number. Analyses that use this approach include diesel range organics (DRO), gasoline range organics (gro), total recoverable petroleum hydrocarbons (TRPH), and oil and grease (O&G). With so many components influencing a single value, significant reduction in certain components can be masked. Furthermore, there is no opportunity to incorporate weighted distinction between those components that do/don't pose health risks. The result may be more cost than is needed to protect human health and the environment.

In some cases, specific compounds have been chosen to represent the compounds of concern within a fuel blend. These compounds are typically volatiles and semivolatiles such as benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene and methyl-naphthalenes. Choosing these compounds as targets for remediation efficiency assessment is desirable since these compounds are easy to detect

and they are among the first compounds to be biodegraded in environmental systems. When these compounds are the targets, remediation systems become more predictable and more finite.

A remediation specialist may be fortunate to have contaminant that is made up of light end TRPH compounds (smaller hydrocarbons, less complexity to the compound's configuration), reaching the endpoint in a timely manner. This specialist can be unfortunate, addressing compounds that are grouped at the heavier end of the spectrum (longer hydrocarbons, more branching), which may result in extended treatment periods. Therefore, knowing the origin of the contaminant and the means by which success will be measured is critical in determining a system's treatment period.

## THE MODELS

The mechanisms behind bioavailability have been explored and are still the subject of significant research efforts (4,5). From a grand scale, three explanations exist. The first is that contaminants are not available for biodegradation because they are physically occluded within the soil and do not have contact with the microorganisms, therefore they are unavailable. This is always true to some extent because contaminant migration over extended periods can result in contaminant located in areas where short-term, aqueous-based treatment supplements cannot penetrate. However, there are many techniques that provide a great degree of soil disruption prior to treatment. These techniques are generally known to produce lower endpoints, but there are occurrences where contaminants still exist at appreciable levels after treatment.

The second model is based on soil type. Sorptive properties of soils vary depending on their characteristics. Figure 1 illustrates the relative bioavailability of contaminants in different soil types. Soils that are sandy generally contain larger soil particles and less of an ionic charge. Contaminants in these soils are more likely to be bioavailable. Soils that contain clay have finer particles and more of an ionic charge.

The third model explaining persistent contamination is molecular hindrance. In this case, the contaminants are composed in such a complex manner that the molecule itself is not available for microbial attack. This model is not influenced by environmental factors. However, at sites where the original source of contamination is not known, detecting these contaminants in a TRPH measurement could be misleading, causing an extended treatment period that may not reach target endpoints. It is likely that limited bioavailability is the primary obstacle as depicted in Figure 2.

## CURRENT PRACTICES

While research and development of the issues surrounding biotreatment endpoints continues, some strategies have been developed to proceed with bioremediation. Regulators have been given some degree of flexibility in determining endpoints based on Risk-Based Correction Action (RBCA) approaches. This new site-specific approach to determine how clean is clean has resulted in acceptance of higher endpoints because the risk to human health and the environment is reduced at that specific site. RBCA has been and will continue to assist in the understanding and acceptance of the limitations of bioavailability.

Stakeholders have begun to consider the grand effects bioremediation has on their site's contamination. Bioremediation certainly decreases the overall concentration of contaminants. However, bioremediation also provides important benefits that reduce the risk of contaminants that remain on-site. By removing the most available compounds, bioremediation reduces the mobility of the remaining contaminants. Similarly, it can reduce the leachability of the contamination. Therefore, even if the analytical value is still detectable, the remaining contamination poses a reduced risk to human health and the environment.

## CONCLUSIONS

While all of the activity dedicated to mitigating organic contamination in the environment continues, policy-makers and scientists must complete the database that persuades cleanup target endpoints. The goals of cleanup should be determined based on the risk to human health and the environment, not on the analytical detection capabilities. Hydrocarbons are a challenge in this regard since evaluating toxicity and health hazards of hundreds of individual compounds is time-consuming and expensive. RBCA techniques have been successful at providing a degree of realism in endpoint decision-making;

however, more effort needs to focus on the benefit of remediation dollars spent to pursue very low endpoints. Further, this cost benefit should be directly related to estimated lives saved.

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TABLES AND FIGURES

Table 1. Analytical Methodology and Fuel Molecular Weight Classes

Fuel Class or Analytical Method	Detectable Carbons Per Molecule Range
Gasoline	C5-C10
Jet Fuel	C9-C16
Diesel	C10-C22
Kerosene	C12-C18
Gas Oil	>C12
Waste Oil	>C18
EPA 8010 (volatiles)	C2-C12
EPA 8015 (TRPH)	C7-C30
EPA 418.1 (TPH)	>C14

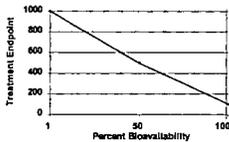


Figure 1. Relationship Between Bioavailability and Treatment Endpoints

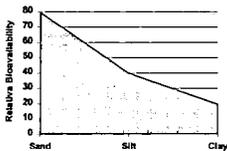


Figure 2. Soil Type Influence on Bioavailability