Lecture 14
Miscellaneous topics in remediation:
New remediation technologies; technical impracticability; and gasoline additives
New remediation technologies

Phytoremediation
Electro-kinetic remediation
Bedrock fracturing
Circulating wells/in-well treatment
In-situ oxidation
Dual-phase vapor extraction
Phytoremediation

- Plant Metabolism
- Plant Uptake
- Root Absorption
- Biodegradation in the Rhizosphere
- Contaminants
Phytoremediation

Phytotransformation – uptake from soil and ground water, transformation within the plant
Rhizosphere bioremediation – augmentation of bacterial processes in plant root zone
Phytostabilization – hydraulic control by pumping action of trees, physical soil stabilization by roots
Phytoextraction – use of metal-accumulating plants to extract metals from soils and concentrate them in roots, stems, or leaves
Rhizofiltration – plant roots acting to sorb, concentrate, or precipitate metals
Artificial wetland constructed in gravel base reduced total explosives (TNT, RDX, HMX) from 9200 to 50 ppb.

Poplar trees for phytoextraction


Courtesy of Melanie Pincus. Used with permission.
Wild mustard plant for metals phytoextraction

Wild mustard plant will hyperaccumulate nickel, reaching shoot concentrations as high as 1.2%.


The ability of Thlaspi goesingense to hyperaccumulate Ni seems to be governed in part by enhanced accumulation of Ni within leaf vacuoles. We have characterized genes from T. goesingense encoding putative vacuolar metal ion transport proteins, termed metal tolerance proteins (TgMTPs). These proteins contain all of the features of cation-efflux family members, and evidence indicates they are derived from a single genomic sequence (TgMTP1) that gives rise to an unspliced (TgMTP1t1) and a spliced (TgMTP1t2) transcript. Heterologous expression of these transcripts in yeast lacking the TgMTP1 orthologues COT1 and ZRC1 complements the metal sensitivity of these yeast strains, suggesting that TgMTP1s are able to transport metal ions into the yeast vacuole in a manner similar to COT1 and ZRC1. The unspliced and spliced TgMTP1 variants differ within a histidine-rich putative metal-binding domain, and these sequence differences are reflected as alterations in the metal specificities of these metal ion transporters. When expressed in yeast, TgMTP1t1 confers the highest level of tolerance to Cd, Co, and Zn, whereas TgMTP1t2 confers the highest tolerance to Ni. TgMTP1 transcripts are highly expressed in T. goesingense compared with orthologues in the nonaccumulators Arabidopsis thaliana, Thlaspi arvense, and Brassica juncea. We propose that the high-level expression of TgMTP1 in T. goesingense accounts for the enhanced ability of this hyperaccumulator to accumulate metal ions within shoot vacuoles.

Electrokinetic remediation

Lasagna process

Electro-osmosis moves contaminant in low permeability environments

The Lasagna™ process works by using buried electrodes to move water through the soil. Applied current drives the water an inch a day from a positive to a negative electrode. The water picks up contaminants and moves them through treatment zones where they are trapped or degraded.

http://www.em.doe.gov/emprog/spr009.html
Thermal treatment (enhanced SVE)

Thermal treatment of PCBs in soil

After thermal treatment

Fracturing of low-conductivity geologic media
Circulating wells

In-well air stripping

Vapors are extracted for ex-situ vapor treatment

Density-driven convection

Vapors are discharged to vadose zone for in-situ degradation

Dual-phase vapor extraction

Dual-phase extraction (DPE) well

Dual-phase extraction

Two-phase extraction

Chemical oxidation

Uses strong oxidizer to chemically destroy contaminants
   Mixed with soil
   Injected into ground water

Oxidating agents:
   Peroxide
   Ozone
   Permanganate
The rate and extent of degradation of a target COC are dictated by the properties of the chemical itself and its susceptibility to oxidative degradation as well as the matrix conditions, most notably, pH, temperature, the concentration of oxidant, and the concentration of other oxidant-consuming substances such as natural organic matter and reduced minerals as well as carbonate and other free radical scavengers. Given the relatively indiscriminate and rapid rate of reaction of the oxidants with reduced substances, the method of delivery and distribution throughout a subsurface region is of paramount importance. Oxidant delivery systems often employ vertical or horizontal injection wells and sparge points with forced advection to rapidly move the oxidant into the subsurface. Permanganate is relatively more stable and relatively more persistent in the subsurface; as a result, it can migrate by diffusive processes. Consideration also must be given to the effects of oxidation on the system. All three oxidation reactions can decrease the pH if the system is not buffered effectively. Other potential oxidation-induced effects include: colloid genesis leading to reduced permeability; mobilization of redox-sensitive and exchangeable sorbed metals; possible formation of toxic byproducts; evolution of heat and gas; and biological perturbation.
Oxidizing agents: Peroxide

Peroxide – usually in form of Fenton’s reagent:

\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \]
\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH} \text{ (radical)} + \text{OH}^- + \text{Fe}^{3+} \]

OH radical is extremely strong oxidizer

Net reaction:

\[ 3\text{H}_2\text{O}_2 + \text{C}_2\text{HCl}_3 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + 3\text{HCl} \]

Requires acidic conditions (pH 2 to 4)
Oxidizing agents: Peroxide

Applicability: most organic compounds
   Not effective against TCA

Application issues:
   Dangerous chemical
   Generates large quantities of heat
   Generates gases (CO$_2$ + O$_2$)
   Other substances may be oxidized, limiting effectiveness
   Transport to oxidation site may be limiting
Field trial of Fenton’s Reagent

Oxidizing agents: Permanganate

Usually potassium permanganate:

$$\text{KMnO}_4$$

but also Ca, Na, and Mg permanganate

Exact mechanism of oxidation unknown

Net reaction:

$$2\text{KMnO}_4 + \text{C}_2\text{HCl}_3 \rightarrow 2\text{CO}_2 + 2\text{MnO}_2 + \text{HCl}$$
Oxidizer comparison

Comparison of Soil Treatment with H₂O₂ (25.5 g/kg), H₂O₂ Plus Iron (25.5 g/kg +5 mM FeSO₄), or KMnO₄ (15.0 g/kg)

Oxidizer comparison

SVOC Treatment Efficiency in Clay Soil Treated for 48 h with H$_2$O$_2$ (39 g/kg), H$_2$O$_2$ Plus Iron (39 g/kg + 5 mM FeSO$_4$), or KMnO$_4$ (16 g/kg) (Initial Concentrations: Naphthalene = 260-337 mg/kg, Phenanthrene = 248-341 mg/kg, and Pyrene = 226-331 mg/kg)

Oxidizing agents: Ozone

Ozone – $O_3$

Ozone gas can be injected by sparging
SITE: Superfund Innovative Technology Evaluation Program

Introduction to the SITE Program

The U.S. Environmental Protection Agency's (EPA) Superfund Innovative Technology Evaluation (SITE) Program was established by EPA's Office of Solid Waste and Emergency Response and the Office of Research and Development (ORD) in response to the 1986 Superfund Amendments and Reauthorization Act, which recognized a need for an "Alternative or Innovative Treatment Technology Research and Demonstration Program." The SITE Program is administered by ORD's National Risk Management Research Laboratory in the Land Remediation and Pollution Control Division (LRPCD), headquartered in Cincinnati, Ohio.

New Solicitations

Updated March 13, 2002

SITE Program Solicitations

New for 2002

Hot Links

Small Business Innovation Research

NEMRL's Land Remediation & Pollution Control Division

U.S. EPA Office of Prevention, Pesticides and Toxic Substances

U.S. EPA/Technology Innovation Office (TIO)

U.S. EPA/Superfund
Federal Remediation Technologies Roundtable

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2 CONTAMINANT PERSPECTIVES

- 2.1 Presumptive Remedies
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Welcome to TechDirect. Since the April 1 message, TechDirect gained 300 new subscribers for a total of 13,681. If you feel the service is valuable, please share TechDirect with your colleagues. Anyone interested in subscribing to TechDirect may do so on CLU-IN at http://clu-in.org/techdirect. All previous TechDirect messages are archived there.

Mention of non-EPA documents or presentations does not constitute a U.S. EPA endorsement of their contents, only an acknowledgment that they exist and may be relevant to the TechDirect audience.

New Video

Introduction to Environmental Geophysics. This video, produced by the U.S. EPA Environmental Response Team, is designed for individuals who have the responsibility for overseeing or planning the collection of site data or waste characteristics. It stresses practical information required to design or supervise geophysical surveys at hazardous waste sites. Run time 9 minutes. See the video section http://clu-in.org/studio

Documents and Websites

Risk Assessment Guidance for Superfund Volume III Part A: Process for Conducting Probabilistic Risk Assessment (RAGS 3A) (OWWER 9285.7-45). This guidance document was issue by the U.S. EPA Office of Emergency and Remedial Response. It was created to establish national criteria to conduct, and review Superfund probabilistic risk assessments in response to the October 1995 Superfund Reform 6A. RAGS 3A was designed to address both human health and ecological probabilistic risk assessments (PRA). It provides flexibility and maintains national consistency in selecting the preliminary remediation goal, based on
Cost estimating resources

• CLU-IN Web Site
  http://www.clu-in.org/
• EPA reports
• Historical cost analysis system (HCAS)
  http://globe.lmi.org/lmi_hcas/
• Environmental Cost-Handling Options and Solutions (ECHOS) – R.S. Means Company
Guidance for Evaluating the Technical Impracticability of Ground-Water Restoration

interim Final

Office of Solid Waste and Emergency Response
U.S. Environmental Protection Agency
Washington, DC 20460
“EPA’s goal of restoring contaminated ground water within a reasonable timeframe at Superfund or RCRA sites will be modified where complete restoration is found to be technically impracticable. In such cases, EPA will select an alternative remedial strategy that is technically practicable, protective of human health and the environment, and satisfies the statutory and regulatory requirements of the Superfund or RCRA programs as appropriate.”
TI Requirements

Identify ARARs to be waived
Specify spatial extent for TI waiver
Develop site conceptual mode
  Provide thorough characterization of site
Evaluate restoration potential
Provide cost estimates
Evaluation of restoration potential

Source control measures
   TI waiver for ground water requires demonstration of source control

Remedial action performance analysis
   High quality, detailed ground-water monitoring
   Effective operation of existing ground-water remedy
   Evaluate remedy modifications
   Evaluate trends over time
Gasoline Additives

Introduced in late 1970s during phase-out of lead additives

Two uses:

- Oxygenated fuel (oxyfuel) – promotes more complete combustion of hydrocarbons
- Reformulated gasoline – reduced benzene and aromatics to reduce ozone formation for air quality
Gasoline Oxygenates

Oxygenates:
- MTBE – methyl tert butyl ether
- ethanol
- ethyl tert butyl ether
- methanol
- tertiary butyl alcohol – TBA
- Oxinol™ – blend of methanol and TBA

Increase octane rating of gasoline
Reduce emissions of air pollutants
Growth in use of MTBE

1960s – first formulated by ARCO
1970 – 39th highest production organic chemical
1998 – 4th highest production

Use of MTBE

Used in 13 states as oxyfuel
  3% of all oxyfuel
  10-15% by volume of oxyfuel gasoline
Used in 18 states as reformulated gas
  85% of all RFG
  11-15% by volume of RFG gasoline
Present in most parts of country as part of gasoline product stream
  88% of Kansas UST sites
Methyl tertiary Butyl Ether - MTBE

CH₃
O
C
CH₃

CH₃

CH₃
MTBE Properties

Extremely soluble:
  4700 mg/L from RFG
  6300 mg/L from oxyfuel

Versus BTEX from conventional gasoline:
  18 mg/L benzene
  25 mg/L toluene
  3 mg/L ethylbenzene
  20 mg/L total xylenes
MTBE Properties

Very low solid partition coefficient ($R_d \approx 1$)
Does not biodegrade readily
Possible human carcinogen
Drinking water advisory – 20 to 40 µg/L
Not highly volatile
Readily partitions from atmosphere to precipitation
Difficult to treat
Prevalence of MTBE

Found at background concentrations of 0.2 to 3 µg/L due to prevalence in precipitation

In USGS national surveys:
  - Found above detection limit in 83% of stormwater samples
  - Found in 27% of ground-water samples

Found at large majority of LUST sites

Significant problems in California including high concentration in Santa Monica public supply wells
Example MTBE Site

Leak in tank valve at fuel storage facility, Woodbury, New Jersey

Hydrogeology: silty sands of moderate hydraulic conductivity
Feb. 1992
Initial release
Dec. 1992
MTBE = 18 ug/L
BTEX < 1 ug/L
Feb. 1993
MTBE = 490 ug/L
BTEX = 27 ug/L

MTBE = 63 ug/L
BTEX < 4 ug/L
June 1993
MTBE = 190 ug/L
BTEX = 2700 ug/L

MTBE = 1.9 ug/L
BTEX < 4 ug/L
Nov. 1993
MTBE = 15 ug/L
BTEX < 4 ug/L