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Preapproval Program Fiscal Update

In the 2009 legislative session, the Florida State Legislature redirected petroleum-tax funds from the Inland Protection Trust Fund (IPTF) into the State's General Fund. The result of these changes is that the Petroleum Preapproval Program will be funded through a bond from which approximately 90 million dollars is anticipated to be available for cleanup activities. Funds from the bond are estimated to be available sometime in the Fall of 2009.

In an effort to preserve the Preapproval Program during the period from July 1, 2009, until the bond funds become available, the Florida Department of Environmental Protection (FDEP) has developed a method to "re-tool" the program. The modifications are presented in a document titled *Revised Petroleum Cleanup Preapproval Program Procedure Modifications to Address the FY 2009-2010 Budget Reduction*. The final version of this document can be found at:

http://www.dep.state.fl.us/waste/categories/pcp/pages/announcements.htm

Some of the main points of this document that affect the normal Preapproval work load are summarized in the following paragraphs.

Effective May 14, 2009, the priority score was raised from 45 to 60. Existing Work Orders and Task Assignments will not be modified. However, proposal preparation can continue for sites scored 56 and above. Proposals for sites with a priority score of 60 or greater will proceed while those with scores between 56 and 59 will be held in the queue pending available funds. Previously requested proposals from sites scored 55 and below will be converted to pay for the proposal preparation fee only. Similarly, Preapproved Advance Cleanup (PAC) work orders can be prepared in anticipation of funding. Work orders will be limited to $150,000 instead of the previous $250,000 cap.

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The approval authority of a Verbal Authorization for Change in Scope of Work (VCO) has changed as well. VCO's can only be considered if deemed necessary to complete the scope of work specified by the Work Order. For example, supplemental site assessment cannot be added to an Operations and Maintenance (O&M) Work Order. The monetary amount of the VCO shall not increase the total value of the Work Order (or split Work Order), so the costs proposed must be offset with a reduction to another part of the Work Order.

New O&M and Post-Active Remediation Monitoring (PARM) Work Orders/Task Assignments will be written for one quarter only. The pre-existing exceptions for continuing work at lower scored sites (greater than 30) will remain in effect.

All sites with active Remedial Action Incentive (RAI) remediation systems are to be evaluated for performance. Those not meeting RAI requirements will be evaluated on a case-by-case basis and a determination will be made as to whether to modify the system or cancel the remaining unperformed work.

For remedial action construction work orders on sites scored 60 and above, it is a requirement to utilize existing state-owned equipment. Chemical or biological remediation proposals will not be processed into work orders unless the prime contractor executes a performance-based cleanup (PBC). Existing systems will be evaluated based on performance. Exceptions may be made on a case-by-case basis to resolve low-level concentrations for the purpose of polishing a site in anticipation of a Site Rehabilitation Completion Order.

The Procedure Modifications Document contains additional details which can be reviewed at the FDEP webpage link shown above. Questions regarding this article can be directed to John J. Gomolka, P.G. at (954) 519-1279 or jgomolka@broward.org.

Searchable City Directories Database Available at Broward's Main Library

Environmental Consultants performing property assessments in Broward County can now utilize a free service allowing easier access to historical city directories through an electronic database available at Broward County's Main Library. These directories can be viewed at the Business, Law, and Government Section on the Fifth Floor of the Main Library at 100 South Andrews Avenue in Fort Lauderdale.

The City Directories database gives the public access to names, phone numbers, and addresses from cities in both Broward and Miami-Dade counties. City directory information in Broward County is available for the Fort Lauderdale, Pompano Beach, Hollywood, and Suburban Fort Lauderdale directories.

The dates of the directories are as follows:

- Fort Lauderdale: 1936-1937 through 1981
- Hollywood: 1940 through 1983
- Fort Lauderdale Suburban: 1975 through 1986
- Pompano Beach: 1955 through 1982

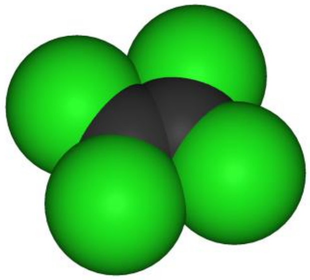
Additionally, those who are interested in Miami-Dade County will find that the database provides information on Miami, Miami Beach, Miami Suburban, Miami North Suburban, and Miami South Suburban. The Miami databases cover 1904 to 1989.

The Broward County Main Library is currently open Monday, Tuesday, and Wednesday from 10:00 a.m. to 8:00 p.m.; Thursday, Friday, and Saturday from 10:00 a.m. to 6:00 p.m.; and Sunday from 1:00 p.m. to 5:00 p.m.

For more information, visit the links below or contact Ray Ledbetter, Ph.D., at (954) 519-1445 or rledbetter@broward.org.

Links: http://www.broward.org/library/pdfs/mn_citydirectories.pdf
http://www.broward.org/library/

Indicator Parameters for Bioremediation of Chlorinated Ethenes in Groundwater



A common method of cleaning up chlorinated solvent contamination in groundwater is through naturally occurring or enhanced bioremediation. Generally, direct anaerobic reductive dechlorination is a biodegradation reaction in which bacteria (halorespirers that can "respire' chlorinated compounds in the same manner aerobic organisms "respire" oxygen) gain energy and grow as a chlorine atom in a chlorinated hydrocarbon (electron acceptor) is replaced with a hydrogen atom in an environment devoid of oxygen. Hydrogen is usually provided by the fermentation of an organic substrate.

Reductive dechlorination of chlorinated ethenes such as tetrachloroethene, trichloroethene, cis-1,2-dichloroethene, and vinyl chloride is a step process in which "parent" compounds transform into "daughter" compounds in generally sequential reactions, with each reaction occurring slower and yielding less energy than the previous reaction. Additional information about chlorinated solvents and the degradation pathways was presented in the January/February 2002 edition of this newsletter, which is available at: http://www.broward.org/pprd/cs_remediationtimes_archive.htm#2002. It is worth mentioning that evidence exists in literature that vinyl chloride biodegradation may better occur in an aerobic (oxidizing) environment, and this must be kept in mind when attempting to generalize the data evaluation paths discussed below.

The basic requirements for a successful anaerobic bioremediation include the presence of sufficient electron acceptors (chlorinated ethenes), electron donors, a source of carbon, adequate groundwater geochemistry, enough nutrients to promote bacteria growth, and a capable microbial community. While anaerobic reductive dechlorination may occur naturally under proper conditions, it can be enhanced by the addition of electron donors, carbon sources, and nutrients, and it can be augmented by the addition of an appropriate microbial community.

There are several common ways to properly collect and interpret data to evaluate if passive or enhanced/augmented anaerobic biodegradation in groundwater impacted with chlorinated ethenes is occurring effectively. The most logical approach is to measure changes in contaminant concentrations and/or mass over time. Since mass or concentration reduction may be influenced by factors other than biodegradation (such as dissolution and dispersion), other lines of evidence are also commonly used. One of these lines of evidence is groundwater geochemistry, which is discussed in this article. If the effectiveness of enhanced/augmented bioremediation is to be evaluated, background conditions must be characterized before the addition of any substances to the aquifer.

The objective of this article is to summarize information already presented in the research literature as referenced. Any analysis should also evaluate the effectiveness of the bioremediation by measuring contaminant concentrations over time, although this aspect is not discussed in this article.

Even though literature attempts to establish values or ranges for individual geochemical indicators that can be indicative of reductive dechlorination, it is recommended that as many parameters as possible be used simultaneously. This approach not only looks at the "big picture", but it also somewhat reduces the variability of results inherent to groundwater sampling and analysis.

INDICATOR PARAMETERS

In reductive dechlorination, chlorinated ethenes compete with native electron acceptors such as dissolved oxygen (DO), nitrate, iron (III), sulfate, and carbon dioxide (from most-to-least thermodynamically favored). These electron acceptors are theoretically used by microbes to biodegrade organic carbon, whether naturally occurring or anthropogenic. Generalizing, in order for the chlorinated ethenes to be preferentially utilized by anaerobic bacteria as electron acceptors, the concentrations of competing electron acceptors need to be naturally low or reduced. Therefore, it is important to have a source of carbon in the aquifer, either natural or enhanced, to satisfy the demand of processes dominated by these competing electron acceptors.

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Dissolved Oxygen (DO)

DO measurements provide an indication if the environment is oxidizing (aerobic) or reducing (anaerobic). DO is the most thermodynamically favored electron acceptor and as such it is quickly consumed in biotic processes. Generally, a DO concentration >0.5 milligrams per liter (mg/l) may prevent anaerobic bacteria from "functioning". Some publications state that at DO values of <2 mg/l, anaerobic conditions may be present. It is reported that DO levels <0.1 mg/l may reflect strong evidence that reductive dechlorination exists.

Nitrate (NO_3^-)

After DO is depleted, the next most predominant competing electron acceptor is nitrate. At nitrate concentrations of greater than approximately 1 mg/l anaerobic dechlorination may not occur, and it is highly unlikely to occur at nitrate concentration >3 mg/l.

Iron

Even though iron (III) is an electron acceptor, it is typically in solid form and therefore it cannot be measured and interpreted in groundwater samples. Since iron (III) reduces (gains electrons) to iron (II), which is soluble in water, iron (II) is used as an indicator of anaerobic biodegradation. It must be kept in mind when evaluating iron (II) that it may precipitate, which would reflect in lower measured concentrations in the groundwater. Iron (II) concentrations of >1 mg/l may be indicative of an environment conducive to reductive dechlorination as it may reflect that competing iron (III) has been reduced.

Sulfate (SO_4^{2-}) and Sulfide (S^{2-})

Anaerobic dechlorination will typically and most effectively occur under sulfate-reducing and methanogenic conditions. As sulfate accepts electrons, it reduces to sulfide. In general, sulfate concentrations of >20 mg/l and sulfide concentration of <1 mg/l may exclude reductive dechlorination from occurring.

Methane

Methane is usually utilized as an indicator for carbon dioxide, as it is a product of reduction. This process is commonly referred to as "methanogenesis". The presence of methane at levels >5 mg/l is strong evidence of reducing conditions, but care should be exercised when evaluating methane because elevated concentrations may be a result of methanogens (organisms that use hydrogen as electron donor and produce methane as a metabolic byproduct in oxygen deficient conditions) acting at the expense of dechlorinating microorganisms.

Oxidation-Reduction Potential (ORP)

ORP is an indicator of the relative tendency of a solution to accept or transfer electrons. Thus, it can be used to indicate oxidizing or reducing conditions in the saturated zone. ORP is expressed as Eh (which is the oxidation potential in relation to the standard hydrogen electrode) and is measured in millivolts (mV). In general, the lower the ORP value is, the more conducive the environment is to reductive dechlorination. Each of the sequential steps of reductive dechlorination (tetrachloroethene to trichloroethene to cis-1,2-dichloroethene to vinyl chloride) requires an environment with a lower ORP. Typically, an ORP of less than -200 mV (sulfate-reducing and methanogenic conditions) is required for reductive dechlorination to be expected to occur.

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ORP values have been generally correlated to each of the different electron acceptor processes previously discussed. Literature such as Reference (1) presents ORP ranges as they correlate to different electron-acceptor processes. When evaluating these ORP values, special attention is needed to determine if measured ORP values and ranges/values presented in the literature are on the same "basis". Discussions in the literature of ORP ranges/values may be presented as measured against a standard hydrogen electrode while field OPR values may use a silver/silver chloride electrode as reference.

A word of caution: ORP is highly sensitive to different parameters, including oxygen. DO and ORP values may provide conflicting results if the sample becomes aerated during collection.

pH

Halorespiring bacteria seem to work in a pH range from 5 to 9 pH units, with an optimal range for reductive dechlorination of 6 to 8 pH units. As microbiological activity increases, hydrogen ions are generated that may cause a lowering of pH.

Alkalinity

The alkalinity concentration (typically expressed as an equivalent concentration of mg/l as $CaCO_3$) is an indicator of a solution's ability to neutralize acids. During microbial respiration, carbon dioxide, carbonate and bicarbonate are produced. Therefore, an increase in alkalinity may be indicative of microbial growth. In addition, organic acids produced during fermentation of organic matter may cause naturally-occurring carbonates in soil (such as calcite and limestone) to dissolve into the groundwater and increase the alkalinity. Alkalinity concentrations that are twice the background concentration may be indicative of biological activity. Alkalinity is an indicator of the buffering capacity of the aquifer, which may be necessary to control pH changes. Alkalinity greater than 300 mg/l is usually sufficient to prevent the pH from decreasing below the optimal range for dechlorination.

Chloride (Cl^-)

In the biodegradation of chlorinated hydrocarbons in groundwater, chloride is a daughter product of the chlorine that is released as a product of reductive dechlorination. A chloride concentration of twice the background concentration may be indicative of reductive dechlorination. Chloride ions exhibit relatively neutral chemical behavior so their migration is controlled by physical processes. Therefore, chloride concentrations can be used as tracers in the estimation of biodegradation rates.

Organic Carbon

Total or dissolved organic carbon can be used as indicators to determine natural carbon levels present in the aquifer as well as the distribution of any substrate carbon source that may have been added. Concentrations of 20 mg/l to 50 mg/l are desired for effective bioremediation.

Hydrogen

Hydrogen is produced by fermentation in which microorganisms decompose organic matter. Hydrogen is the primary electron donor utilized in reductive dechlorination. Hydrogen levels between 2 and 11 nanomols per liter (nM/l) are conducive to efficient reductive dechlorination. Hydrogen is also very useful in determining different zones of a contaminant plume that may be undergoing different electron-acceptor processes. Table 2.5 in Reference (2) presents hydrogen concentrations characteristic to each of the electron-acceptor processes.

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Indicator Parameters, continued from Page 5

SUMMARY

The table below very generally summarizes the guidelines for evaluating whether the bioremediation indicator parameters discussed in this article are conducive to reductive dechlorination. Different literature sources present varying values for these parameters, so the values listed below should be utilized as rules-of-thumb and not as absolute criteria for remediation design.

Indicator Parameter	Guideline Values for Anaerobic Dechlorination
Dissolved Oxygen (DO)	Should be < 0.5 mg/l
Nitrate	Should be < 1 mg/l
Iron	Fe(II) should be > 1 mg/l
Sulfate and Sulfide	Sulfate should be < 20 mg/l Sulfide should be > 1 mg/l
Methane	Should be > 5 mg/l
Oxidation-Reduction Potential (ORP)	Should be < -200 mV
pH	Should be between 6 and 8
Alkalinity	Concentrations that are twice the background concentration may indicate biological activity. Should be > 300 mg/l for pH buffering
Chloride	Concentrations that are twice the background concentration may indicate reductive dechlorination. Can be used to trace biodegradation
Organic Carbon	Should be between 20 mg/l and 50 mg/l
Hydrogen	Should be between 2 and 11 nanomols/l

By no means is it the intent here to present all parameters that may be useful in evaluating reductive dechlorination. Others, such as fatty acids, microbial population, and nutrients (such as nitrogen and phosphorous) are also available as indicators. It is recommended that as many indicators as possible be used simultaneously to evaluate whether dechlorination is occurring.

Questions regarding this article can be directed to Norman Arrazola, P.E., at (954) 519-1237 or narrazola@broward.org.

References

(1) Interstate Technology & Regulatory Council. August 2002. "A Systematic Approach to In Situ Bioremediation in Groundwater".

(2) Environmental Protection Agency. September 1998. "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater". Office of Research and Development, EPA/600/R-98/128.

(3) Environmental Protection Agency. July 2000 (revised). "Engineered Approaches to *In Situ* Bioremediation of Chlorinated Solvents: Fundamentals and Field Applications". Solid Waste and Emergency Response, EPA 542-R-00-008.

(4) Interstate Technology & Regulatory Council. December 1998 (final). "Technical and Regulatory Requirements for Enhanced In Situ Bioremediation of Chlorinated Solvents in Groundwater".

(5) Interstate Technology & Regulatory Council. October 2005. "Overview of In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones".