



## **TRAP & TREAT® - BOS 200®**

Based on years of experience using a variety of injectable technologies, ranging from augmented bioremediation to Fenton chemistry using hydrogen peroxide, it became clear that a better mousetrap was needed. As a consequence of this line of thought, an idealized product was defined having the following characteristics.

1. Can reduce contaminant concentrations quickly to regulatory standards.
2. Works in a variety of soil and groundwater conditions.
3. Is non-toxic and has no adverse impact on soil properties or groundwater quality.
4. Is applicable to a variety of contaminants.
5. Is reasonably cost-effective, at least in comparison to existing remedies.
6. Is a passive system, easily installed using equipment common to the industry.

The above six characteristics are the heart and sole of RPI's Trap & Treat® concept. The trap portion is designed around an immediate and predictable impact, observable in groundwater and soil after installation of the product. This aspect of BOS 200® is due to the presence of activated carbon in the product. In other words, the "Trap" is absorption by the activated carbon. Significant reductions in contaminant concentrations are typically realized in a matter of hours.

BOS 200® does not stop at stabilization of contamination. Absorption is just the first step in the process. Treatment is accomplished through biodegradation of the absorbed contaminants. In general, whenever the following conditions are present,

Microorganisms + Electron Donors + Electron Acceptors + Nutrients.

The result is metabolic by-products + energy + new microorganisms (Wiedemeier, 1999).

In this case, petroleum-degrading microorganisms are the "bugs" and hydrocarbon contaminants are the electron donors. Hydrocarbon degraders are very robust and can thrive under a wide range of conditions. In fact, they have been known to withstand pressures of hundreds of bars, pH conditions ranging from 1 to 10, temperatures from 0° to 75° C, and salinities greater than normal seawater (Freeze and Cherry, 1979). In the last decade, a great deal of research has been conducted on the role and importance of electron acceptors and nutrients within hydrocarbon plumes and the consensus is that the rate of biodegradation is limited by a lack of electron acceptors rather than a lack of nutrients. BOS 200® contains selected nutrients including phosphorus and nitrogen, and it contains a variety of electron acceptors that can be utilized under aerobic or anaerobic conditions.

A complete story of the electron acceptors must begin in the mixing tank. The product is shipped as a dry powder, which is mixed with water in the field to prepare an injectable slurry. One feature of activated carbon is that it has quite an affinity for oxygen. It adsorbs oxygen as the BOS 200® is manufactured, stored, and from the aerated water during the mixing operation. In short, the product is saturated with oxygen before injection into the contaminated formation. The product contains additional electron acceptors in the form of nitrate, ammonia and a time-release source of sulfate. The source of the time-release sulfate is gypsum or calcium sulfate.

Gypsum has been used by farmers for centuries as a soil conditioner and is not very soluble in water. However its solubility is such that a low but persistent concentration of sulfate can be maintained in groundwater for a number of years with a single application. A hidden benefit of this chemistry has to do with phosphorus. During manufacture, a small amount of ammonium phosphate is blended into the mix. This readily dissolves when mixed with water. However, calcium phosphate is virtually insoluble in water and so the available phosphate is rapidly precipitated out of solution, into and onto the activated carbon during the mixing operation. This provides a bio-available form of phosphorus (an essential nutrient) to the microorganisms that cannot be washed out by groundwater seep.

For thermodynamic reasons, microorganisms preferentially utilize those electron acceptors that provide the greatest amount of free energy during respiration (Bower 1992). The driving force for the biodegradation of petroleum hydrocarbons is the transfer of electrons from the donor (hydrocarbon) to the electron acceptor. The organism derives energy from this process and the more energy it can derive, the more attractive the process becomes. The high end of the energy spectrum is represented by aerobic utilization of oxygen as the electron acceptor. An overview of the next stops along the energy path is given by the following.

Nitrate reduction, Fe<sup>+3</sup> reduction, Sulfate reduction, and the last stop is given by methanogenic respiration.

The concept of respiration is important in that the organism literally breaths nitrate or sulfate while oxidizing hydrocarbons. In each case above, the energy derived decreases as one moves down from nitrate toward methanogenic respiration. It is clear that if oxygen is available, it will be the preferred electron acceptor. The catch is that organisms must be present that can take advantage of prevailing conditions at any given time. When the material is first injected, it is saturated with oxygen. Consequently, no matter what the prevailing condition is within the plume, the prevailing condition within the BOS 200® is initially aerobic. Once the oxygen is consumed, nitrate will become the next favored electron acceptor, finally settling into sulfate reduction along with some methanogenic respiration. This process can be short-circuited by a persistent source of a higher energy acceptor. For example, if a sustainable source of oxygen is available, the dominant mechanism for degradation will remain aerobic.

This points to an important concept. Much discussion in the literature is devoted to the apparent advantage indigenous microorganisms have over cultured bacteria that one might add to the mix. It is widely held that existing organisms have become accustomed to the prevailing condition and already “occupy the niche”. As a result, it is very hard for a new organism to take

over or to even get a foothold in the existing biocosm. In fact, the BOS 200 represents a new niche that is very attractive to bacteria. Bugs love activated carbon. We take advantage of this by mixing bacteria with the product when preparing the injectable slurry. The product is inoculated with bacteria before it is installed. This is an important step because the new niche is already occupied by bacteria designed to degrade hydrocarbons before it is installed. Shortly after installation, hydrocarbons are adsorbed and the niche is full.

RPI recommends and uses a specific blend of microorganisms with its product. It is a customized culture of facultative anaerobes that can take advantage of the wide swing in conditions presented by the installed BOS 200<sup>®</sup>. As a result, there are organisms present that can use the oxygen initially present. Further, there are nitrate reducers, iron reducers, sulfate reducers, fermenters, and methanogens. No matter what condition exists within the activated carbon, there are microorganisms present to take advantage.

Metabolic by-products vary depending on what metabolic pathway is being used for hydrocarbon degradation. Carbon dioxide and water are common although many other compounds are possible, including various alcohols and volatile fatty acids. Acetate turns out to be produced by aerobic conditions as well as by anaerobic fermentation, and under methanogenic respiration. Other products include lactate, formate, butyrate, isobutyrate, pyruvate, and propionate along with methane.

When BOS 200 is mixed with water, the resulting slurry has elevated concentrations of nitrate, sulfate, and chloride. This results in elevated concentrations in the groundwater wherever the material is injected. Under normal conditions, contaminant levels drop literally overnight. Initially, nitrate levels within the treatment area range from 50 ppm to perhaps as high as 250 ppm with sulfate ranging from 200 ppm to 1500 ppm. Chloride is initially somewhere between 50 ppm and 150 ppm. At first, microbes utilize oxygen. When oxygen is depleted, nitrate is the next highest energy electron acceptor. The first step in the de-nitrification is the formation of nitrite. Over the first month or two (post injection), nitrate levels typically drop and low levels of nitrite are often observed. The nitrite and nitrate are normally consumed within the first two months and nitrate falls to levels below regulatory standards. At about the same time, measurable levels of acetate can begin to show up. Finally, fermentation, sulfate reduction, and methanogenic respiration become the dominant pathways.

Regulators often postulate that the disappearance of nitrate is simply due to the natural dispersion from groundwater movement and diffusion. Chloride can be used as an internal measure of these effects as there are no biological demands for this species nor are there chemical demands that are commonly encountered in groundwater plumes. As a result, the behavior of chloride over time is a good indication of natural forces such as groundwater seep and diffusion. It should be noted that neither chloride nor nitrate is adsorbed by activated carbon. In fact, activated carbon is virtually transparent to charged inorganic species. As described above, nitrate typically plummets over the first two months, falling from an initial value of over 100 ppm to less than 5 ppm. Chloride, on the other hand, typically remains fairly stable over this same time period. Given such performance, it is hard to argue that the disappearance of nitrate is not due to its consumption in anaerobic respiration.