BIOREMEDIATION: ENVIRONMENTAL GROUNDWATER REMEDIATION

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BACKGROUND:

BIOREMEDIATION TECHNOLOGIES

BIOREMEDIATION OR BIODEGRADATION IS THE USE OF MICROORGANISM METABOLISM TO REMOVE POLLUTANTS. TECHNOLOGIES CAN BE GENERALLY CLASSIFIED AS IN SITU OR EX SITU. IN SITU BIOREMEDIATION INVOLVES TREATING THE CONTAMINATED MATERIAL (SOIL OR GROUNDWATER) IN PLACE, WHILE EX SITU INVOLVES THE REMOVAL OF THE CONTAMINATED MATERIAL (SOIL OR GROUNDWATER) TO BE TREATED. SOME EXAMPLES OF SPECIALIZED BIOREMEDIATION TECHNOLOGIES INCLUDE PHYTOREMEDIATION, BIOVENTING, BIOLEACHING, LANDFARMING, BIOREACTOR, COMPOSTING, BIOAUGMENTATION, RHIZOFILTRATION, AND BIOSTIMULATION. SAGE HAS EXTENSIVE EXPERIENCE IN DEVELOPING AND IMPLEMENTING BOTH NATURAL AND NUMEROUS TYPES OF SPECIALIZED BIOREMEDIATION PROGRAMS AND PROCESSES.

Bioremediation can occur on its own (natural attenuation or intrinsic bioremediation) or can be spurred on via the addition of nutrients to increase the bioavailability within the matrix material (biostimulation). Recent advancements have also proven successful, including the addition of matched microbe strains to the matrix material to enhance the resident microbe population's ability to break down contaminants. Microorganisms used to perform the function of bioremediation are known as bioremediators. It should be noted that not all contaminants are easily treated by bioremediation using microorganisms, including heavy metals such as cadmium and lead, which are not readily absorbed or captured by microorganisms.

Numerous field and laboratory studies have shown that organic-degrading microorganisms are pervasive in the subsurface environment and that these microorganisms can degrade a variety of organic compounds that are commonly associated with industrial facility groundwater contaminant plumes. Research conducted by the U.S. Air Force Center for Environmental Excellence, the Lawrence Livermore National Laboratories, Chevron Research and Technology Company, and the Texas Bureau of Economic Geology show that the majority (greater than 85 to 90%) of the organic dissolved-phase plumes present in the shallow subsurface of the United States are at steady-state equilibrium or are receding due to microbial biodegradation. In addition, Sage has performed numerous small and large scale bioremediation evaluations, developed and negotiated plans for regulatory approval, and implemented attenuation investigations that have identified the types and numbers of microbial colonies in groundwater which have transformed several mid and large-scale production remediation system into natural remediation monitoring-only programs.

MICROBIAL ATTENUATION

General water quality parameters measured in the field such as pH, temperature, oxidation-reduction potential (ORP), and specific conductivity are very helpful in evaluating if there is at least the potential that microbial attenuation is taking place in and near the dissolved-phase plume. Bacteria generally prefer specific environments in order to flourish; however, bacteria that degrade organics have been found to withstand pH conditions ranging from 1 to 10 standard units, temperatures from 10°C to 70°C, and salinities greater than those of normal seawater. All of these factors directly affect the solubility of oxygen and other geochemical species, as well the metabolic activity of bacteria. Biological activity roughly doubles for every 10°C increase in temperature over the temperature range between 5°C and 25°C.

The ORP of groundwater is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or transfer electrons. The ORP of groundwater changes with the predominant terminal electron-accepting process, with conditions becoming more reducing through the sequence Oxygen → Nitrate → Iron → Sulfate → Carbonate or:

$O_2+4e^-+4H^+ \rightarrow 2H_2O$	Oxygen	↗	$CaCO_3$
		↓	
$2NO_3^-+10e^-+12H^+ \rightarrow N2+6H2O$	Nitrate	↗	Nitrite
		↓	
$Fe(OH)_3+e^-+3H^+ \rightarrow Fe^{2+}+3H_2O$	Ferric Iron (Fe III)	↗	Ferrous Iron (Fe II)
		↓	
$SO_4^{2-}+8e^-+10H^+ \rightarrow H_2S+4H_2O$	Sulfate	↗	Sulfide
		↓	
		↓	
$2CH_2O \rightarrow CO_2+CH_4$	Methanogenesis	↗	Methane
		↘	
		↘	Alkalinity ↑↑↑

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This sequence is directly related to the depletion of electron acceptors and nutrients by microbial activity during the biodegradation of organics. Sage conducts minimal sampling of plume area wells in order to determine if (1) natural attenuation is occurring and to what degree, and (2) what stage of natural attenuation the plume is in. This information is then utilized to develop an attenuation plan and monitoring program for the purpose of determining when remediation is complete. The following is a general discussion of the key attenuation stages that need to be evaluating when determining a natural attenuation monitoring program:

OXYGEN: AEROBIC BIODEGRADATION

Data indicators that are usually available from typical compliance/detection/post-unit closure monitoring programs include dissolved oxygen and ORP. Contaminants are biodegraded aerobically when indigenous hydrocarbon-degrading microorganisms are supplied with the oxygen and nutrients necessary to use the contaminant as an energy source. As an example, in hydrocarbon impacted plumes, aerobic biodegradation changes aromatic hydrocarbons to carbon dioxide and water, and involves the use of oxygen as a co-substrate during the initial stages of hydrocarbon metabolism and, later in the process, as the terminal electron acceptor for energy production. Aerobic biodegradation primarily occurs around the edges of an organics plume because groundwater brings "fresh" supplies of oxygen to the periphery of the plume. The reduction of molecular oxygen is one of the most favorable and fastest of the oxidation-reduction reactions involved in dissolved organics biodegradation. Typically, aerobic biodegradation is readily taking place in the plume areas with dissolved organics and dissolved oxygen concentrations greater than 2 mg/L. Between 0.1 and 2 mg/L oxygen, biodegradation will take place but will be drastically limited by available oxygen.

NITRATE: DENITRIFICATION

Secondary indicators of natural attenuation include electron acceptors and their reduction products. Electron acceptors available for organic metabolism under anaerobic conditions include nitrate, sulfate, ferric iron, and carbon dioxide. Carbon dioxide, water, nitrogen gas, ferrous iron, hydrogen sulfide, and methane are some of the metabolic byproducts typically produced from the biodegradation of dissolved organics. The biodegradation of organics is limited primarily by electron acceptor availability. The purpose of collecting and evaluating these secondary indicator parameters is to determine the maturity or stage that the bioattenuation processes are at in the breakdown of the organic plume.

After almost all oxygen has been removed from an aquifer via aerobic respiration and anaerobic conditions dominate the dissolved plume geochemical landscape, nitrate is used as an electron acceptor by microorganisms that break down the organic plume via denitrification. A dissolved-phase plume of organics that does not contain nitrate indicates that the adaptation of the necessary bacterial population is occurring and quickly consuming the ambient concentrations of nitrate. Consequently, increasing concentrations of nitrite (the reduced form of nitrate) indicate which areas of the

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plume have experienced denitrification and which areas might be low on naturally occurring nitrate.

FERRIC IRON

Ferric iron is used as an electron acceptor after all the available oxygen and nitrate in an aquifer have been depleted. The best form of ferric iron for microbiological reduction is generally abundant in sedimentary systems, thus providing a large reservoir of potential electron acceptors to facilitate biodegradation of organics. The reduction of insoluble ferric iron (Fe III) by bacteria occurring in most groundwater systems produces soluble ferrous iron (Fe II). As with the nitrate:nitrite relationship discussed above, increasing concentrations of ferrous iron along with decreasing concentrations of ferric iron will indicate which areas of the plume have utilized all available oxygen, nitrate and iron in the biodegradation processes.

SULFATE

After available oxygen, nitrate, and ferric iron have been depleted in the groundwater system, sulfate-reducing bacteria can begin degrading organics. Decreases in ORP, along with dissolved oxygen and nitrate depletion, favor sulfate-reducing bacteria. Although the oxidation of organics by sulfate to sulfide reduction is thermodynamically favorable, it is not as favorable as aerobic respiration, denitrification, or iron. Areas of decreased sulfate corresponding to increased concentrations of sulfide indicate those areas that have used all available oxygen, nitrate, iron, and sulfate in the biodegradation processes.

METHANOGENESIS

If ideal conditions for sulfate reduction are not met, then methanogenesis will likely result in the biodegradation of the dissolved-phase hydrocarbon plume. Research shows that BTEX and a variety of other compounds can be degraded when methanogenesis is the terminal electron-accepting process. Methane gas samples are collected from the groundwater in and around the organic plume. The presence of methane in the groundwater at elevated concentrations is a good indicator of methane fermentation and is a positive indicator that natural attenuation is an ongoing and active process despite the lack of other nutrients.

Portions of an organics plume in which natural attenuation is actively occurring can be identified by an increase in alkalinity. An increase in alkalinity can be initiated by the production of carbon dioxide during the biodegradation of organic carbon. An increase in alkalinity, measured as $CaCO_3$, in an area with organic concentrations elevated over background conditions can be used to indicate the mass of organics destroyed through aerobic respiration, denitrification, Fe(III) reduction, and sulfate reduction.

Sage can develop a strong indication if a mobile portion of an organic plume has been removed by evaluating the existing historical mass and plume area information previouisly collected at a facility. Once the mass and area have stabilized over a period of time, it becomes much harder for the contaminants left to come out of the formation

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matrix, even under active remediation production. Sage can determine strong indications of what is happening within the plume can be determined by reviewing and evaluating the indicators of bioattenuation.

OUR SERVICES AND APPROACH:

BIOREMEDIATION EVALUATIONS

Sage has extensive experience in assisting clients through both the development and implementation of bioremediation evaluations based on both developing data and/or on existing historical data. Sage uses that evaluation to determine the best bioremediation process, develop a program of utilization, and negotiate the use of that process with the regulatory agencies, including the evolving an existing engineered remediation program into a natural attenuation monitoring program. We also take ongoing monitoring information and develop reports and system evaluations required by regulatory agencies.

Additional information concerning the use and process of bioremediation in groundwater remediation can be found in:

Sherrill, R., 2007, LNAPL Remediation – When is Enough, Enough?; Proceedings of The National Petroleum Refiners Association [NPRA}, ENV-07-110