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Risk assessment and management frameworks

This article summarizes the key points from a comparative analysis of seven major risk assessment/risk management frameworks from the United States, Canada, the United Kingdom, the Netherlands, Australia and New Zealand *(Power and McCarty, 1998)*.

One of the most important environmental policy developments in the past decade has been risk assessment/risk management. People now recognize that their activities depend upon and have consequences for the environment. Human activity has impacts on "sociopolitical institutions and environmentally dependent systems such as the economy, human health and natural ecosystems at different spatial and temporal scales. The resulting range of issues that need to be considered when assessing potential impacts has driven the development of environmental assessment frameworks in many countries" *(Power and McCarty, 1998).*

Power and McCarty compared the risk assessment/risk management frameworks of seven government organizations:

- The Netherlands
- The U.S. EPA
- Australia/New Zealand
- U.K. Department of the Environment
- U.S. National Research Council
- Canadian Standards Association
- U.S. Risk Commission

These frameworks were initially designed to prevent or reduce risk and supply information to the risk management process. More recent frameworks have improved risk management in terms of risk characterization, decision making and management.

Researchers found that all of the frameworks stressed "the fundamental importance of appropriately conducted and reviewed scientific practice. Not all [frameworks] agree on the primacy or separation of science from policy. . . Some frameworks view science as not wholly objective because it is capable of influencing and being influenced by the social milieu in which it operates." According to Power and McCarty *(1998), "*Frameworks that favor isolating science from management tend to place little emphasis on stakeholder consultations or the inclusion of anything other than technical information in assessment scoping. In such frameworks, societal views are recognized but are incorporated into the assessment/management process separately from science . . . The temporal trend has been toward the development of more inclusive processes, less dominated by technocratic practice, which ask those affected by risk to participate in the selection of risk management options capable of meeting multiple social goals. Proposed changes to the EPA framework are consistent with this trend."

Environmental risk initially focused on quantitative estimates; now the risk assessment focus is on "balancing multiple social interests to achieve consensus. . ." Attitudes toward risk characterization, uncertainty analysis and incorporation of socioeconomic information have changed. Limited resources for risk management and improved risk assessment have made it necessary to ensure that risk reductions are achieved at reasonable cost. Thus, a cost-benefit analysis is usually included in the decision making. Power and McCarty state that "while recognizing the role of economic analysis, frameworks that include it are careful to note that it should not be the overriding determinant in decision making."

"All frameworks agree that the uncertainty associated with risk estimates must be stated. At issue is whether such statements should be primarily qualitative or quantitative in nature. . . The earlier frameworks do not explicitly recognize iteration between analytical steps, although the proposed EPA guideline changes have specifically stressed iteration. They allow for limited iteration within steps and view monitoring as a quality control issue, not a trigger for assessment revision. In part, this is because earlier frameworks viewed assessment as a technocratic exercise dominated by logical deductive processes. In contrast, later frameworks have stylized risk assessment/management as a largely deliberative decision-making process."

The authors stress that "deliberative processes by nature involve information exchange, refinement of views, and evolution toward a consensus. They are dynamic and should include feedback loops within and between analytical phases. . . . A lack of understanding of risk and inability to predict it precisely mandate a more cautious approach to management issues. More important, they point to the need to include human values, to act prior to achieving scientific consensus and to confront the essentially political, social and economic roots of environmental issues."

Reference

Power, M. and L.S. McCarty, "A Comparative Analysis of Environmental Risk Assessment/Risk Management Frameworks," *Environmental Science & Technology*, May 1, 1998; 703-552-0685; http://www.pubs.acs.org.

Low-level and synergistic chemical exposure

Some scientists are beginning to question the human health impact of low-level chemical exposure in the environment. This article summarizes some ideas derived from editorials published in *Environmental Science & Technology* and *Ground Water Monitoring and Review*.

Ashford and Miller *(1998)* contend that evidence indicates "that human exposure to chemicals at even low levels can be harmful. Such exposures are linked with adverse biological effects, which include

- endocrine disruption
- chemical sensitivity
- cancer

According to the authors, "Prior susceptibility of an individual, whether inborn or environmentally induced, followed by other lifetime exposures, can cause irreversible injury. Unfortunately although emerging scientific knowledge associated with these exposures indicates a need to change the way we think about chemicals and health, new theories are slow to emerge. We are just now beginning to recognize the link between chemicals and new public health problems that challenge the tenets of traditional toxicology and medicine." These emerging health problems share characteristics that fall into the following categories:

- nature
- cause
- time
- nonclassical explanation
- disease processes

Nature. These health problems involve the endocrine system, the immune system and the neurological system rather than specific organs of the body.

Cause. "No single cause has been identified for each of these conditions. Often there are no clear biomarkers for either exposure or disease. Consequently, classical epidemiology is less able to identify susceptible or sensitive subgroups."

Stages. "Disease becomes manifest after two or more stages or events occur. . . It has been hypothesized that Toxicant-Induced Loss of Tolerance (TILT, a new theory of disease), leading to chemical sensitivity, also proceeds via a two-stage process: an initial exposure to high levels of certain chemicals (or repeated exposures at lower levels) followed by triggering of symptoms by everyday chemical exposures at levels that do not appear to affect most people."

Time. "The time between the first and subsequent stages of disease can be long enough to obscure the connection between exposures and ultimate disease. . . Chemical sensitivity reportedly can develop months after the initial exposure and remain manifest for years. The timing of the initiating dose does appear important. Loss of tolerance does not always require a high initial dose; smaller doses, strategically timed, might also cause pathological loss of tolerance."

Nonclassical explanation. "Classical approaches and models used in both toxicology and epidemiology, premised on single agents disrupting individual organs, do not explain these diseases. Moreover, the relationship between the initiating exposure and ultimate health effects is not monotonic [uninterrupted repetition]. . . Endocrine disruption (ED), TILT and some cancers appear to represent a failure in functional and adaptive processes in important systems or networks as a result of chemical exposures that are concentrations 3 to 6 orders of magnitude lower than those associated with classical toxic effects in normal individuals. Moreover, individuals simultaneously exposed below safe thresholds to multiple xenobiotics, as in a sick building, are affected."

Disease processes. "Endocrine disruption (ED), TILT and some cancers may be interrelated. ED disrupts normal development and possibly the immune system, which results in increased susceptibility to certain cancers. ED might also affect the neurological system, leading to increased susceptibility to sensitization by chemicals. TILT manifests itself as a loss of tolerance to everyday chemical, food and drug exposures in affected persons, possibly leaving these individuals more susceptible to other diseases. . . [and] key systems of the body appear to lose their ability to adapt to low-level chemical exposures. Finally, cancer proceeds when adaptive, homeostatic repair processes and the immune system no longer function as they should, although the cause of this loss of protective function is not well understood" *(Power and McCarty, 1998)*

Developing a new policy

Ashford and Miller *(1998)* assert that "Lack of clear biomarkers and the time lag between initiating exposures and ultimate disease make it technically and politically difficult to develop evidence needed for regulating many chemicals. . ." They advocate adoption of a "precautionary principle" because it acts "preventively in the face of uncertainty." They stress that endocrine-disrupting chemicals have negatively impacted human health and that addressing problems now gives the opportunity to act quickly. "Some aspects of the endocrine disruption and other systemic damage or injury remain uncertain, and potentially regulated industries are opposed to costly controls. Nonetheless, rapid intervention to prevent the next generation of developmentally compromised or chemically intolerant individuals is possible and advisable. Uncertainty and economic concerns may appear to pose a dilemma for environmental legislators and regulators (they may fail to regulate a chemical that is later discovered to be harmful, or they may, at cost to industry and consumers, regulate a chemical and later find that the chemical is safe to use), but potentially harmful chemicals should be regulated when scientific evidence, although imperfect, is compelling."

Ashford and Miller *(1998)* advocate the following:

- policies that are harmonized and coordinated among the major stakeholders
- a new corporate stewardship that is harmonized with the customers' and the public's expectations that companies will adhere to the precautionary principle
- government's return to its role as a trustee of the environment, public health, and sustainability and direct its interventions and research support to all phases of multistage disease
- accurate media reporting of the complexities of scientific understanding
- public-interest-group and non-governmental-organizations efforts to strengthen linkages among disparate groups and to continue their role as educators and advocates for precautionary protections
- commitment of the international community to a program of relevant research and to multilateral environmental agreements

Complacency?

In another editorial from *Ground Water Monitoring and Remediation*, Dr. Micheal Barcelona *(1999)* warns groundwater professionals not to be complacent. "Real gains have been made in balancing costs and benefits in subsurface remediation programs. However, more in-depth understanding of the behavior of contaminant mixtures, even in 'simple' hydrogeologic systems, is needed to minimize long-term environmental or human health risk. It's definitely not a time to become complacent with our current understanding of contaminant fate and transport processes. . ."

Barcelona cites two reasons for cautioning groundwater professionals against "historical myopia":

- approved analytical methods for organic contaminants mainly detect volatile or sparingly soluble compounds
- there are always unforeseen hydrogeologic, chemical, or biological consequences of active treatment processes

Approved analytical methods for organic contaminants mainly detect volatile or sparingly soluble compounds. "Rarely has more than 10 percent of the dissolved organic content of groundwater been identified. Very soluble compounds (e.g. acids, alcohols, aldehydes, amines, ketones, etc.) with considerable biological and chemical reactivity are almost never reported or considered in risk estimates for their impact on possible remedial options. Numerous observations of MTBE in groundwater, which are associated with dissolved fuel components, should alert us to the presence of unreported compounds that influence oxygen, iron III, nitrate and other electron acceptor concentrations, sorption and source release terms, and overall biological activity or biomass within plumes. These compounds may be responsible for synergistic or agonistic effects in exposures. Either effect would render meaningless our estimates of reference dosages or cancer slope factors for risk determination. We should be clear in our qualified definition of and solutions to problems where BTEX compounds (or TPH for that matter) alone have been documented" *(Barcelona, 1999)*.

There are always unforeseen hydrogeologic, chemical, or biological consequences of active treatment processes. Chlorine used to disinfect drinking water, for example, reacts with natural organic compounds in the water to produce by-products such as chloroform, trihalocetonitriles, and chlorophenols. These chemicals can significantly affect human health. "Given the complexity of petroleum products, industrial formulations or landfill leachate mixtures in sediments or groundwater, we should all be well advised to keep up with the literature in other fields that may alert us to unintended treatment consequences. For example, in the petroleum hydrocarbon area, the growing use of forensic analysis methods to supplement "approved" methods has been quite fruitful in source estimation and product differentiation" *(Barcelona, 1999)*.

References

Ashford, N.A. and C.S. Miller, "Low-Level Chemical Exposures: A Challenge for Science and Policy," *Environmental Science & Technology*, November 1, 1998; 703-552-0685; http://www.pubs.acs.org.

Barcelona, M.J., "Beyond BTEX," *Ground Water Monitoring and Remediation*, Winter, 1999; 614-898-7791; http://www.ngwa.org/journals.

New ASTM/OUST guidance

RBCA Fate and Transport Models: Compendium and Selection Guidance, funded and technically coordinated by OUST, has recently been published by the American Society of Testing and Materials. This guidance provides a compendium of commonly used fate and transport models and information on model selection for risk-based corrective action (RBCA) processes. Audiences with varying levels of experience in fate and transport modeling will find the guidance helpful. It addresses all chemical fate and transport pathways including vapor migration, soil leaching and groundwater transport pathways. It also gives easy-to-use comparison tables, and matrices and flowcharts that compare model specifics such as governing equations, applicability, key/sensitive input parameters, model output format and model limitations.

States, EPA and National Partnership in RBCA Implementation (PIRI) reviewed the guidance. It is available to government and the public at no cost by contacting EPA's National Service Center for Environmental Publications, 800-490-9198.
The private sector may obtain copies by contacting ASTM at 610-832-9685. The document can also be downloaded from OUST's home page at http://www.epa.gov/oust/rbdm/rbdmfnt.htm.

Aquatic risk assessment

This article, by an ecotoxicologist with the Centre for Environment, Fisheries and Aquaculture Science, United Kingdom, questions if risk assessments adequately address the contaminant problems of ecosystems. The author describes some misperceptions concerning risk assessments and, in particular, risk assessments of aquatic environments.

Current scientific efforts promote the view that the use of risk assessments "provides the best practical approach for ecosystem protection. Ever more complex assessment strategies are being developed, refining knowledge of hazards as well as predictions of environmental exposure and combining them in increasingly sophisticated ways to produce risk estimates. Much of this undertaking has been driven by public concerns, such as that which arose in response to environmental disasters caused by poor management practices and imperfect knowledge of chemical modes of action and behavior. Ecotoxicologists and environmental chemists responded to these emergent problems by developing improved testing regimes designed to eliminate or better manage future uses of harmful materials. Although far from being a reliable science, the assessments are definitely screening out some undesirable chemicals or at least their risky uses" *(Matthiessen, 1998)*.

Matthiessen questions if the risk assessment approach prevents significant environmental degradation and if the use of even more sophisticated testing programs will be justified. "Few environmental investigations and monitoring programs are explicitly designed to test whether chemical risk assessments are working as intended." From this, the author raises the following points:

- significant fallacies are embedded in the risk assessment models
- the significance of environmental mixtures is generally ignored
- risk assessors, by default, generally assume scenarios in which new chemicals enter a pristine ecosystem—one into which anthropogenic chemicals have not previously been discharged
- it is difficult to account for the effects of chemical mixtures in the environment

The author makes the following observations:

- one estuary in the United Kingdom is acutely toxic primarily because of contamination by at least seven different organic substances; researchers have not found that toxicity in estuaries or offshore is due solely to a single contaminant
- the consistent and more or less ubiquitous nature of water and sediment toxicity in industrialized estuaries suggests that contamination cannot generally be attributed to occasional accidental spills; rather it must be largely the result of routine contemporary discharges of a mixture of mainly synthetic chemicals
- substances usually being discharged in individually harmless concentrations are acting together in discharges and receiving water to produce lethal and sublethal consequences
- a proportion of this toxicity must be caused by chemicals that have never received any risk assessment or management

The above observations suggest that "reliance upon currently formulated risk assessments is not entirely an effective measure for preventing environmental impacts" *(Matthiessen, 1998)*. The author finds this situation unacceptable, yet he does not advocate a comprehensive ban on chemical discharge; rather, he advocates using sentinel organisms to warn the environmental agencies of potential ecological deterioration. "Only biological systems can provide the integrated information that tells us whether a particular effluent or waterway contains a harmful mix of chemicals, and only bioassay-led chemical fractionation investigations can identify which substances are responsible for the observed effects."

In conclusion, Matthiessen *(1998)* states: "Environmental risk assessments of chemicals have flaws that probably cannot be addressed by tinkering with models. Rather than relying solely on increasingly sophisticated risk assessments, we should consider. . . performing direct toxicity assessment (DTA) of complex discharges and quality assessment of receiving waters . . . The use of DTA responds to the insufficiency of chemical risk assessment and monitoring for preventing environmental impacts. DTA detects and identifies major pollutant problems before they have a chance to cause extensive damage. . . Environmental risk assessment of chemicals is working, but only up to a point. We must recognize its limitations and emplace additional measures that can identify substances that are slipping through the net."

Reference

Matthiessen, R., "Aquatic Risk Assessment of Chemicals: Is it Working?" *Environmental Science & Technology*, October 1, 1998; 703-552-0685; http://www.pubs.acs.org.

Iron and sulfate mineralogical analyses for natural attenuation studies

Quantifying the amount of iron (Fe^{3+})and sulfate (SO_4^{2-}) reduced in some bioremedial environments may be important. This information could be used to

- determine which microbiological redox processes are or have been active
- evaluate the mass of hydrocarbon (or organic contaminant) that has been destroyed for a specific redox condition, expressed as capacity
- estimate the future ability of an aquifer system to degrade hydrocarbons through specific redox processes (i.e., assimilative capacity)

Kennedy and others *(1998)* recently developed a method that involves quantifying mineralogical changes to more accurately track Fe^{3+} to Fe^{2+} and sulfide species reductions. This article briefly describes this method, but more importantly, it describes the iron and sulfate geochemistry of subsurface environments.

Review of oxidation/reduction (redox) reactions

Intrinsic bioremediation is that part of natural attenuation involving interaction between the chemical contaminants and bacteria. Reactions between the bacteria and chemicals are simple oxidation/reduction (redox) reactions.

According to Daintith *(1990),* "Originally oxidation was simply regarded as a chemical reaction with oxygen. The reverse process—loss of oxygen—was called reduction. Reaction with hydrogen also came to be regarded as reduction. Later, a more general idea of oxidation and reduction was developed in which oxidation was loss of electrons and reduction was gain of electrons . . . These definitions of oxidation and reduction apply only to reactions in which electron transfer occurs—i.e., to reactions involving ions. It can be extended to reactions between covalent compounds by using the concept of oxidation number (or state). This is a measure of the electron control that an atom has in a compound compared to the atom in the pure element."

An oxidation number has two parts:

- its sign, which indicates whether the control has increased (negative) or decreased (positive)
- its value, which gives the number of electrons over which control has changed

"The change of electron control may be complete (in ionic compounds) or partial (in covalent compounds). For example, in SO_2 the sulfur has an oxidation number +4, having gained partial control over 4 electrons compared to the sulfur atoms in pure sulfur. The oxygen has an oxidation number –2, each oxygen having lost partial control over 2 electrons compared to oxygen atoms in gaseous oxygen. Oxidation is a reaction involving an increase in oxidation number whereas reduction involves a decrease. Thus in

$$2H_2 + O_2 \rightarrow 2H_2O$$

the hydrogen in water is +1 and the oxygen is –2. The hydrogen is oxidized and oxygen reduced" *(Daintith, 1990)*.

Oxidation/reduction reactions with emphasis on iron and sulfate

Organic contaminants being bioremediated donate electrons, that is, the organic contaminants are oxidized. The electron acceptors, listed by ease of redox, are by convention:

- O_2 (oxygen)
- NO_3^- (nitrate)
- Mn^{4+} (manganese)
- Fe^{3+} (iron III)
- SO_4^{2-} (sulfate)
- methanogenesis

Thus, O_2 will preferentially gain electrons before the nitrate and so on. Kennedy and others *(1998),* however, suggest that iron may be an exception to this rule. "Fe^{3+}-reducing organisms may slowly reduce crystalline Fe^{3+} forms, such as goethite and hematite, in systems that are otherwise dominated by sulfate reduction or even methanogenesis . . . However, this redox succession is believed to be thermodynamically related. The amount of free energy (delta G^o) that can be generated for each of these oxidation/reduction reactions decreases for each successive electron acceptor couple. The bacterial type capable of deriving the most energy per unit organic redox acceptor reduced has a natural advantage over the other types and may dominate the local environment. A lower energy-yielding electron acceptor is substantially utilized only if an electron acceptor of a higher energy level has been substantially consumed."

Fe^{3+} reduction may depend on the following:

- the form or state of the iron
  - dissolved or chelated iron may be more biologically reactive than solid forms
  - amorphous Fe^{3+} will be reduced preferentially over more crystalline forms, depending on the different amounts of free energy that the iron provides to bacteria; in ascending order of crystallinity are the following iron forms:
    - ferrihydrite rust (FeOOH)
    - lepidocrocite and akageneite λ- and β-FeOOH
    - goethite α-FeOOH
    - hematite α-(Fe_2O_3)
- environmental conditions; for instance, Fe^{3+} is very insoluble in near-neutral pH conditions usually found in groundwater; it is required for optimum heterotrophic bacterial growth

- surface area available; decreased surface area of the more crystalline forms may decrease biological utilization
- spatial distribution to permit microbial access; for instance, if Fe^{3+} appears as a coating on silicate minerals, only the outermost coating may be immediately accessible to bacteria
- time; the total amount of Fe^{3+} reduced may be ultimately time dependent; sites contaminated for years show continued Fe^{3+} reduction, suggesting continued slow utilization of native Fe^{3+}

Only a portion of the total iron present in an aquifer, however, is amenable to direct enzymatic reduction; thus, the term "biologically available iron," although convenient, is difficult to quantify because of the variables involved. Furthermore, the product of Fe^{3+} reduction is Fe^{2+}; Fe^{2+} is poorly represented in aqueous samples because it tends to

- precipitate as mineral forms (including FeS, FeS_2, siderite, $FeCO_3$, magnetite, Fe_3O_4, vivianite, $Fe(PO_4)^2$ x $8H_2O$
- exchange with ions on clay minerals

Aqueous Fe^{2+} concentrations are further affected by

- pH; low pH causes elevated aqueous concentrations
- chelating agents, which can cause elevated aqueous concentrations
- groundwater saturated with respect to Fe^{2+}, which may allow for buildup of Fe^{2+}

The presence of large amounts of mineral Fe^{3+} aids sulfate reduction. "Nonenzymatic reduction of Fe^{3+} by HS^- during SO_2^- reduction is well documented. . . For natural attenuation studies, measuring aqueous HS^- usually underestimates the degree of SO_4^{2-} reduction. Much of the produced HS^- reacts with mineral iron to generate authigenic mineral iron sulfides" *(Kennedy and others, 1998)*. The precipitated iron sulfide minerals, known as acid volatile sulfides, AVS, include iron sulfide, mackinawite, gregite and pyrrhotite. (The AVS readily dissolve in hydrochloric acid.) The presence of AVS species will therefore indicate recent sulfate reduction. If the AVS is enriched relative to FeS_2, this may indicate recent or ongoing SO_4^{2-} reduction. Remediators can analyze aqueous SO_4^{2-} to verify that SO_4^{2-} reduction occurred; however, because HS^- precipitates as a solid, a better assessment of assimilative capacity would incorporate a mineralogical analysis.

Natural attenuation studies

Natural attenuation studies typically sample groundwater to quantify aqueous-phase electron acceptors. According to Kennedy and others *(1998),* "for O_2 and NO_3^- analysis, this approach may be valid; however, microbially mitigated Fe and S redox reactions often involve solid/aqueous interactions that may not be assessed adequately if the data are obtained only from water analyses. In addition, with respect to assimilative capacity, concentrations of O_2 and NO_3^- are usually small in groundwater (typically < 8 mg/L and <10 mg/L, respectively) but comparatively large amounts of SO_4^{2-} (ranging from 50 to ~ 1,000 mg/L) can be found. Even greater electron-accepting capacity is potentially available when just modest amounts of solid Fe^{3+} are present. Therefore, Fe^{3+} and SO_4^{2-} could dominate the electron acceptor pool in many aquifer systems."

In summary, researchers state that "reduction of Fe^{3+} and SO_4^{2-} largely results in the precipitation of reduced Fe and S mineral forms that cannot be detected adequately using groundwater analysis alone. Aqueous SO_4^{2-}, upon reduction, often produces mineral iron sulfide. The magnitude and distribution of SO_4^{2-} reduction can be determined best by mineral iron sulfide analysis. For iron reduction, solid Fe^{3+} usually is microbially reduced to form one of several types of solid Fe^{2+} minerals. Considerable Fe^{3+} reduction could occur in an aquifer with little noticeable change in water chemistry with respect to iron. When evaluating Fe^{3+} reduction for a natural attenuation study, solid mineral analysis may be very important."

Sample collection, preservation and analysis

Researchers believe that iron and sulfate mineral analyses are not widely used because of the difficulties in

- solid sample collection
- preservation
- analysis

Solid sample collection. Researchers recommend minimal exposure to air since many reduced Fe^{2+} and iron monosulfide minerals oxidize. This might involve obtaining samples with continuous coring and collecting samples within the same plastic core sleeve. Or cores can be transferred immediately to storage bottles.

Preservation. Samples collected should be kept in anoxic environments, preferably in containers that have N_2 gas atmospheres.

Analysis. Identification by X-ray analysis of Fe minerals is difficult because the minerals are either finely particulate or poorly crystalline. Researchers adapted chemical scenarios to quantify biologically available Fe^{3+} and biogenically produced Fe^{3+}. Basically the techniques consisted of extracting Fe^{2+} using a mild acid (.05N HCL). Then a portion of the extractant was analyzed spectrophotometrically for total Fe and Fe^{2+}. Results are converted to dry weight per unit soil mass. Stronger acid, 6N HCL, was used to extract Fe^{3+} and sulfides. An additional chromium extraction and zinc precipitation is required to quantify the sulfide in a sample.

These procedures are outlined in detail in the authors' paper.

Conclusions

Researchers applied their analyses to a fuel-contaminated aquifer, a natural-gas-contaminated aquifer and a landfill-leachate-contaminated aquifer. They found the following:

- as predicted, many microbial processes that involve Fe and S are expressed in mineral form
- SO_4^{2-} is usually aqueous; its reduction often results in deposition of AVS or chromium-extractable sulfide solids
- little Fe^{3+} is aqueous at normal pH, and most Fe^{2+} precipitates in mineral forms
- the 0.5N HCL extraction technique recovered most of the biogenically produced Fe^{2+} mineral species without overly extracting the bulk matrix iron largely comprised of Fe^{3+} species
- during microbial reduction, some of the original Fe^{3+} mass is used to form new Fe^{2+} minerals
- due to the nonspecific nature of the extraction process, and many other factors, a chemical determination of the biologically available Fe^{3+} or biogenically produced Fe^{2+} is largely subjective
- Fe^{3+} minerals that are prone to microbial reduction are more easily extracted by weak acid attack
- certain precipitated Fe^{2+} minerals can also be extracted with some degree of specificity
- evaluating the ratio of Fe^{2+} to total Fe can help to identify zones of significant Fe^{3+} reduction
- interpretation is still required to discriminate between Fe^{3+} reduction from naturally occurring organics vs. that occurring as a result of organic contamination; this technique may not work in iron-limited sediments where the amounts of total Fe extracted using 6 N and 0.5N HCL are similar
- the resulting AVS data are used as general indicators of recent SO_4^{2-} reduction; AVS plus the chromium extractable sulfide yields a total Fe sulfide mass number that can be used to determine capacity in natural attenuation studies

Researchers also recommend that, where possible, remediators examine the Fe^{2+} ratios from the non-contaminated portions of the aquifer to establish background conditions." . . . obtaining such sediment samples from different geographic areas of an aquifer is not necessarily ideal because true background conditions may not be represented due to the spatial heterogeneity in the mineralogical composition inherent in any aquifer" *(Kennedy and others, 1998)*.

References

Daintith, J. "A Concise Dictionary of Chemistry," 1990, Oxford University Press Inc., 200 Madison Avenue, New York, New York 10016.

Kennedy, L.G., Everett, J.W., Ware, K.J., Parsons, R. and V. Green, "Iron and Sulfur Mineral Analysis Methods for Natural Attenuation Assessments," *Bioremediation Journal,* Vol. 2 , 1998; 800-272-7737; http://www.estd.battelle.org/Journal.htm.

Information sources

Recent publications

An Introduction to Applied and Environmental Geophysics, by J.M. Reynolds, is available from John Wiley & Sons; see the website, http://www.wiley.com.

Bibliography of Field Applications of Permeable Reactive Barrier Technology: see the website, http://www.rtdf.org/public/permbarr/barrdocs.htm.

Environmental Guide to the Internet, 4th Edition, is available for $55 from Government Institutes, 4 Research Place, Ste. 200, Rockville, Maryland 20850; phone 301-921-2323 or fax 301-921-0373 or e-mail giinfo@govinst.com.

Geotechnical and Environmental Geophysics, Vol. I, II and III, edited by Stanley Ward, is available from the Society of Exploration Geophysicists, P.O. Box 702740, Tulsa, Oklahoma 74170.

Global Environmental Diplomacy, by M.K. Tolba and I. Rummel Bulska, is available from MIT Press for $27.50; call 617-253-5645, or see the website, http://mitpress.mit.edu/index.html.

Introduction to Ground-Water Hydraulics—A Programmed Text for Self-Instruction is available as an electronic book at http://www.scisoftware.com.

International Oil Spill Conference Proceedings (API Publication No. 4684A) CD-ROM is available from API for $30; call 202-682-8375.

Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface is available from John Wiley & Sons, Inc. Distribution Center, 1 Wiley Drive, Somerset, New Jersey; call 800-225-5945 or see websites http://catalog.wiley.com or Barnes and Noble, http://barnesandnoble.com.

Remediation Case Studies is available from http://www.frtr.gov, or call 800-490-9198 or 513-489-8190 or fax request to 513-891-6685. Reports include

- *Ex-situ Soil Treatment (bioremediation, solvent extraction, thermal desorption)*
- *Soil Vapor Extraction*
- *Groundwater Pump and Treat – Nonchlorinated Contaminants*
- *Innovative Groundwater Treatment Technologies*
- *On-Site Incineration*
- *Debris and Surface Cleaning Technologies and Other Miscellaneous Technologies*

Soil and Groundwater Hydrology, an electronic book, is available at the author's home page, http://ahti.hut.fi/~tkarvone/.

Sustainable Reservoir Development and Management is available from the International Association of Hydrological Sciences, Wallingford, Oxfordshire OX10 8BB, UK phone: +44-1491 692442, fax +44-1491 692448/692424 or e-mail jilly@iahs.demon.co.uk. Also available are

- *Groundwater Quality: Remediation and Protection*
- *Karst Hydrology*
- *Hydrology, Water Resources and Ecology in Headwaters*
- *Water Resources Variability in Africa During the 20th Century*
- *Hydrology in the Humid Tropic Environment*

The Application of Heat and Chemicals in the Control of Biofouling Events in Wells is available from Lewis Publishers for $79.95. Write Lewis Publishers at 2000 N.W. Corporate Blvd., Boca Raton, Florida 33431-9868; call 800-272-7737, fax 800-374-3401 or e-mail orders@crcpress.com.

The EPA Environmental Assessment Sourcebook, edited by J. Russell Boulding, is available for $69.95 from Ann Arbor Press Inc., 121 S. Main St., P.O. Box 310, Chelsea, Michigan 48118; phone 313-475-8787 or 800-858-5299 or fax 313-475-8852.

The following publications are available from the National Ground Water Association (call 800-551-7379, fax 614-898-7786 or e-mail ngwa@ngwa.org):

- *A Mathematical Primer on Groundwater Flow: An Introduction to the Mathematical and Physical Concepts of Saturated Flow in the Subsurface*, by John F. Hermance
- *Remediation of Petroleum-Contaminated Soils: Biological, Physical and Chemical Processes*, by Eve Riser-Roberts
- *The Proceedings of the 1998 Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Remediation*

EPA publications and information

EPA REACHIT, a searchable internet-based database designed to assist remediation professionals in treatment, characterization and monitoring. Available from the following website http://www.epareachit.org.

Emerging Technology Summary Report: Simultaneous Destruction of Organics and Stabilization of Metals in Soils (EPA/540/SR-98/500). View or download at http://www.epa.gov/ORD/SITE/reports/sr98500.html; for hard copies call 800-490-9198 or 513-489-8190 or fax request to 513-891-6685.

Gasoline Spill Demonstration Project at Lawrence Livermore National Laboratory. View or download at http://www-ep.es.llnl.gov/www-ep/aet/dynstrip/dynstrip.html.

Ground Water Currents (EPA 542-N-99-002), the most recent issue of which concerns innovative permeable reactive barriers. View or download from http://clu-in.org/techdrct/techpubs.htm.

Groundwater Issue: Design Guidelines for Conventional Pump-and-Treat Systems (EPA 540-S-97-504). View or download from http://www.epa.gov/ada/issue.html.

Monitored Natural Attenuation in Wisconsin and Illinois. View or download from http://clu-in.org/techpubs.htm.

Oil Spill Program Update. View or download at http://www.epa.gov/oilspill/docs/index.htm.

Permeable Reactive Barriers Technologies for Contaminant Remediation (EPA 600-R-98-125). View or download at http://www.rtdf.org/public/permbarr/barrdocs.htm. To request hard copies call 800-490-9198 or 513-489-8190 or fax request to 513-891-6685.

SITE Technology Documents contain reports and fact sheets on specific technologies used at contaminated sites. View or download at http://www.epa.gov/ORD/SITE/reports/.

Soil Sampling Technologies Verification Statements and Reports and Monitoring Technology Pilot. View at http://clu-in.org/techpubs.htm. The six reports reviewed are

- *AMS Dual Tube Liner Sampler (EPA 600-R-98-093)*
- *JMC Environmentalist's Subsoil Probe (EPA 600-R-98-091)*
- *Large Bore Soil Sampler (EPA 600-R-98-092)*
- *EMFLUX Soil Gas System (EPA 600-R-98-094)*
- *Core Barrel Sampler (EPA 600-R-98-094)*
- *GORE-SORBER Screening Survey (EPA 600-R-98-095)*

Soil Screening Guidance, Technical Background Document. Available from http://www.epa.gov/oerrpage/superfnd/web/resources/soil/introtbd.htm.

Subsurface Containment and Monitoring Systems: Barriers and Beyond, an overview of subsurface barriers. Available from http://clu-in.org/techdrct/techpubs.htm.

Three-Dimensional NAPL Fate and Transport Model (EPA 600-R-99-011) describes the development, testing and validation of a comprehensive flow and transport simulator (UTCHEM) that can model fate and transport of NAPLs and remediation processes. View or download at http://www.epa.gov/ada/reports.html.

Websites

American Chemical Society (ACS) Division of Environmental Chemistry, free software to calculate numbers of samples for site investigations, http://www.acs-envchem.duq.edu

American Institute of Professional Geologists (AIPG) http://www.aipg.org

Association of State Boards of Geology http://www.asbog.org/index.htm

Biocatalysis/biodegradation database http://www.labmed.umn.edu/umbbd/index.html

BioRedox, a 3-D multi-component transport model, capable of modeling coupled biodegradation-redox processes in groundwater, http://www.rovers.com/natural_attenuation.htm

Disaster Prevention Management: An International Journal, http://www.mcb.co.uk/dpm.htm

Electro-Chemical-Ge-Osication (ECGO) and CleanOx (in-situ chemical oxidation using Fenton's chemistry) http://www.CanRem.net

Environmental Software Solutions has a version of SEQUENCE, a program that allows for visualizing natural attenuation trends for petroleum hydrocarbons, chlorinated solvents and redox indicators such as oxygen, nitrate, iron and manganese, sulfate and methane, http://www.enssi.com

Geotechnical and Geoenvironmental Software Directory gives details of more than 1,000 computer programs in the fields of geophysics, earthquake engineering, soils dynamic behavior, engineering geology, data analysis and data visualization, http://www.ggsd.com

International Association of Hydrological Sciences (IAHS), http://www.wlu.ca/~wwwiahs/index.html

Material safety data sheets, http://www.env-sol.com/solutions/MSDS.HTML

Minnesota 1998 statutes, http://www.revisor.leg.state.mn.us/stats/326/02.html

National Environmental Publications Information System http://www.epa.gov/ncepihom.catalog.html

Nuclear waste technology cleanup, http://www.flowtc.com

SIRI material data safety sheets, http://www.hazard.com/

Strategic Programs on Environmental Endocrine Disrupters '98, http://www.eic.or.jp/eanet/e/end/sp98.html

U.S. Geological Survey groundwater modeling http://water.usgs.gov/nrp/gwsoftware

Waste Policy Institute website, Microsoft PowerPoint tutorial with examples, http://www.wpi.org/wpiprodser

Where to Geo on the World Wide Web http://www.wheretogeo.com

Woods End Group, information on C:N:P ratios http://www.woodsend.org

Discussion groups and new bulletin boards

Water Systems is dedicated to the discussion of all aspects of water systems including sources, treatment, distribution and protection of water systems. To join, send an e-mail to water–subscribe@topica.com. To post, send e-mail to water@topica.com.

Well Drilling is dedicated to drilling topics such as monitor well drilling, vertical and horizontal drilling. To join, send e-mail to drill-subscribe@topica.com. To post, send a message to drill@topica.com.

Soils Web Bulletin Board, where messages may be posted and viewed, http://www.soilvision.com. Topics include unsaturated soils, water in soils, soil properties and contaminant hydrogeology.

UTTU obtained many of these sites and other information from the Groundwater Mailing List (http://groundwater.com), the Bioremediation Discussion Group (http://biogroup.gzea.com) and TechDirect (http://clu-in.com/techdrct.htm). UTTU thanks the moderators/editors from these groups—Ken Bannister of Groundwater, Richard Schaffner of Biogroup and Jeff Heimerman from U.S. EPA's TechDirect.

The view from U.S. EPA: program direction for 1999 and beyond

by Sammy Ng

With the passing of the 1998 deadline for owners to comply with requirements for upgrading, replacing, or closing substandard USTs, we have heard comments that the UST program work is now complete. Information from states and the Petroleum Equipment Institute suggest that the rate of compliance with the 1998 deadline is approximately 80 percent nationwide and continuing to increase. While it is true that some of our work is complete, we still need to ensure that all owners comply with the technical requirements. For example, although owners installed leak detection equipment on their tanks, a significant percentage of leak detection systems may not be operated or maintained properly. EPA wants to prevent the next generation of leaking USTs and will work closely with states to improve compliance rates. EPA will continue to work cooperatively with owners, industry, and regulators to ensure that preventing releases from USTs becomes a common business practice. If releases do occur, the EPA will address them appropriately and cost-effectively.

Over the past year, OUST has gathered stakeholder feedback that confirms we still have much work to do on certain issues:

- preventing leaks
- addressing the approximately 170,000 cleanups yet to be completed
- ensuring that human health and the environment are protected

We have identified the following priority work areas:

- UST system evaluation
- operation and maintenance of UST systems
- temporarily closed tanks
- corrective action
- USTs in Indian country

UST system evaluation. A significant challenge to the UST program is to prevent leaks by ensuring that tank systems are safe and managed properly. EPA will work to help states evaluate the effectiveness of UST systems—especially leak detection, cathodic protection and tank lining—to ascertain that they operate properly and to identify ways in which these systems can be improved.

Anecdotal evidence suggests that UST systems performance has improved greatly over the last decade. We need to conduct a more comprehensive effort to validate and verify claims and identify areas that require improvement. EPA is particularly interested in field performance over time vs. factory testing, which gives only the best possible results.

Initial evaluation steps include the following:

- conducting a study of leak detection system performance (under the aegis of the University of California-Davis)
- gathering qualitative input from experienced people
- compiling existing studies and databases

Operation and maintenance of UST systems. To achieve the goal of preventing another generation of LUSTs, EPA wants to establish that owners/operators are properly operating and maintaining their UST systems and using quality tank management practices. Owners/operators often do not have adequate knowledge of equipment usage and procedures. To resolve this dilemma, we have begun by forming an EPA-state workgroup whose goal is to share and develop ideas. In addition, EPA is assisting the U.S. Postal Service in developing their O&M plan. Over the next few months, EPA will gather O&M information and work with EPA offices, states, industry and trade associations to improve implementation of quality O&M ideas.

Temporarily closed tanks. To meet the 1998 upgrade requirements, many owners temporarily closed their tank systems. EPA estimates that as of February 1999, 73,000 tanks were temporarily closed. Temporary closure of substandard systems may not exceed 12 months unless the implementing agency grants an extension. Owners who temporarily closed tanks should now make efforts to close permanently, upgrade, or replace their USTs. State and federal regulators will be working to ensure that owners take appropriate action regarding these USTs.

Corrective action. EPA's work in the corrective action area has been and will continue to be extremely important to the UST program's success. As of March 1999, approximately 170,000 cleanups had not been completed; EPA estimates that as many as 80,000 additional releases may be confirmed before 2005. The UST program has a reputation for innovation, as well as serving as a model for other environmental programs. Thus, we are continuing our corrective action efforts in two innovative areas: risk-based decision making (RBDM) and pay for performance (PFP).

EPA advocates using RBDM at corrective action sites. RBDM provides UST implementing agencies with a reliable process to help them determine management, extent and urgency of corrective actions. Progress in this area is indicated by cooperation of the various stakeholders (federal, state, and private sector) to foster change. EPA is measuring RBDM performance in pilot programs by analyzing the effects of RBDM on the following:

- reducing risk
- expediting closure of impacted sites
- improving cost control and resource allocation

Early results suggest that states using RBDM have realized increased closure rates and benefited from a decreased backlog of releases.

Additionally, EPA is championing the use of the PFP approach to UST cleanups. The PFP concept is based on the premise that states pay cleanup contractors only for actual contamination reductions. The data show that PFP cleanups can reach environmental goals in half the time required by traditional ways of paying for UST cleanups. In addition, PFP cleanups can be 35 to 50 percent less costly. EPA is working with stake-holders on creating and operating PFP cleanup programs, as well as continuing to document effectiveness and efficiency.

EPA is also developing strategies for reusing UST fields, those commercial and industrial sites where gasoline and other regulated substances from USTs contaminated the environment. After corrective action work has been completed, UST field properties can be restored and reused, serving as a community asset. EPA is working to prevent future UST fields and encouraging states to use scientifically sound, rapid, and cost-effective corrective action at LUST sites.

USTs in Indian country. EPA has primary responsibility to implement the UST program in Indian country. Approximately 3,000 active USTs exist and 3,700 closed USTs may require additional remediation work. These UST owners/operators often do not have sufficient funds to fulfill O&M and cleanup requirements. EPA is taking steps to ensure that these owners/operators will continue to make progress despite institutional barriers to providing funds in Indian country.

Continuing the partnership

We greatly appreciate the exemplary efforts over many years from owners, industry and regulators who have worked diligently to prevent and clean up leaks from USTs. Together we have made significant progress. We can be quite proud of our accomplishments. By continuing to work together, we will make advances in ensuring that leak prevention is a common business practice.

Sammy Ng is the acting director of the U.S. Environmental Protection Agency's Office of Underground Storage Tanks (OUST). He previously served as the office's director of the Policy and Standards Division and as chief of the Regulatory Analysis Branch. Sammy has worked in OUST since its inception in 1985.

Underground Tank Technology Update

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