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March 2002

Phytoremediation:
State of the Science Conference
U.S. Environmental Protection Agency

Boston, Massachusetts
May 1, 2000

United States Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory
Cincinnati, OH

NOTICE

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here under Contract 68-D7-0001 to Eastern Research Group. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director

National Risk Management Research Laboratory

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Stephen D. Luftig
Director
Office of Emergency and Remedial Response
U.S. Environmental Protection Agency

Steve Luftig is the Director of the U.S. Environmental Protection Agency's Office of Emergency and Remedial Response. This office manages Federally-funded emergency response and longer-term cleanup activities at hazardous waste sites under the Superfund program, and EPA's implementation of the Federal Oil Pollution Act. Steve has helped implement wide-reaching reforms that have dramatically increased the pace of cleanup work, and has received numerous awards for innovative management. In 1999, Steve received the prestigious Presidential Rank Award, given to only a handful of federal executives each year. In his career with EPA, he has managed a variety of federal environmental programs both in New York, where he started in 1972, and in Washington, D.C. headquarters, where he has been since 1990. Steve is a licensed professional engineer and member of Tau Beta Pi, the National Engineering Honor Society. He graduated (Magna Cum Laude) from the City College of New York, with a Bachelor of Engineering (Chemical) Degree, and has a Masters Degree in Civil (Sanitary) Engineering from New York University.

SUPERFUND'S VIEWPOINT ON PHYTOREMEDIATION

Stephen Luftig, Director
Office of Emergency and Remedial Response

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Examples of Superfund Environmental Response Team Recent Successes

- Portland, OR (TCE polishing and park)
- Leadville, CO (mine tailings in-situ)
- Aberdeen PG, MD (TCE and restoration projects)
- Naples, UT (gasoline spill - polishing)
- Lovell, WY (PAHs - polishing)
- Tibbitts Road Site, NH (polishing and site restoration)
- Davis Liquid Chemical, RI (polishing and restoration)
- Kauffman Minteer, NJ (polishing)
- Sears Property, NJ (polishing)

Superfund's Viewpoint on Phytoremediation

- Early projects have shown promising results
- Not a panacea - has certain concerns and considerations
- Attractive because it is effective and inexpensive
- Rarely used alone - can be under certain conditions
- Usually part of a treatment train as a polishing step
- Can be both a remediation tool and used for restoration

Superfund's Viewpoint on Phytoremediation

Phyto Considerations

- Requires site specific testing and design
- Specific to contaminant concentrations and is chemical dependent
- Seasonal/geographical/climatic dependent
- Can take long time - growth rate dependent
- Depth dependent - on root systems
- Seems to work well for small, shallow plumes

Superfund's Viewpoint on Phytoremediation

Phyto Considerations

- Food chain exposure concerns
- Attractive nuisance issues
- Down time if damage occurs
- Need to use Native plants (Executive Order)
- Need to manage for invasive aliens (EO)

Superfund's Viewpoint on Phytoremediation Regulatory Issues

- Few Federal impediments, but must comply with NCP
- Nine-criteria drive remedy selection
- ITRC is working on Guidance to overcome state regulatory impediments
- Some State ARARs may need to be addressed
- Evapotranspiration caps for landfills

The Science and Practice of Phytoremediation

Steven C. McCutcheon, Ph.D., PE
US EPA National Exposure Research Laboratory
Ecosystems Research Division
Athens, Georgia

Plenary Session I Phytoremediation: State of the Science Conference US Environmental Protection Agency Boston, Massachusetts May 1, 2000

Dr. Steven C. McCutcheon is an internationally known expert on water quality, watershed hydrology, hydrodynamics, sediment transport, cleanup of toxic organic chemicals and metals, phytoremediation, ecological engineering, and environmental planning. He authored the 1989 book, Water Quality Modeling, Vol. 1, by CRC press, co-authored in 1999 Hydrodynamics and Transport for Water Quality by Lewis Publishers and CRC press, and was editor of the American Society of Civil Engineers, Journal of Environmental Engineering. He is on the editorial board of Ecological Engineering by Elsevier, International Journal of Phytoremediation by CRC, and was on the Board of Hazardous, Toxic, and Radioactive Waste Practice Periodical, a new journal by the American Society of Civil Engineers. He is currently writing and editing Phytoremediation: Scientific Advances to Manage Contamination by Organic Compounds for Wiley and Sons. The 1997 EPA Science Achievement Award in Chemistry by the American Chemical Society and EPA, and 1995 EPA Science Achievement Award in Waste Management by the Association for Air and Waste Management and EPA, was awarded Dr. McCutcheon (with others) for innovative advances in permeable barriers to clean up ground water and development of a new component of phytoremediation. The 1994 Richard R. Torrens Award by the American Society of Civil Engineers (outstanding editor among the 21 editors in the Society), the Engineer of the Year in the U.S. Environmental Protection Agency selected by National Society of Professional Engineers, and the Young Civil Engineer in Government in 1984 by the American Society of Civil Engineers have been given him as well. Consulting experience includes designing and conducting stream and ground water quality assessments in Italy, arid lake and harbor water quality assessments in western and eastern China, and reviews of basin water quality studies, including review of plans for the Han River in Korea prior to the 1988 Olympics. As a registered engineer in Louisiana, Dr. McCutcheon has served as an expert witness on the 1983 flooding in New Orleans in a precedent setting class action. The Detroit District of the Corps of Engineers engaged him as a consultant to testify at a ,401 Water Quality Hearing by the State of Wisconsin. In a tenure-track position at Clemson, he advised the State of South Carolina and Home Builders Association on sediment control regulations, and International Paper on water quality standards for the Sampit River. He was involved in the bioremediation cleanup of the EXXON VALDEZ oil spill in Alaska, and the emergency response modeling of a chemical spill in the Sacramento River. Dr. McCutcheon has been involved in risk and exposure assessments at a number of hazardous waste sites involving metals and organic chemical contaminated sediments and soils. As a leader in phytoremediation, Dr. McCutcheon is at the forefront in developing new uses of plants to clean up hazardous waste sites and control contaminant releases to reduce clean up costs at U.S. military facilities. He supervised student research at Clemson University and the University of Georgia in nonpoint source pollution, forest management to control water quality, hydrodynamics, and estuary water quality modeling. Dr McCutcheon is known for guiding university research to meet immediate needs in water quality management in South Carolina and Oregon. He developed and wrote guidance for the US Environmental Protection Agency on regulating waste loads into estuaries and streams. For the internationally reviewed Handbook of Hydrology, he is the lead author of the chapter, Water Quality. He has authored over 167 articles, papers, chapters, books, and reports, including international consulting reports. Steve holds the Ph.D. and M.S. degrees from Vanderbilt, and a B.S. in Civil Engineering from Auburn University.

Dr. McCutcheon serves on the Florida Bay Science Oversight Panel for ecosystem restoration by the National Park Service, NOAA, USGS, Corps of Engineers, South Florida Water Management District, and State of Florida. He has served on four-peer review panels on South Florida Ecosystem Management, Circulation Modeling in Florida Bay, and the Florida Bay Model Evaluation Group. He chaired the peer panel for temperature modeling of the central Platte River to resolve conflict between the EPA Administrator and Governor of Nebraska. In addition to service on a hazardous and radioactive waste management panel advising the Department of Energy for the National Academies, he has served on more than 35 other advisory panels for universities and government agencies.

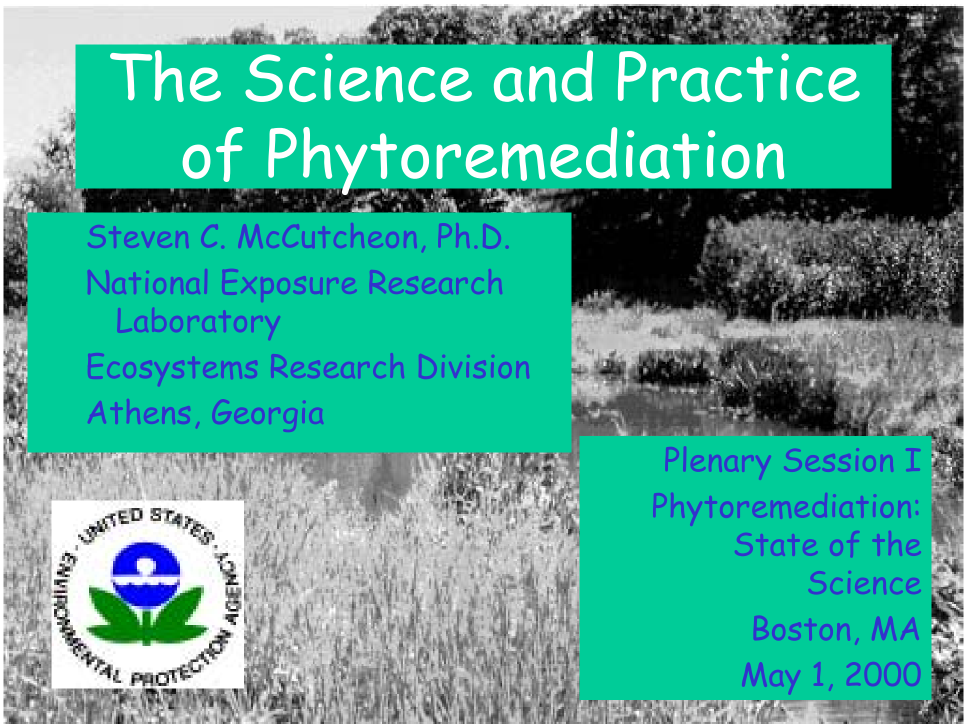
Abstract

This presentation will briefly review terminology, and define the types, benefits, and limitations of phytoremediation. A review of where phytoremediation fits in the scheme of hazardous waste management serves as a lead into an overview of the scientific advances on which the practice of phytoremediation is based.

Based on the advances and application of

- phytoaccumulation of metals and other contaminants
- rhizosphere biodegradation of organic compounds
- phytodegradation of organic contaminants
- phytovolatilization of metalloids, metals and some organic compounds
- phytostabilization of metals and organic contaminants
- rhizofiltration of metals

This presentation defines broadly the application of phytoremediation as a niche or polishing technology and when the approach can be used as a primary treatment. Secondary benefits for nonpoint source treatment in air and water, effluent treatment, erosion control arid site management, and ecosystem restoration will be put into context with the general scientific and ecological engineering knowledge of the art. The fundamental understanding of plant and rhizosphere biochemistry and contaminant fate and transport will be contrasted with the field and pilot studies that represent the current proof of concepts and proof of principles that justify use of phytoremediation. The practice is summarized as those approaches that are ready for application (given the appropriate pilot and feasibility investigations for specific sites), promising treatments expected to be tested soon, and conceivable phytoremediation approaches that require intensive development. Finally, the intrinsic strengthens of phytoremediation and future potential for the technology will be reviewed for the regulatory applications in hazardous waste management.


The Science and Practice of Phytoremediation
Steven C. McCutcheon, Ph.D.
National Exposure Research Laboratory
Ecosystems Research Division
Athens, Georgia
Plenary Session I
Phytoremediation: State of the Science
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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

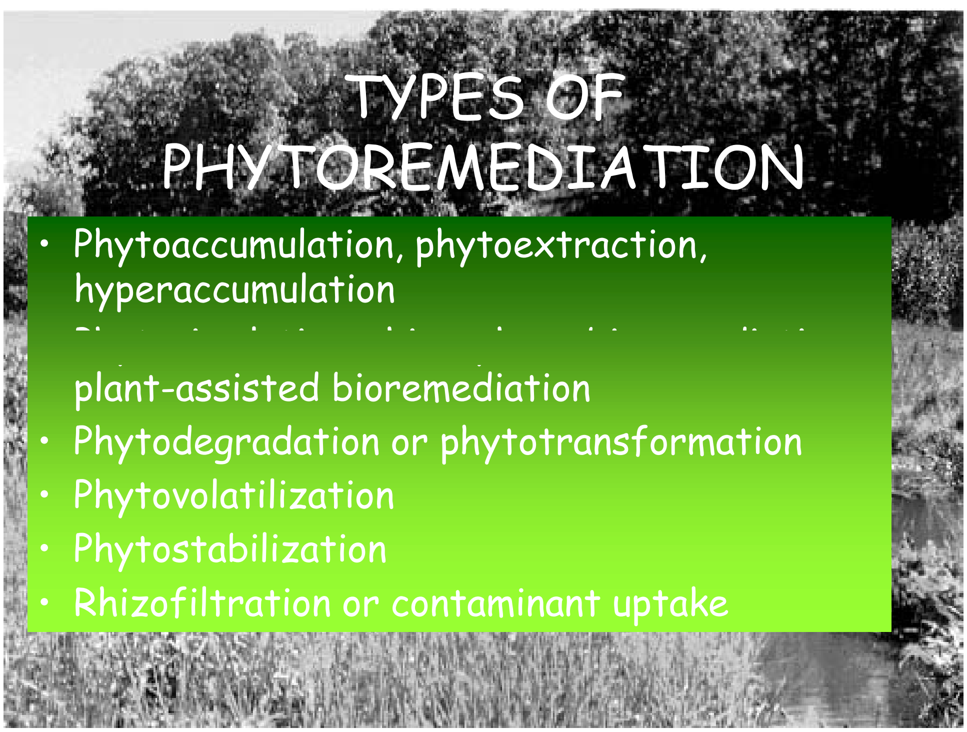

Overview
• History and Types of Phytoremediation
• Strengths and Limitations
• Phytotransformation
• Rhizosphere bioremediation
• Accumulation of Metals and Other Compounds
• Phytovolatilization
• Phytostabilization
• State of the Technology

PHYTOREMEDIATION: use of green plants or vascular plants to clean up or control hazardous wastes.

Coined in 1991 by Raskin (metals accumulation)

Schnoor et al. (1995) seems to be first recognition that plants are very effective in degrading organic chemicals for remediation

Growing element of ecological engineering -- the use of the self-engineering ability of plants



BENEFITS OF PHYTOREMEDIATION

- Aesthetically pleasing ecosystem restoration
- Solar energy driven, passive, in situ
- Plants self-engineer soil and water environment (moisture, pH, redox, organic matter, nutrients)
- Highly evolved enzymes for detoxification, energy extraction, and nutrient management
- Complete break down and recycling of some organic wastes
- Cost effective in some cases

Limitations of Phytoremediation

- ✓ **Shallow soils, ground water and streams**
- ✓ **Slower than excavation, incineration, thermal desorption, and chemical oxidation**
- ✓ **Mass transport limitations like bioremediation**
- ✓ **Winter shutdown -- seasonal rates**
- ✓ **Phytotoxicity limits to lower concentrations**
- ✓ **Multimedia transfer to air & ground water possible**
- ✓ **Bioaccumulation and product toxicity not well understood for many chemicals**
- ✓ **Unfamiliar to many regulatory agencies**

Where Phytoremediation Fits

- Niche technology and polishing step to control and treat hazardous waste sites
- Complete technology for some nonpoint source pollution (water & air), & industrial waste streams
- Widespread, cost effective treatment of moderate to low concentrations
- Long-term treatment and control
- Consistent with erosion control, site management, and ecosystem restoration
- Some hot spot treatments possible

CONTAMINANTS SUITABLE FOR PHYTOREMEDIATION

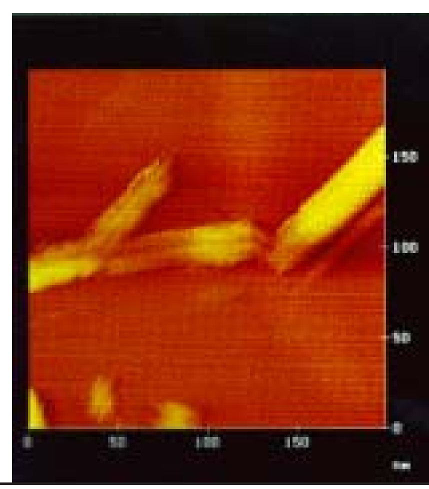
- Heavy metals: Pb, Ni, Zn, Cd, Cr
- Other inorganics: ClO_4, Se, Ar, radionuclides
- BTEX, PAH, petroleum hydrocarbons, PCB
- Munitions (TNT, RDX, HMX), other nitroaromatics
- Phosphorus based pesticides and nerve agents
- Chlorinated aliphatics (TCE, PCE and others)
- Pesticides (atrazine, cyanided compounds, DDT, methyl bromide)
- Nitriles and phenols
- Methyl Tetra Butyl Ether (MTBE)

The Science of Phytotransformation

- Isolated and now forecast the plant enzymes that degrade organic contaminants
- Conducted mass balance and pathway analyses to prove complete degradation and estimate potential toxicity of intermediates
- Axenic tissue cultures establish some plant and microbial enzymatic processes are powerful tools to engineer cleanup and control

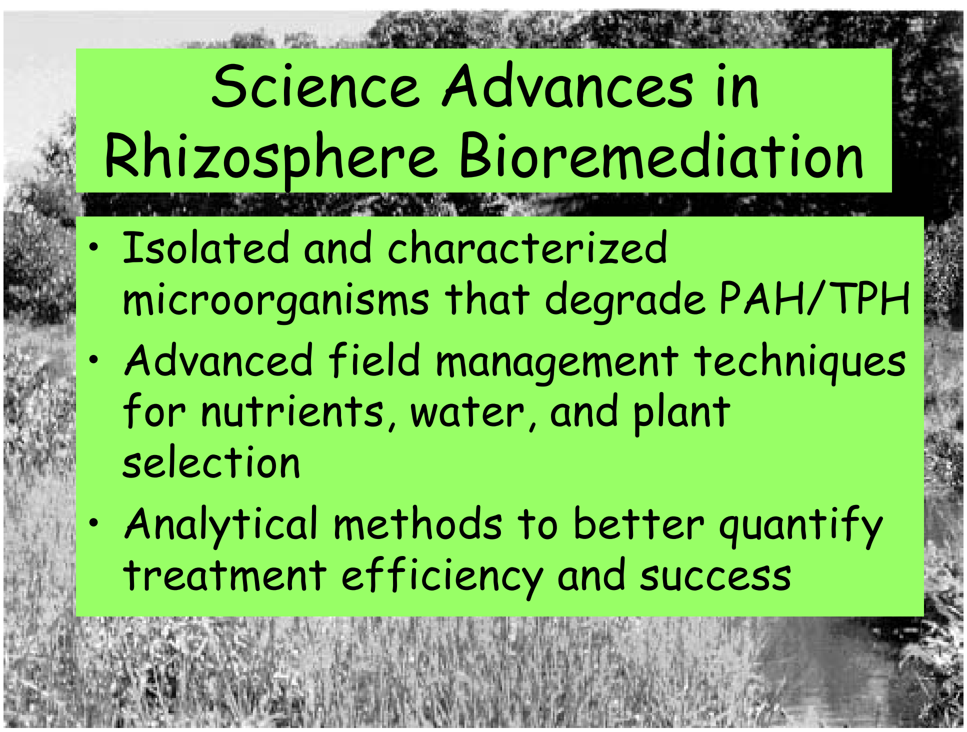
Biotechnology Tools

- ELISA field kits to select native vegetation
- Immunofluorescence to locate oxidative and reductive sites to better engineer created wetlands and plantations



Proof of Principle -- Organic Degradation

- Field proof of principle for TNT and RDX at Iowa AAP (Milan AAP ambiguous)
- Lab proof of principle for pink water and soil
- Feasibility of intrinsic remediation at Joliet AAP
- Lab proof of concept for chlorinated solvents



Science Advances in Rhizosphere Bioremediation

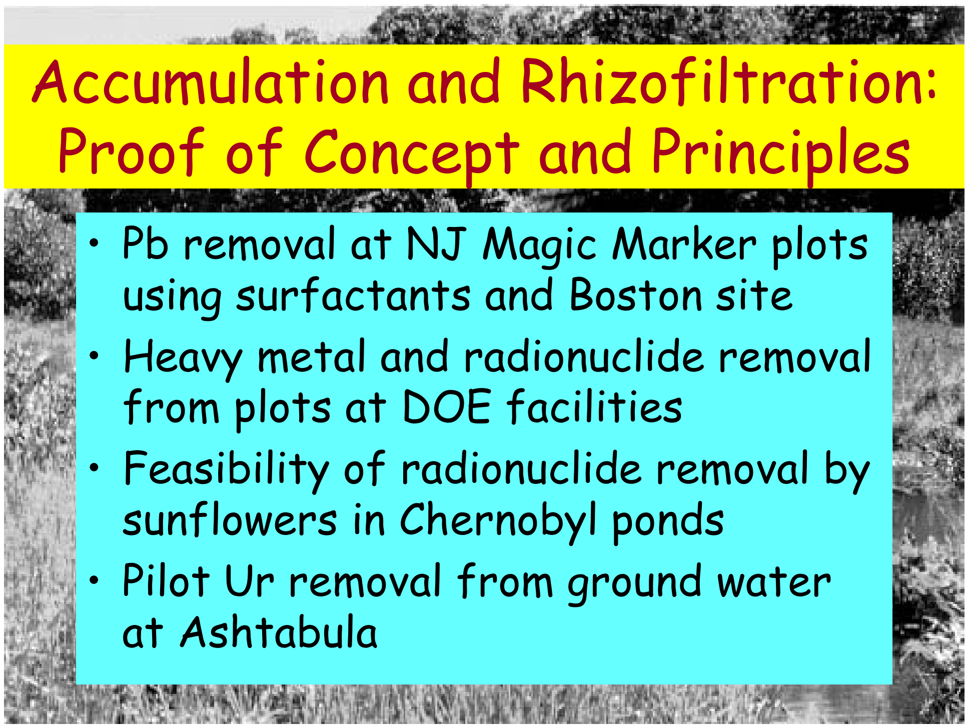
- Isolated and characterized microorganisms that degrade PAH/TPH
- Advanced field management techniques for nutrients, water, and plant selection
- Analytical methods to better quantify treatment efficiency and success

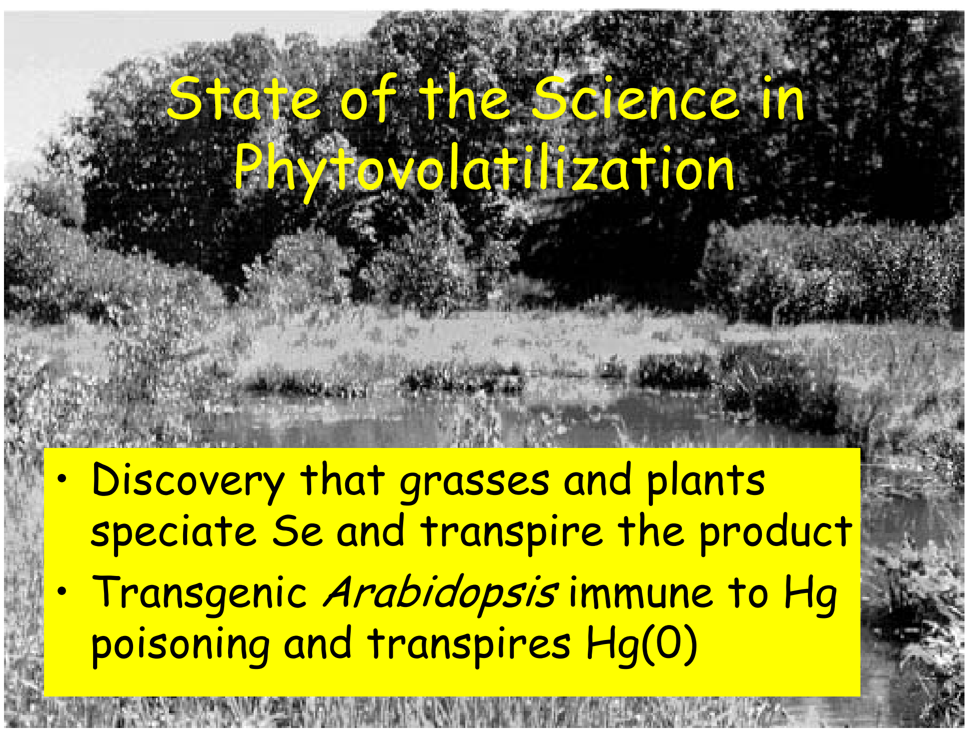
Proof of Principle -- Rhizosphere Remediation

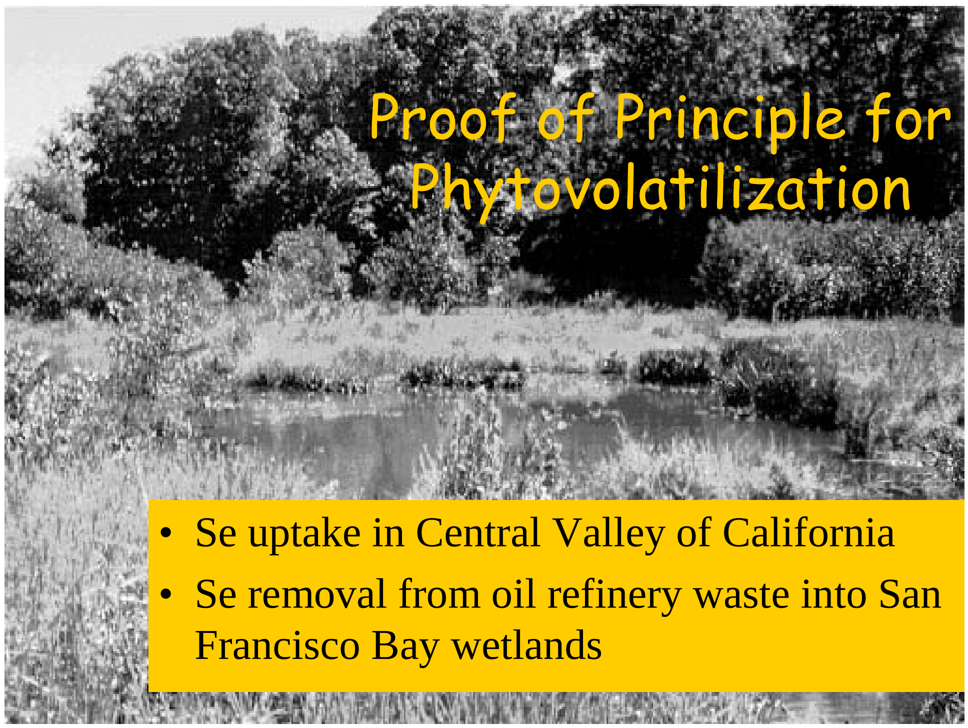
- Craney Island and Gulf Coast Proof of Principle for PAH/TPH
- Field proof of concept for chlorinated solvents: NW, Hill AFB, Carswell AFB TX, Cape Canaveral, (Orlando feasibility expected soon)
- Field proof of concept for TNT and RDX removal at Milan AAP

Phytoextraction and Rhizofiltration Science

- Botanical prospecting dating to the 1950s in the USSR and US
- Cataloged over 400 species of hyperaccumulators worldwide
- Field test kits for metal hyperaccumulation
- Uptake and segregation processes using cation pumps, ion transporters, Ca blocks, metal chelating exudates and transporters, phytochelatin peptides, and metallothioneins


Accumulation and Rhizofiltration: Proof of Concept and Principles
• Pb removal at NJ Magic Marker plots using surfactants and Boston site
• Heavy metal and radionuclide removal from plots at DOE facilities
• Feasibility of radionuclide removal by sunflowers in Chernobyl ponds
• Pilot Ur removal from ground water at Ashtabula


State of the Science in Phytovolatilization
• Discovery that grasses and plants speciate Se and transpire the product
• Transgenic *Arabidopsis* immune to Hg poisoning and transpires Hg(0)


Proof of Principle for Phytovolatilization
• Se uptake in Central Valley of California
• Se removal from oil refinery waste into San Francisco Bay wetlands


Proof of Concept for Stabilization
• Canadian mining waste stabilization
• Zn contaminated smelter sites
• Pb, Zn, Cd, Ni at industrial sites

Summary of the Technology Available

- Control and accumulation of Pb and Ni
- Treat munitions contaminated water and waste water
- Treat PAH/TPH contaminated soil
- Control and treat shallow chlorinated solvent plumes
- Se control in soils and wetlands
- Radionuclide control and treatment of soil
- Water balance and leachate control for landfills

Promising Technology

- Perchlorate treatment
- MTBE control
- Stabilization for Pb, Cu, Zn, Ni in soils

Possible With Intensive Development

- Accumulation and disposal of Zn, Cr, Cd
- PCB removal from soil
- Accumulation of PCP
- Pesticides and nerve agent treatment
- Nitriles
- Phenols

What to Look for in a Phytoremediation Strategy

- Indigenous aquatic and terrestrial communities that self engineer waste sites and unit processes and have dominant species with the effective enzymatic processes or spur effective rhizosphere degradation and do not require energy-intensive intervention or co-factor and nutrient supplements
- Rapid growing single metal accumulators carefully using surfactants to overcome soil binding

Long-Term Promise -- continued

- Plant breeding to accumulate several metals and degrade organic contaminants simultaneously
- Full exploration of the multitude of plant enzymatic and self engineering processes (allelopathy, natural insecticides, pioneering plants, detoxification, herbs and other unusual plants, unique nutrient control)

Long-Term Promise -- concluded

- Enzyme and co-factor production by biotechnology and agronomic practices
- Symbiotic communities supporting fungi and unusual microbes
- Paleoecology to prove decadal long intrinsic remediation by plants
- Transgenic plants and genetically engineered microbes

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- EPA Superfund, HSRC, DOD SERDP, Navy Southern Facilities Command and Air Force Restoration Division

Interstate Technology Regulatory Cooperation: Making It Easier for Regulators

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Robert Mueller has a B.S. in Psychobiology from Albright College and an M.S. in Environmental Science from Rutgers University. He has worked as an environmental scientist for 25 years in both the public and private sector.

Robert Mueller is currently employed by the New Jersey Department of Environmental Protection as a Research Scientist. He is working in the Division of Science, Research and Technology in the Office of Innovative Technology and Market Development. His office is working within the New Jersey Department of Environmental Protection (NJDEP) and with other states to develop methods to share information on innovative technologies and break down barriers to the deployment of these technologies. One such effort is the Interstate Technology and Regulatory Cooperation (ITRC). The ITRC is a group of over 30 states dedicated to this mission. Mr. Mueller is leading the phytoremediation team within the ITRC.

Abstract

The Interstate Technology & Regulatory Cooperation (ITRC) Work Group was created through the Western Governors Association to expedite the use of innovative hazardous waste and remediation technologies. Currently the ITRC has expanded to include more than 30 states, three federal partners, stakeholders, and two state associations. In January 1999, the Environmental Research Institute of the States (ERIS) became the new host of the ITRC.

The ITRC:

- Provides a forum for states to exchange technical information;
- Creates a network of state contacts to promote the use of innovative technologies;
- Identifies interstate barriers to the deployment of technologies;
- Benchmarks state perspectives about innovative technologies;
- Develops consensus among state regulators, with input from industry and public stakeholders, on technical regulatory aspects of using innovative technologies.

Through these mechanisms, the ITRC develops guidance documents intended to help regulatory staff conduct an expeditious review of the use of a specified technology and to help technology developers/vendors collect performance data that can be used to support regulatory approval.

To see if the ITRC has developed any guidance documents that are useful to you, you may access the ITRC website at *www.itrcweb.org.* If you have already identified a site where one of the ITRC guidance documents can be used to deploy an innovative technology, please contact the ITRC State Point of Contact (POCs) for the state in which the site is located. These POCs are listed in the website also.

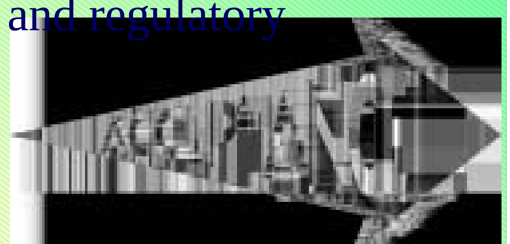
For more information please feel free to contact Mr. Brian Sogorka, NJ, or RocLer Kennett, NM, Managing Co-Directors of the ITRC, or Rick Tomlinson, ITRC Project Manager, c/o The Environmental Council of the States, 444 North Capital Street, Suite 305, Washington DC 20001, (202) 624-3669 (phone), (202) 624-3666 (fax).

Promoting Innovative Environmental Technologies

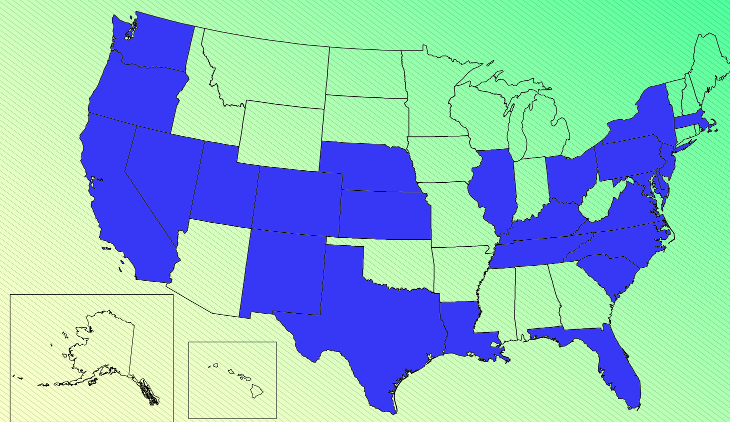
Purpose of ITRC

ITRC is a state-led, national coalition of regulators working with industry and stakeholders to:

- improve state permitting processes and
- speed deployment of technologies through interstate and regulatory collaboration.



Participating States



Other Participants

- Industry representatives
- Public Stakeholders
- Federal agencies

DOE

EPA

DOD

- Host organization

Environmental Council of States

- State organizations

Western Governors' Association

Southern States Energy Board

Products & Services

- Regulatory and Technical Guidelines
- Technology Overviews
- Case Studies
- Training Courses
- Peer Exchange
- Technology Advocates

Document Contents

- Site Characterization
  - –Pre-Treatment Sampling
  - –Site Modeling
  - –Exposure Analysis
  - –Historical Data about Site Use
  - –Data Requirements
  - –Analytical Methods
  - –QA/QC
- Performance Data
  - –Treatability Studies
  - –Test & Demonstration
  - –Monitoring for Treatment Goal and Fugitive Emissions
  - –System Operating Requirements
  - –Health & Safety Requirements
  - –Feed Limitations
- Clean-Up Levels
  - –Closure Criteria
  - –Intended Use
  - –Receptors
  - –Surrounding Community

Benefits to States

- Access to peers & experts in other regulatory agencies
- Shortened learning curve by obtaining advance knowledge of new and used technologies
- Cost-effective involvement in demonstrations conducted in other jurisdictions
- Sounding board for problem solving
- Information and technology transfer
- Maximize limited resources
- Personal & professional development

Benefits to Industry

- Forum conducive to advancing technology & solutions
- Insight into the regulatory world
- Access to multiple state entities
- Opportunity for broader review of technology
- Unique & cost-effective approach to demonstration & deployment of new technology
- Mechanism to identify and integrate regulatory performance expectations amongst states

Benefits to DOD

- Facilitates interactions between DOD managers and state regulators
- Increases consistency of regulatory requirements for similar sites in different states
- Can help reduce uncertainties when preparing cleanup plans
- Addresses contaminants of concern to DOD (heavy metals, VOCs, PAHs, organic pesticides, solvents, etc.)
- One technical team is dedicated to UXO, a problem unique to DOD

Benefits to DOE

- Facilitates interactions between DOE managers and state regulators.
- Increases consistency of regulatory requirements for similar cleanup problems in different states.
- Can help reduce uncertainties when preparing cleanup plans.
- Addresses DOE's remediation needs (metals, organics, asbestos, mixed waste).
- One technical team, Radionuclides, is dedicated to a problem of particular concern to DOE.

Benefits to USEPA

- Forum to facilitate idea sharing between regulators at the federal and state levels.
- Unique & cost-effective approach to demonstration & deployment of new technology.
- Mechanism to identify and integrate regulatory performance expectations amongst states.

State Engagement –Points of Contacts

- Serve as liaisons between states and ITRC
- Help gain state concurrence on documents
- Encourage use of ITRC products/services
- Document use of ITRC documents (38 examples to date)
- Record institutional changes resulting from ITRC (46 examples to date)

Technical Teams

- Accelerated Site Characterization
- Enhanced In Situ Bioremediation
- Low Temperature Thermal Desorption
- Metals in Soils
- Permeable Reactive Barriers
- Plasma Technologies
- Verification

NEW in 1999-2000:

- Dense Nonaqueous Phase Liquids
- Enhanced In Situ Biodenitrification
- Phytoremediation
- Radionuclides
- Unexploded Ordnance

Accelerated Site Characterization

Value: Offers the potential to reduce the time and costs of characterizing a site before a cleanup plan is chosen

Products: 2 Technology Overviews
2 Guidelines on technical requirements for
- SCAPS - LIF
- SCAPS - VOCs

Status: Closed out in 1998

Success: Document helped TX use SCAPS-LIF at an EPA Superfund creosote site

Enhanced In Situ Bioremediation

Value: Usually less expensive and more acceptable than aboveground options

Products: 4 Guidelines including *Natural Attenuation of Chlorinated Solvents in Groundwater - Principles and Practices.*
Technology Overview
Case Study
Offered natural attenuation courses in 1998

Status: Team conducting training as requested

Success: Courses reached more than 900 regulators and 500 consultants

Low Temperature Thermal Desorption

Value: Removes hazardous solvents from mixed waste, reducing waste volume and lowering disposal costs

Products: 3 Guidelines on technical requirements for
- petroleum/coal tar/gas plant wastes
- chlorinated organics
- mixed waste and/or mercury

Status: Team closed out in 1998

Success: Contributed to $100/ton savings for treatment in NY

Metals in Soils

Value: Treatment could help avoid costly excavation, transportation, disposal at waste facility, capping, and monitoring

Products: Overviews of three emerging technologies
- phytoremediation
- electrokinetics
- in situ stabilization

Soil Washing Guideline issued in 1997; updated in 1999

Success: Facilitated community acceptance of soil washing and phytoremediation at Ft. Dix, NJ

Permeable Reactive Barriers

Value: Offers potential to restore many types of sites to the standards that can't be met by conventional groundwater treatments

Products: 3 documents on remediation with PRBs
- regulatory guidance for (1) chlorinated solvents and (2) inorganics and radionuclides
- design guidance for chlorinated solvents

Status: Offering training courses in 1999 and 2000

Success: Process—from design through installation — took less than four months in NJ

Plasma Technologies

Value: Thermal treatments that have potential to treat hazardous, radioactive, military, and medical wastes

Product: Technology Overview

Status: Team closed out in 1998

Verification

Value/ Success: Technology verification programs are incorporating state verification needs into their programs, making it easier for states to approve technologies

Product: A matrix of data provided by 16 states on the elements necessary in a verification program to increase knowledge and evaluate confidence in the verified technology

Status: Accumulating examples of verification being used to improve technology deployment

Dense Nonaqueous Phase Liquids

Value: If not removed, DNAPLs could contaminate groundwater for centuries

Planned Product: An overview of technologies capable of characterizing and treating DNAPLs

Partner: USEPA's Superfund Innovative Technology Evaluation (SITE) program

Status: New team in 1999

Enhanced In Situ Biodenitrification

Value: May be used to treat contamination caused by nitrogen fertilization, concentrated animal feeding operations, explosives manufacture, wastewater treatment, and UXO

Planned Product: A technology overview

Status: New team in 1999

Phytoremediation

Value: Offered commercially, but many details still need to be studied to explain the process and guarantee reliability

Product: A decision tree to help determine when phytoremediation is appropriate

Planned: Product Technology overview and regulatory issues

Status: New team in 1999

Radionuclides

Value: A concern particularly at DOE sites as a result of nuclear weapons production

Planned Products: A catalog of state, federal, and international radionuclide organizations and their activities
A glossary of radionuclide terms

Status: New team in 1999

Unexploded Ordnance

Value:	Examining the problem of military munitions contaminating federal (DOD) and private sites
Planned Product:	Case studies examining ways to remove Barriers to using innovative UXO remediation technologies
Status:	New team in 1999

Contacts

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The Future of Phytotechnologies

Steven Rock

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Steve Rock manages field projects using phytoextraction, phytodegradation, and hydraulic control with trees. He is the author of several phyto publications, including acting as team leader on the EPA's Introduction to Phytoremediation, and a chapter in the Standard Handbook of Environmental Engineering. He co-chairs the RTDF Action Team on Phytoremediation, and has three subgroups researching the phytoremediation issues of petroleum hydrocarbons, chlorinated solvents, and vegetative covers for waste containment. He participates in EPA in-house research, and provides technical assistance to EPA regional staff on questions of phytoremediation.

The Future of Phytotechnologies

Steve Rock, US EPA

Planted systems have a potentially bright future

Clearly phyto
is a
growing
endeavor.

It is fertile ground
for research or commerce

With experts from many backgrounds who are frequently out standing in their fields.

Experts who go to great lengths to...

...dig up new information.

In this field you need to keep your sense of humus…

Because with living systems,

Sometimes you just get stumped.

Phyto - Technologies - Using Plants as Engineering Tools

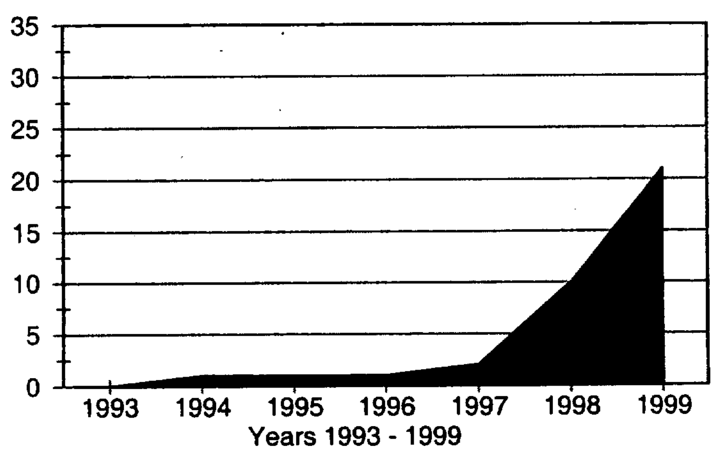
- Phytoremediation: Cleaning soil or groundwater
- Landfill Cover Systems
- Mine Site Reclamation
- Industrial and Municipal Wastewater Treatment
- Erosion control

The plants are an essential component of the system.

Plants as Tools

- Deep planted trees to intercept groundwater
- Wetlands to enhance degradation
- Shallow plantings to enhance degradation
- Metals extraction & concentration
- Prairie or tree based evapotranspiration covers

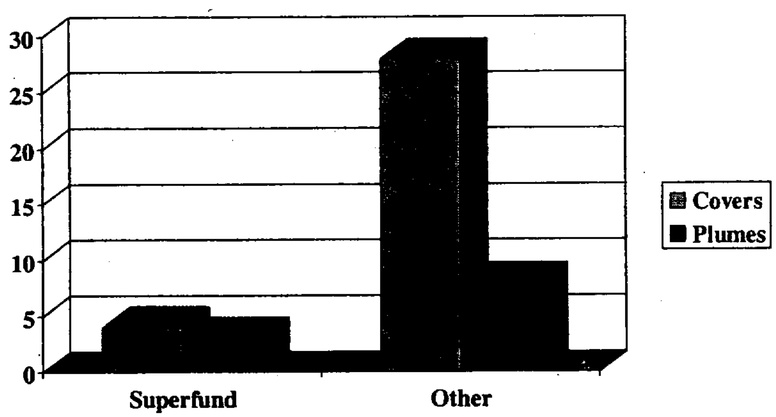
Historical Trend



SUPERFUND SITES

Site Name, State	Date Initiated	Plant	Contaminant/Matrix
Former Carswell Air Base, TX	1996	Eastern cottonwood tree	TCE/groundwater at 4-12 ft
Aberdeen Proving Ground, MD	1996	Hybrid poplar trees	TCE/groundwater
French Limited, LA	1996	Phreatophytes	Solvents, hydrocarbons
Edward Sears Site, NJ	1996	Hybrid poplar trees	TCE/groundwater at 8 ft
Ammunition Army Depot, IA	1997	Wetland and terrestrial plants	TNT/soil and pond water
Fort Wainwright, AK	1997	Felt left willow	Pesticides/soil and groundwater
Kaufman Minter, NJ	1997	Hybrid poplar trees	TCE/groundwater
SRS, CT	1998	Hybrid poplar trees	Solvents/groundwater
Army Ammunition Plant,	1998	Wetland	TNT groundwater
Del Monte, HI	1998	Koa haole	Pesticides/soil and groundwater
Bofors-Nobel, MI	1999	Various trees and wetland plants	Residual sludge in waste lagoons

Full Scale Installations To Date



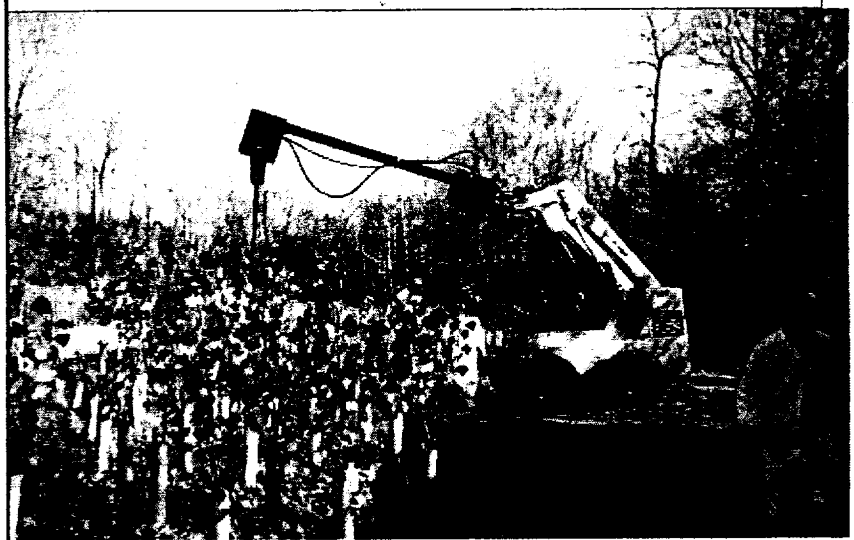
Disadvantages of Planted Systems

- Vegetation to contamination relationship varies
- Lack of broadly applicable performance data
- Seasonally, climatically dependent

Site Specific Design and/or
Treatability Studies

= High information cost (one time)
+ Low installation and operating cost

Show me the DATA!!!



Sample, sample, sample

But data is not information,
information is not knowledge,
and knowledge is not wisdom...

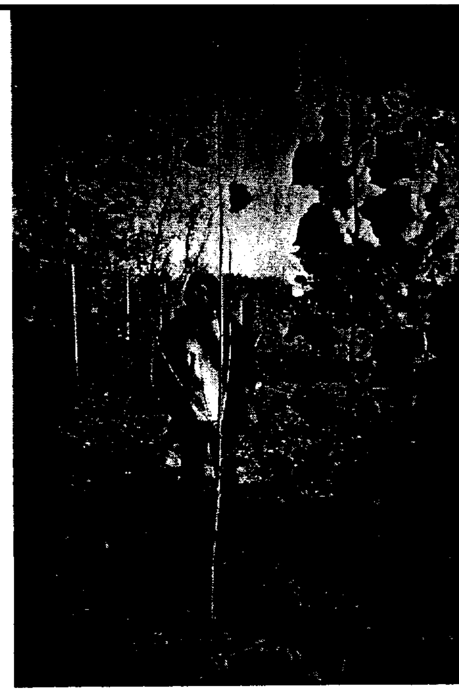
One future of phytotechnologies is integration.

Integration of Goals

- Integrate goals i.e.- Region 3 project in Pennsylvania in which *CAFOs* (feed lots) send biomass to *coal mine damaged lands* for *reforestation* and to *sequester atmospheric carbon.*

Integration of Uses

Superfund site with pump and treat supplemented by upgradient phyto, wetland enhancement, and a bike path.



Integrate Disciplines

- Engineering, soil science, agronomics/silviculture, climate change, many regulatory aspects, environmentalism, and entreprenuership.

<u>Natural Capitalism</u>

by

Amory Lovins, Paul Hawken, and Hunter Lovins

Rocky Mtn. Institute rmi.org

FUNDAMENTAL PROCESSES OF PLANTS AND SOILS

Transport of Contaminants in Plant and Soil Systems

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Dr. Erickson is presently professor of chemical engineering and director of the Great Plains/Rocky Mountain Hazardous Substance Research Center. He has been conducting research on the beneficial effects of vegetation in contaminated soil since 1991. He is editor of the Journal of Hazardous Substance Research, an online journal published by Kansas State University at www.engg.ksu.edu/HSRC/

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Abstract

The transport of contaminants in soil and plant systems depends on the properties of the contaminant, aqueous phase flow, soil properties, and size and growth of the plants. There is convective flow of the aqueous phase in soil, plant roots, and plant stems because of differences in the pressure of water or matrix potential as a function of position. Significantly larger quantities of water are lost to the atmosphere through evapotranspiration when growing plants are present. Contaminants are transported to the soil surface in plant roots and in the soil.

Contaminants such as trichloroethylene (TCE) and methyl-tert-butyl ether (MTBE) diffuse through the walls of roots and stems. Volatile compounds such as TCE diffuse through the gas phase in unsaturated soil into the atmosphere. In small roots, TCE transported upward in the aqueous phase may diffuse out through the walls of the roots into the unsaturated soil and to the atmosphere. In large mature trees, TCE has been found in the xylem in locations where the groundwater is contaminated with TCE. The concentration of TCE decreases with height because the TCE diffuses out through the plant cells between the xylem and bark of the trees.

Since MTBE is more soluble in water and less volatile than TCE, it is transported through the roots into plant stems of alfalfa. The loss of MTBE through the walls of the stems appears to be limited by diffusion through the plant cells in the stem wall. This process has been modeled with a transport model.

Introduction

The fate and transport of water and contaminants in soil with growing vegetation has been the subject of research in our laboratories for more than nine years. Since much of the information contained in the oral presentation is available in other manuscripts and publications, the primary purpose of this manuscript is to identify these publications and provide information on the significant transport processes which have been observed in our investigations.

Methods

Most of the experimental research has been conducted using plant growth chambers in a laboratory setting. These chambers include two identical U-shaped channels, each 10 cm wide, 35 cm deep, and approximately 180 cm in axial length (Narayanan et al, 1995a and 1995b; Narayanan et al., 1999a) and a six channel system (Zhang et al, 1998a; Zhang et al, 1999). Each of the six channels was 10 cm wide, 110 cm long and 65 cm deep with 60 cm of soil. Measurements have been made of the contaminant concentration in the inlet and outlet groundwater, the gas phase leaving the surface, and at points within the chambers. Experiments have been conducted with toluene, phenol, trichloroethylene, and methyl tert-butyl ether.

Models have been developed and computer simulation has been used to provide additional information on the processes that are affecting the fate of the contaminants.

Results

The fate and transport of organic contaminants depends on the physical and chemical properties of the contaminants. In the early work with toluene and phenol, biodegradation in the soil appeared to be the primary mode of disappearance. Toluene degradation appeared to be limited to aerobic conditions (Davis et al., 1994; Erickson et al., 1994: Narayanan et al., 1995a; Narayanan et al., 1998a and 1998b). Phenol may have been biodegraded anaerobically as well as aerobically. There was no evidence that toluene and phenol were lost to the atmosphere (Davis et al., 1994).

In the research with trichoroethylene (TCE), biodegradation was observed in the early research (Narayanan et al., 1995b), but it did not appear to be significant in the later research (Narayanan et al., 1999a). Experiments were conducted to investigate the diffusion of TCE in plant systems (Davis et al., 1999). Values of diffusivity of TCE in plants were found to be about 0.1 to 0.3 of the value of the diffusivity of TCE in liquid water. For small roots, TCE which moves upward with soil water in plant roots may move out of the roots near the soil surface by diffusion. Narayanan et al. (1999a) has shown that the concentration of TCE is very low at the soil surface because of gas phase diffusion in unsaturated soil. With alfalfa plants in TCE contaminated soil, there is little evidence of TCE moving up into the plant stem; however, Vroblesky et al.(1999) has shown that TCE does move up into large trees. While the estimated diffusivity for TCE is similar in the trees, the radial distances are larger and thus, the concentrations of TCE in the xylem are detectable and significant.

Plants impact transport by removing water from the soil. The gas phase diffusion in the unsaturated zone varies with the fraction of gas phase volume. As plants remove water from the soil, they increase the fraction of gas phase volume in the surface soil which enhances the transport of oxygen and volatile contaminants. When plants are present the movement of contaminants and the drying rate following precipitation are different than when plants are not present.

When methyl tert-butyl ether (MTBE) is the contaminant, there is a greater tendency for the contaminant to be found in the plant because of the greater solubility in water and the lower value of the Henry constant compared to TCE. In our research with MTBE, values of diffusivity for MTBE in plant stems were found to be about two orders of magnitude smaller than those for MTBE in water (values were about 0.008 to 0.02 of those for MTBE in liquid water) (Zhang et al., 2000; Zhang, 1999).

The loss of volatile contaminants to the atmosphere has been investigated experimentally and through modeling and simulation (Davis et al, 1994; Davis et al., 1998b; Narayanan et al, 1999b). If the contaminant is transformed rapidly in the atmosphere and if the degradation products are environmentally acceptable, phytovolatilization may be a desirable process to move the contaminants from the soil and groundwater into the atmosphere. Narayanan et al. (1999b) has shown that volatile organic concentrations in the atmosphere are usually well below the threshhold limit values where health concerns become significant. The rate at which contaminants are moved from the soil to the atmosphere is limited by the dissipation of water vapor into the atmosphere. Thus, when the contaminant and water move upward together, the rate is limited by the rate of evapotranspiration which is limited by the dissipation of the soil water into the air. For example, for TCE in soil water at a concentration of 1 mmol/L or 131 mg/L, the corresponding concentration for TCE in water saturated air is 0.56 ppm by volume at 25 C. There is a significant dilution because of the expectation that all of the transpired water must be dissipated into the air.

The volume of water that is transpired by plants is significant (Davis et al., 1998a). When the roots can find adequate water, alfalfa, poplars and willows may use as much as 2 meters of water in one year (2 cubic meters per square meter of area). Zhang (1999) has shown that water use in planted chambers is significantly greater than that in the unplanted chamber (Zhang et al., 1998b and 1999). There is significant interest in using plants as solar driven pumps to contain plumes and the vegetation as the treatment system. While the degree of treatment depends on the contaminant, it has been shown that for many contaminants, plants may be used as part of a pump-and-treat system (Davis et al., 1998a: Erickson et al., 1997: Narayanan et al., 1999b).

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Acknowledgement

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Transport of Contaminants in Plant and Soil Systems

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Qizhi Zhang, and Muralidharan Narayanan

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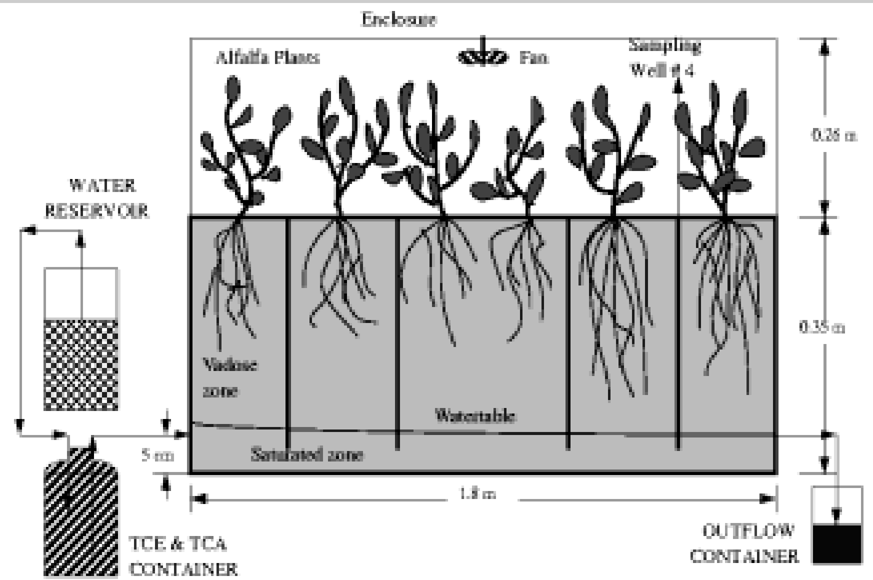


Fig. 1. Schematic view of the axially extended experimental setup.

Table 2: Mass balance for contaminant carbon (mmol/day).

Compound	Inflow carbon (mmol)	Outflow carbon (mmol)	Carbon disappearing (mmol)
Toluene	34.0	8.2	25.8
Phenol	27.0	0.3	26.7

Table 3: FTIR estimates of CO_2 in the headspace of the chamber (mmol/day).

CO_2 with C feed (mmol)	CO_2 without C feed (mmol)	CO_2 due to Contaminant Degradation (mmol)
85.0	57.0	28.0

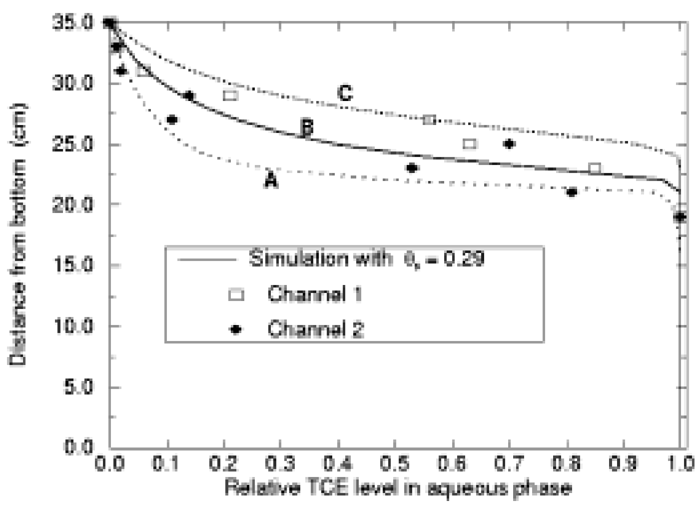
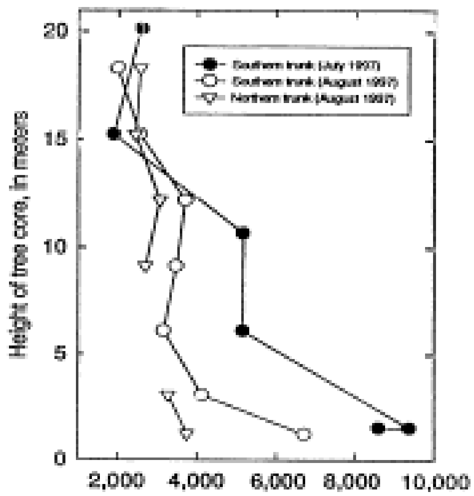


Fig. Experimentally measured and numerically simulated TCE conc. profiles in the system. Lines **A**, **B**, and **C** are TCE profiles for θ_s = 0.25, 0.29, and 0.32, respectively. Experimentally measured profiles in the aqueous phase are shown as hollow squares and filled diamonds.



Trichloroethene concentration in tree cores, in
nanomoles of gas per liter of core water

Trichloroethene concentration in cores along the trunk of tree 7 (bald cypress). Cores from the northern trunk were not collected in July 1997.
(From Vroblesky et al., Environ. Sci. & Technol., 33: 510 (1999).)

Estimated values of diffusivity for trichloroethylene in trees

Tree	Diffusivity cm^2/s	Source of data
Poplar	1.6×10^{-6} 1×10^{-6} 2×10^{-6} 3×10^{-6}	Hu Davis *et al.* Davis *et al.* Davis *et al.*
Willow	1.6×10^{-6} 1.5×10^{-6} 2×10^{-6} 3×10^{-6}	Hu Davis *et al.* Davis *et al.* Davis *et al.*
Bald Cyprus	3×10^{-6}	Vroblesky *et al.*

Diffusivity of trichloroethylene in water is 1×10^{-5} cm^2/s.

Comparison of confined and unconfined gas phase concentrations of trichloroethylene (TCE) for several different concentrations in ground water at 25°C and 1 atmosphere.

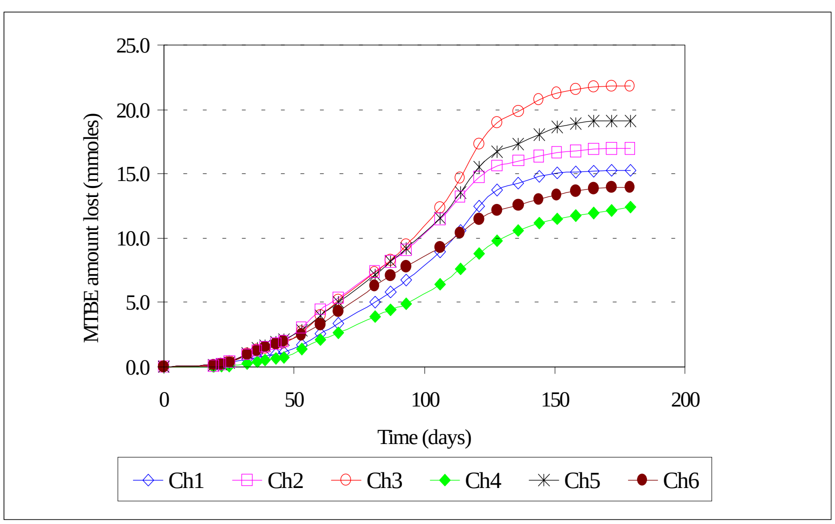
Concentration in ground water		Concentration in gas phase		
mmol/L	mg/L	Confined,* ppmv	TCE in water** vapor, ppmv	TCE in water** saturated air, ppmv
1.0	131	9,100	18	0.56
0.1	13.1	910	1.8	0.056
0.01	1.31	91	0.18	0.0056
0.001	0.131	9.1	0.018	0.00056

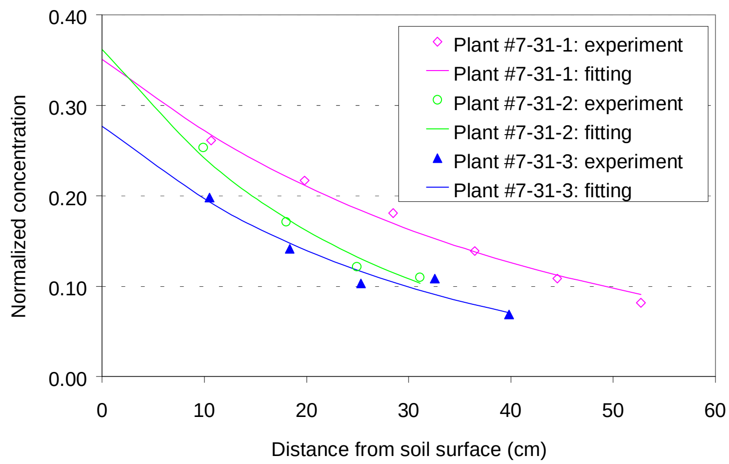
ppmv = parts per million by volume.

* Confined gas phase concentrations are assumed to be in equilibrium with the liquid phase.

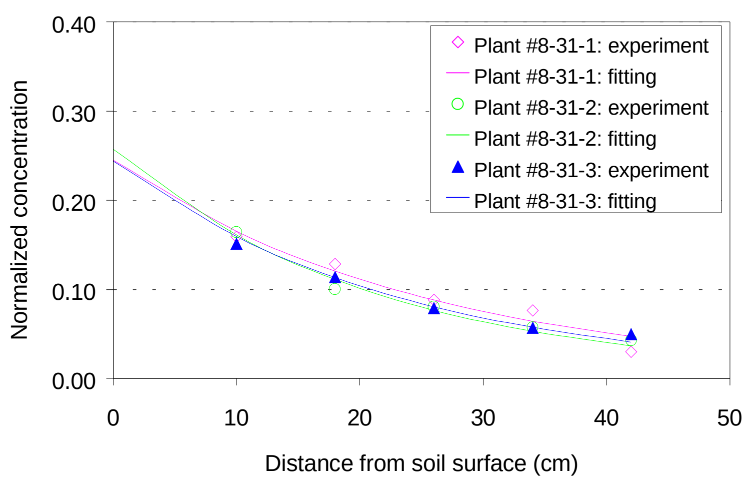
**Unconfined gas phase concentrations are based on evaporation of water vapor and TCE together.

Integrated amount of MTBE lost to the atmosphere over time from the soil surface of six channels.

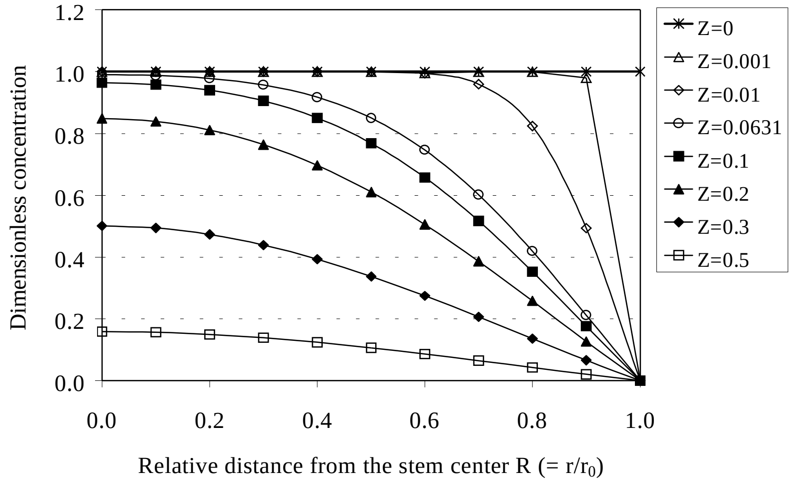




MTBE concentration in plant water as a function of stem position from the soil surface. The points are experimental data and the solid lines are the exponential fittings of form $c = c_0 \exp(-\alpha z)$. The concentration is normalized to the inlet concentration (0.844 mM).



MTBE concentration in plant water as a function of stem position from the soil surface. The points are experimental data and the solid lines are the exponential fittings of form $c = c_0 \exp(-\alpha z)$. The concentration is normalized to the inlet concentration (0.844 mM).



Concentration distribution within the plant stem as a function of the characteristic distance $Z\ (= \frac{\theta_w Dz}{u r_0^2})$, with uniform concentration at Z = 0. Concentration is reduced to the overall concentration at Z = 0.

J. R. Philip (1958) &
D. A. Rose (1981):

diffusion between an individual cell and a large body of solution in which it was placed

$$\tau_{1/2} = \frac{D t_{1/2}}{r_0^2} = 0.0631$$

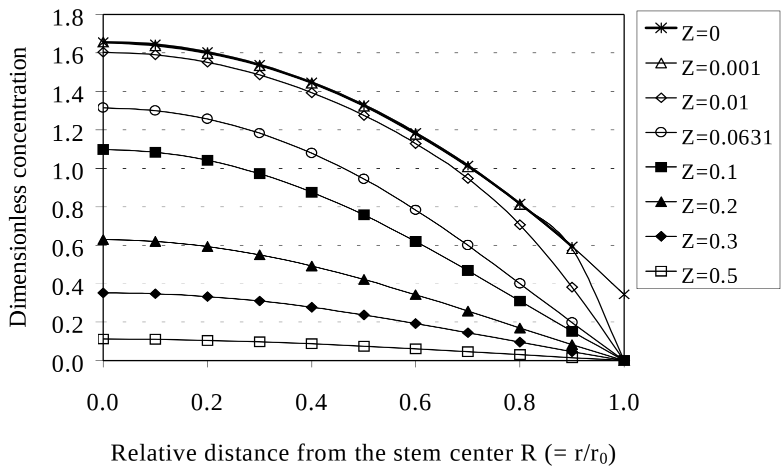
Our Results:

diffusion between a porous plant stem and the atmosphere

$$Z_{1/2} = \frac{\theta_w D z_{1/2}}{u r_0^2} = 0.0631$$

MTBE diffusion coefficient D (with uniform concentration at Z = 0):

$5.88 \times 10^{-8} \sim 1.11 \times 10^{-7}$ (cm^2/sec)



Concentration distribution within the plant stem as a function of $Z\ (=\frac{\theta_w Dz}{ur_0^2})$ for plant #7-31-1, with non-uniform concentration at Z = 0. Concentration reduced to the overall concentration at Z = 0.

Results--*for non-uniform starting conditions*

$$Z'_{1/2} = \frac{\theta_w D' z_{1/2}}{ur_0^2} = 0.0919$$

MTBE diffusion coefficient D':

$8.57 \times 10^{-8} \sim 1.62 \times 10^{-7}$ (cm^2/sec)

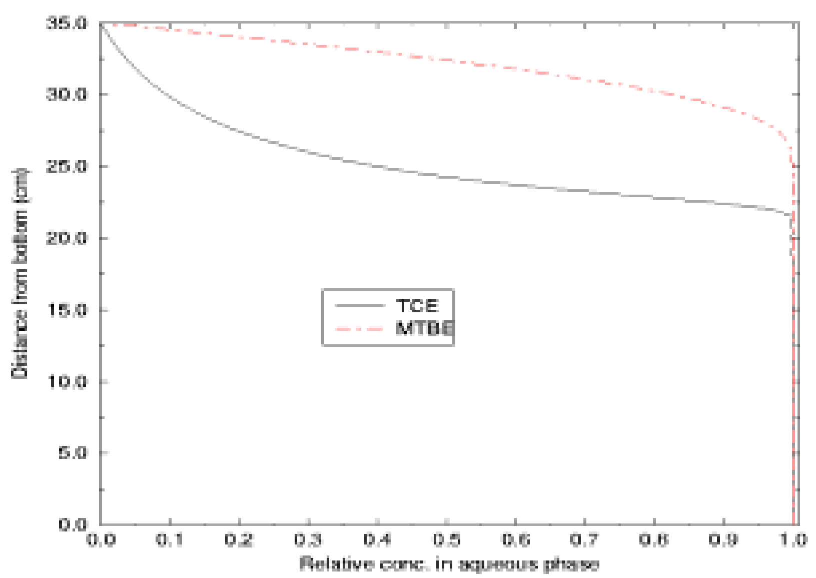
Comparison of Standard Deviations of Two Model Solutions from the Experimental Data

Plant#	7-31-1	7-31-2	7-31-3	8-31-1	8-31-2	8-31-3
uniform	0.0753	0.0782	0.0748	0.0929	0.0771	0.0676
non-uniform	0.0452	0.0524	0.0519	0.0608	0.0373	0.0253

Mass balance of water and estimated fraction of MTBE transpired by plants during the three- months test period.

Channel #, description	**1, planted and aerated**	**2, planted but not aerated**	**3, planted but not aerated**	**4, unplanted and not aerated**	**5, planted but not aerated**	**6, planted and aerated**
Total water added (L)	186	192	191	185	199	197
Evapotranspired water (ET) (L)	81	116	109	37*	106	108
Estimated average plant uptake of MTBE (fraction)	**0.015**	**0.029**	**0.024**	**0.0****	**0.032**	**0.035**
Estimated greatest plant uptake of MTBE (fraction)	**0.035**	**0.068**	**0.056**	**0.0****	**0.075**	**0.080**
Corrected recovery	0.78	0.69	0.80	1.0	0.85	0.71
Recovery with average plant uptake	**0.80**	**0.72**	**0.82**	**1.0**	**0.88**	**0.75**

* There was only evaporation of water in this unplanted channel.
**No plant uptake for this channel.



Simulated aqueous phase concentration
of MTBE and TCE for $\theta_s = 0.29$

Key Publications

1. Zhang, Qizhi, L.C. Davis, and L.E. Erickson. "Effect of Vegetation on Transport of Groundwater and Nonaqueous Phase Liquid Contaminants," *Journal of Hazardous Substance Research*, Vol. 1, No. 8 (1998), http://www.engg.ksu.edu/HSRC.
2. Narayanan, Muralidharan, J.C. Tracy, L.C. Davis, and L.E. Erickson, "Modeling the Fate of Toluene in a Chamber with Alfalfa Plants 1. Theory and Modeling Concepts," *Journal of Hazardous Substance Research*, Vol. 1, No. 5 (1998), http://www.engg.ksu.edu/HSRC.
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Rhizosphere Remediation of Recalcitrant Soil Contaminants: An Important Component of Long-term Sustained Biosystem Treatment

John Fletcher

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John S. Fletcher

John Fletcher holds a B.S. from Ohio State University, an MS from Arizona State University, and a Ph.D. in Plant Physiology from Purdue University. He is a Professor of Botany in the Dept. of Botany and Microbiology at the University of Oklahoma in Norman, OK. During his 30 year tenure at the University of Oklahoma he and his graduate students have studied the metabolism of nonphotosynthetic plant tissues, root uptake of xenobiotics, ecological risk assessment (including PHYTOTOX and UTAB database development), and rhizosphere remediation of PCBs and PAHs. In 1997 Dr. Fletcher received a level 1 Research Award from EPA's Office of Research Administration for phytotoxicity research he conducted in collaboration with persons at the EPA Laboratory in Corvallis, Oregon. His current research is focused on rhizosphere remediation of PAHs at a former industrial sludge basin in Texas and several PCB-contaminated field sites in the Czech Republic. Both projects are being conducted with the cooperation of industrial partners. Dr. Fletcher's professional service activities related to environmental issues include: Plant Editor for the Journal of Environmental Toxicology and Chemistry, member of the Chemical Manufacture Association's Technical Implementation Panel for Ecological Risk Assessment Research, and member of EPA's Scientific Advisory Panel for the Federal Insecticide, Fungicide and Rodenticide Act.

Sustained Rhizosphere Remediation of Recalcitrant Contaminants in Soil: Forensic Investigations with Laboratory Confirmation

John S. Fletcher, Dept. of Bot. and Micro., Univ. of Oklahoma, Norman, OK 73019

A conservative estimate of the volume of PAH contaminated soil in the US (based on U.S. Dept. of Commerce Reports) is 1 billion ton. Biosystem Treatment relying on the integrated action of plants and microbes over extended time periods has the potential of reducing cleanup costs by >90%, and lead to pollutant degradation rather than just containment that leaves the burden of cleanup for future generations. The three components of Biosystem Treatment are plant evapotranspiration, plant-microbe rhizosphere degradation, and natural attenuation of groundwater by microbes. The least studied and therefore poorest understood of these three components is rhizosphere degradation.

Rhizosphere research in our laboratory has addressed the hypothesis: "Roots of some plant species enhance the degradation of recalcitrant, organic soil contaminants (i.e. PCBs and PAHs) by releasing cometabolites and facilitating soil aeration, both a result of fine root turn over". Published results from our laboratory supporting this hypothesis are: (1) purified natural plant compounds (i.e. flavonoids) stimulate the growth and activity of PCB and PAH degrading bacteria, (2) flavonoid compounds are present in mulberry fine roots, (3) flavonoid compounds accumulate in aging/dying mulberry roots, (4) over 50% of the fine roots turnover (die) annually. Demonstration of statistically significant reductions in the concentrations of high molecular wt, low water soluble contaminants in laboratory pot studies have failed. This is attributed to several factors: (1) pot-study artifacts (i.e. unnatural root distribution), (2) limited soil-root contact at any one time, (3) long time (several seasons) necessary for extensive soil exploration through fine root turn over. For these reasons, the only valid test of rhizosphere remediation of recalcitrant, slightly water soluble contaminants (PCBs and high molecular wt PAHs) are long term (15-20 yr) field studies. Because of the inability to gain authorization to conduct such a study we resorted to an alternative, forensic examination of naturally revegetated sites. At a revegetated former sludge basin we have shown a 50-90% reduction of PAHs (including slightly water soluble benzo(a)pyrene) in the 120 cm root zone of 12-16 yr old mulberry trees where over two hundred PAH degrading bacteria isolates have been recovered.

Currently available laboratory and forensic field data justifies initiation of carefully monitored long-term Biosystem Treatment projects. During early stages of treatment (first 5 years) the monitoring should establish that the components of the system (roots and degrading bacteria) are in place with monitoring shifting to analysis of contaminant disappearance after 5 years. It is gratifying that a Biosystem Treatment strategy has been adopted at Bofors Nobel Site in Michigan. The most pressing need to advance the Biosystem Treatment concept is improved assessment tools to monitor the biological components of the integrated system. To that end, our current research is focused on development of improved field assessment tools. Our approach is: identify working rhizosphere systems at existing revegetated sites, study the components of these working systems in the laboratory, develop assessment methods in the laboratory, and return to the field to validate, and use the newly developed methods.

Rhizosphere Remediation of Recalcitrant Soil Contaminants: An Important Component of Long-term Sustained Biosystem Treatment

John S. Fletcher, Department of Botany and Microbiology
University of Oklahoma, Norman, OK 73019

A conservative estimate of the volume of PAH contaminated soil in the US (based on US Dept; of Commerce Reports) is 1 billion tons with some associated with former manufactured gas plant sites dating back 150 years. Biosystem Treatment relying on the integrated action of plants and microbes over extended time periods has the potential of reducing cleanup costs by > 90%. Furthermore, the end result would be pollutant degradation rather than just containment, characteristic of capped cells where unfavorable water and oxygen conditions prevent biological degradation, thus preserving the waste and leaving the burden of cleanup for future generations. Three important components of Biosystem Treatment are plant evapotranspiration, plant/microbe rhizosphere degradation, and natural attenuation of groundwater by microbes. The least studied and therefore poorest understood of these components is rhiosphere degradation.

Underpinning our research approach to phytoremediation is the realization that although plants in natural ecosystems produce polyaromatic compounds (flavaniods, coumarins, etc.) in their leaves, stems and roots, these compounds have not accumulated in the soil to concentrations reflective of their annual production over thousands of years (Figure 1). There is only a limited understanding of the production and recycling of carbon associated with naturally occurring polyaromatic compounds in terrestrial ecosystems (i.e. tannins in oak forests, Figure 1). However, it is apparent that since they have not accumulated to astronomic amounts over the last millennium, mechanisms do exist within nature to degrade and recycle carbon present in thousands of naturally occurring polyaromatic compounds many of whose structures resemble those of recalcitrant pollutants such as PCBs, and PAHs (Figure 2). The obvious question is, "Will the biological mechanisms in nature that degrade natural polyaromatic compounds also degrade recalcitrant organic pollutants (i.e. PCBs and PAHs)?" If so, what soil ecosystems associated with what plants are most active against pollutants? How should we introduce and manage these natural, multi-organismic systems to optimize their degradative properties towards recalcitrant pollutants? All of these questions deserve attention and should be resolved in order to develop dependable sustained phytoremediation technology. First however, there is a need for a better understanding of rhizosphere degradation properties and its relationship to xenobiotic compounds. To that end, our research has addressed the hypothesis: "Roots of some plant species enhance the degradation of recalcitrant, organic soil contaminants (i.e. PCBs and PAHs) by releasing cometabolites and facilitating soil aeration, both a result of fine root turn over".

The emphasis of our research over the past 15 years has been placed on understanding the mechanism of rhizosphere degradation of PCBs and PAHs with secondary attention given to the disappearance of these recalcitrant contaminants from contaminated soil. The rational for placing emphasis on mechanistic studies was that the results collected not only served to test the hypothesis but also provided a level of understanding that is necessary to improve the performance of phytoremediation and develop monitoring tools to facilitate field implementation, the importance of which is described later in this summary (Figure 3). Published results from our laboratory supporting the hypothesis and providing a mechanistic understanding of rhizosphere degedation are: (1) purified natural plant compounds (i.e. flavaniods) stimulate the growth and activity of PCB degrading bacteria (Donnelly, etal. 1994); (2) Plant roots release phenolic compounds that support the growth of PCB degrading bacteria, but all plant species are not effective (Fletcher and Hegde, 1995; Fletcher etal. 1995, Hegde and Fletcher, 1996); (3) Flavanoid compounds that support the growth of PAH- degrading bacteria accumulate in aging/dying fine roots of mulberry (Leigh, etal. 1998); (4) field studies have shown that fine mulberry roots grow in contact with PAH-contaminated sludge at 1 meter depths (Olson and Fletcher 1999). The combined interpretation of these data is that the roots of some plant species are capable of growing to immobile soil contaminants (PCBs and high mol. wt. PAHs) and deliver cometabolies (i.e. flavaniods) upon fine root death. These natural cometabolites foster the growth and activity of degredative microbes. The dead/decayed roots also create soil cavities that facilitate soil aeration. Thus, in order for roots to foster the degradation of immobile soil contaminants

(PCBs and PAHs) it is not necessary for the water insoluble contaminants to move to the root, because fine roots (<0.5mm in diameter) grow to the contaminants, and upon root death serve as soil injectors of bacterial cometabolites and facilitators of soil aeration (Figure 4). Based on this mechanistic understanding, the performance of rhizosphere remediation can be improved by increasing both root synthesis of cometabolites and the rate of fine root turnover.

Efforts on our part to demonstrate statistically significant reductions in the concentrations of high molecular wt, low water soluble contaminants in laboratory pot studies have failed. This is attributed to several factors: (1) pot-study artifacts (i.e. unnatural root distribution), (2) limited soil-root contact at any one time (<5%), and (3) long time (several seasons) necessary for extensive soil exploration through fine root tur over (growth followed by death). For these reasons, it is our contention that long-term (15-20 year) field studies are the only valid test of rhizosphere remediation of recalcitrant, slightly water-soluble contaminants (PCBs and high molecular wt PAHs). Because of the inability to gain authorization to conduct such a study we resorted to an alternative, forensic examination of naturally revegetated sites. At a revegetated former sludge basin we have shown a 50-90% reduction of PAHs (including slightly water soluble benzo(a)pyrene) in the 120 cm deep root zone of 12-16 yr old mulberry trees where over two hundred PAH degrading bacteria isolates have been recovered (Olson and Fletcher, 1999; Olson et.al., 2000.)

Based on current data available from laboratory mechanistic studies and forensic field data that have been collected on recalcitrant soil contaminants, we believe carefully monitored long-term Biosystem Treatment projects (15-20 years) should be initiated. Because of the long time required for roots to have a statistical influence on the degradation of immobile soil contaminants for reasons explained earlier, we propose that during early stages of treatment (first 5 years) the monitoring should establish that the components of the system (roots and degrading microorganisms) are in place with monitoring shifting to analysis of contaminant disappearance after 5 year (Figure 3). Monitoring the existence and operation of the degratative system instead of the product of the system (compound disappearance) is a more sensitive way to establishing that slow but sustained rhizosphere remediation is working. We are in the process of developing chemical and molecular methods to monitor the existence and function of rhizosphere degradation in the field. The development of these methods is capitalizing on basic research that was conducted in our laboratory to understand mechanistic features of the plant rhizosphere.

It is gratifying that ideas and phytoremediation data gained at the University of Oklahoma were instrumental in designing and promoting the Biosystem Treatment strategy that has been adopted at Bofors Nobel Superfund site in Michigan. Implementation of the Biosystem Treatment at Bofors will be an example of capitalizing on the combined action of plant evapotranspiration, plant-microbe rhizosphere degradation, and natural attenuation by groundwater microbes for the long-term sustained treatment of contaminants across space and time, typical of natural ecosystems.

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BROWNFIELDS APPLICATION AND BENEFICIAL USE OF LAND

Integrating Remediation Into Landscape Design

Niall Kirkwood

Niall G. Kirkwood is Program Director and Associate Professor at Harvard University's Graduate Design School, where he has taught since 1993. He supervises research, executive education, curriculum development and teaching in the areas of landscape technology, land reclamation, and innovative site engineering. In addition, he is Director of the recently established Harvard Center for Environment and Technology.

Prior to his academic appointment, he was in private practice in the United States and Europe as an architect, landscape architect and urban designer working on urban regeneration projects in Barcelona, London, Riyadh, Los Angeles, Columbus, Ohio and Manhattan.

Professor Kirkwood's current research focus includes environmentally disturbed sites in industrial and developing countries, and landfill and brownfields redevelopment. Current study projects include the reuse of the Fresh Kills Landfill, Staten Island, NY and brownfield sites in New England, Mexico and Asia. Superfund research at Tar Creek, Ottawa County, Oklahoma is is carried out in collaboration with Harvard Medical School and the Harvard School of Public Health.

He is a member of the board of The Clean Land Fund, a non-profit revolving loan fund based in Rhode Island and serves on the Harvard Committee on the Environment.

Abstract

The presentation will focus on four topics related to the application of phytoremediation on Brownfields.

- An overview of the development of phytoremediation in relationship to land use and development.
- An introduction to landscape design processes and their relationship to the use and application of living plant material.
- The application of phytoremediation on Brownfields- the issues of context, site and implementation.
- An introduction to the larger urban issues surrounding Brownfields and their impact on phytoremediation.

INTEGRATING REMEDIATION INTO LANDSCAPE DESIGN

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Niall Kirkwood
Harvard Graduate School of Design

SESSION IIIA
BROWNFIELDS APPLICATIONS AND BENEFICIAL USE OF LAND

EPA Phytoremediation: State of the Science Conference, Boston, MA May 1-2, 2000

TOPICS TO BE ADDRESSED

- Phytoremediation and Landscape Design
- What is the Landscape Design Process?
- Phytoremediation and Brownfields
- Further Issues in Brownfield Design

PHYTOREMEDIATION POTENTIAL

- Regional, City Parks & Community Recreational Open Space
- Commercial/Industrial Parks and Biotechnology Centers
- Housing: Assisted and Private
- 'Green Infrastructure': open space/roads/utility/rail corridors
- Landfill Parks and Golf Courses
- Urban Arboretum, Environ. Education & Growing Centers

THE LANDSCAPE DESIGN PROCESS

- **Site Analysis** (*site identification, economic and site assessment*)
- **Conceptual Design** (*project development and financing)*
- **Schematic Design and Design Development** (*project planning*)
- **Documentation and Bidding**
- **Implementation** (*cleanup execution and redevelopment of land*)
- **Maintenance and Post-Occupancy Evaluation**

(source: AIA. Document B163)

PHYTOREMEDIATION

➢ **SELECTED IMPLEMENTATION ISSUES** (source: L. Jackson, 1997)

- **Refine Select-a-Plant Chart**
- **Use Phytoremediation to go beyond Site Closure**
  whole ecosystem approach
  use of native plants & habitat restoration
- **Managing Wildlife Issues: Balance Habitat and Treatment**
- **Increase Net Environmental Benefit and Value**

BROWNFIELDS

➢ **SELECTED CURRENT ISSUES** (source: J. Ackerman, VHB 1999)

- **Sustainable Economics- urban planning/'smart growth'**
- **Treating Social Malaise- livable neighborhoods/employment**
- **Environmental education- 'tools for schools'**
- **Technology Trends- innovations in assessment & remediation**

PHYTOREMEDIATION/BROWNFIELDS

➢ **TIME LINE- TWO DEVELOPMENT TRACKS**

1. **Anticipated Development (9 months - 3 year)**
   phytoremediation system is implemented as part of delivery of usable site and construction program.

2. **Long Term (30 year)**
   phytoremediation 'embedded' in evolving interim and temporary land-use programs

PHYTOREMEDIATION/BROWNFIELDS

➤ THREE KEY POINTS

Perception
phytoremediation derived from agricultural-scale (crops, fields and hedgerows) rather than urban scale (bosque, allee, garden)

Time
relationship of phytoremediation to temporary and interim brownfield uses and site programs.

Brown Cities and Brownfields
nature, scale, complexity and location of site areas.

PHYTOREMEDIATION/BROWNFIELDS

- **ISSUES**
  - Urban Context
  - Existing Site Conditions- soils/groundwater
  - Other Engineering Activities not Remediation
  - Plant Growth Concerns- microclimate/soils
  - Adjacent Community Concerns
  - Proposed Site Program
  - Implementation Concerns
  - Disposal Methods
  - Time-line- 2 tracks

Goals for Brownfields Pilots - O'Sullivan Island

John Podgurski

John Podgurski is currently the Brownfields Coordinator for EPA-Region I with responsibility for implementing the EPA's New England brownfields efforts.

John has over fifteen years of regulatory experience working in hazardous waste management and site remediation. In addition, he has worked in the chemical manufacturing industry as a chemical engineer in research & development and production operations.

John has been involved with EPA's brownfields initiative continuously since its inception in 1995.

EPA Phytoremediation: State of the Science Conference

May 1-2, 2000

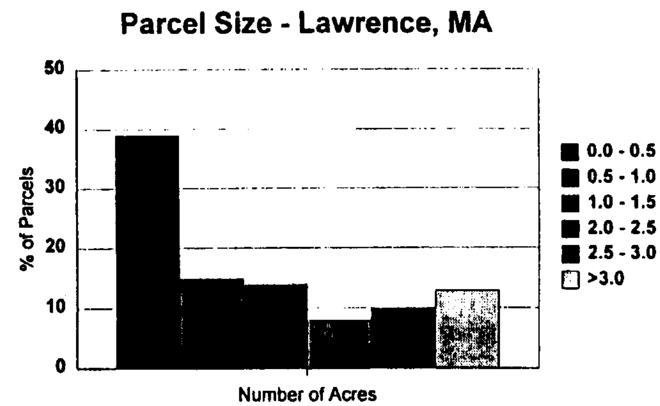
What is a brownfield?

- ▲ Vacant or under used industrial/commercial facility
- ▲ Redevelopment is complicated by real or perceived contamination.

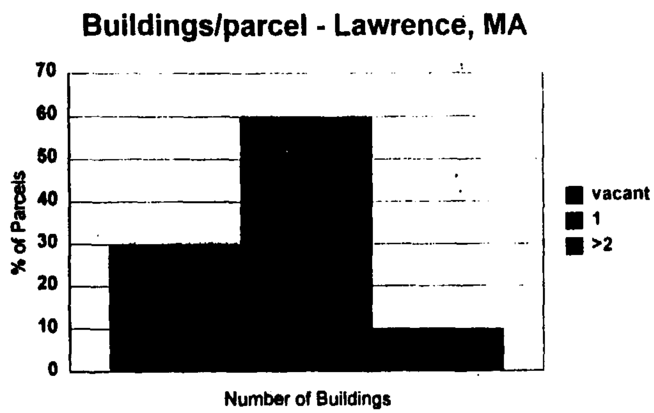
What is a brownfield?

- ▲ Estimated Number of Sites
- ▲ Distribution
- ▲ "Typical" Profile (Urban)

"Typical" Urban Brownfields Profile



"Typical" Urban Brownfields Profile



Common Brownfields Issues (Contamination-related)

- ▲ "Pre-decisional" investment
- ▲ Site investigation/clean-up <u>costs</u>
- ▲ Site investigation/clean-up <u>time frames</u>
- ▲ Additional engineering/design requirements
- ▲ Potential delays caused by public concerns
- ▲ Process uncertainties
  - undetected contamination
  - ineffective remediation
  - changing regulatory climate and standards

Some of the "Other" Issues

- ▲ Location
  - Local property values
  - Existing infrastructure (e.g., utilities, roadways, etc.)
  - Surrounding socio-economic stability
  - Security/safety
- ▲ Existing structures
  - Structural integrity
  - Physical layout/retrofitting
- ▲ Financial encumbrances

Phytoremediation and the Urban Setting - An Opportunity?

- ▲ Focus on publicly- vs. privately-controlled sites
- ▲ Part of broader strategy to address multiple public needs
  - Flexibility with future reuse options
    - open space
    - commercial/industrial
    - residential
  - Exposure reductions
    - "low cost" stabilization option
    - long term (remediation)
  - Aesthetic enhancement
- ▲ Some "economy of scale" possible
- ▲ Potential O&M cost reductions

Phytoremediation and the Urban Setting - Potential Issues

- ▲ Small parcel sizes
- ▲ Existing structures/surfaces
- ▲ Complicated ownership status
- ▲ Difficult growing conditions
  - Soil types/debris
  - Shading
  - Microclimates

Potential Issues *(continued)*

- ▲ Site Security/Vandalism
  - May be located in high crime areas
  - High usage areas
- ▲ Equipment access
- ▲ Public concerns regarding exposure

RADIONUCLIDES

Capturing a "Mixed" Contaminant Plume: Tritium Phytoevaporation at Argonne National Laboratory

M. Cristina Negri, Ray Hinchman, and James Wozniak

MARIA CRISTINA NEGRI

As a soil scientist and agronomist, M. Cristina Negri (University Degree 1981, Dottore in Agricultural Sciences, 110/110 Cum Laude, University of Milan, Italy) shares the leadership of the phytoremediation activities at Argonne National Laboratory (ANL) since 1990. Active or completed phytoremediation projects at ANL include the deployment of a deep-rooted [30'] groundwater phytoremediation project for hydraulic control and VOC and tritium remediation; investigation on the potential for using plants to remove Cs-137 and inorganics from soils at Argonne-West at the INEEL, Idaho; zinc, lead and arsenic phytoremediation studies; and the study of plant systems for the treatment of salt brines produced in the natural gas and oil extraction processes.

Other activities include developing a proprietary technology for the decontamination of cesium-137 contaminated milk from the Chernobyl area, and the study and scale-up of a soil washing technology for the decontamination of a Pu-contaminated DOE soil. Since 1991 M.C. Negri is the appointed Convener of a working group within CEN (the European Standardization Organization) aimed at creating human and environmental safety standards for growing media and soil improvers, both traditional and waste-derived. From 1979 to 1991 M.C. Negri worked in the private industry sector in Italy. Her activities related to the study of chemical and microbiological aspects and environmental impact of the recovery of biomass and industrial waste.
Publications available upon request.

Abstract

Large green plants have the capability to move significant amounts of soil solution into the plant body through the roots and evaporate this water out of the leaves as pure water vapor in the transpiration process. It is known that tritium, as tritiated water, is partly directly incorporated in biological tissues, and partly transpired by plants as tritiated water vapor.

An innovative application of engineered phytoremediation has been deployed at the Argonne National Laboratory (ANL) site in Illinois. At this site, tritium is present as a co-contaminant with Volatile Organic Compounds (VOCs) in the groundwater, approximately 30 ft (10 m) deep in the glacial subsoil. In 1999, the U.S. Department of Energy (DOE), through the Accelerated Site Technology Deployment (ASTD) Program funded the deployment of a phytoremediation system in the 317/319 areas with the objectives of minimizing water infiltration into the source soils, stabilizing the treated soil surface to prevent erosion, runoff, and downstream sedimentation; hydraulically contain tritium and VOCs migration with the groundwater, and continuing remediation of the residual VOCs in the plume.

The phytoremediation system installed involves the use of high-transpiring, deep-rooted phreatophytes to provide hydraulic control of the contaminated plume. While the fate of the VOCs in a phytoremediation system has already been demonstrated in a number of cases, this installation is pioneering the use of phytoevaporation for the removal of tritium from the subsoil.

A preliminary evaluation conducted by ANL prior to the inception of the project indicated that even assuming that all of the tritium (at the highest concentration in the plume) were transpired by plants, air emissions of tritium would result in an inconsequential exposure for a person at the site boundary, and be well within the National Emission Standards for Hazardous Air Pollutants (NESHAPS).

Soon after DOE funded the project, the U.S. EPA and DOE agreed to include this remediation technology deployment in the projects evaluated by the EPA Superfund Innovative Technology Evaluation (SITE) Program. Under this program, the EPA is independently monitoring and evaluating the technology's performance at the ANL-E 317/319 sites, in addition to the scheduled monitoring activities conducted by ANL.

Phytoremediation at the 317/319 areas at Argonne was deployed in the summer of 1999 achieving a significant, 33% cost saving over the baseline traditional technology of capping and extraction wells. As the plants mature, performance data will validate further predicted cost savings on operations and maintenance, as the existing extraction wells will be closed and the plants will generate no secondary waste.

Capturing a "Mixed" Contaminant Plume: Tritium Phytoevaporation at Argonne National Laboratory's Area 319

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Introduction

Tritium is a soft (low-energy) beta emitter radionuclide. As such, it is easily shielded by human skin, paper, and approximately 6 mm of air. It is, however, hazardous when taken internally via ingestion, inhalation, and absorption. It decays to Helium-3 and has a half-life of 12.6 years. As it shares the chemical and physical properties of hydrogen, it is found as an environmental concern typically as tritiated water. As for most of the radionuclide contaminants, its radiological hazard exceeds the chemical hazard and thus levels of environmental concern in terms of radioactivity translate into minute amounts in terms of mass. Sources and an estimated inventory of tritium are reported in Table 1 (from: www.hfbr.bnl.gov/hfbrweb/hdbl1079a.html#ZZ5).

Table 1. Sources and estimated inventory of Tritium.

Source	Inventory
Natural (cosmic rays, m steady state)	70×10^6 Ci
Nuclear test explosions (1945-1975)	3×10^9 Ci (most decayed)
Nuclear power and defense industry releases	$1\text{-}2 \times 10^6$ Ci/year
Commercial devices (radioluminescent, neutron generating)	1×10^6 Ci/year

Tritium is known to be directly incorporated in water and biological tissues. Its average biological half life in the human body is 7.5 to 9.5 days. In plants, it is taken up as tritiated water and subsequently mostly transpired as tritiated water vapor (IAEA, 1981). Studies conducted by the University of Heidelberg in natural ecosystems suggested that heavy plant growth might pull water from the soil at a rate so fast to considerably reduce tritium diffusion and therefore isotopic mixing in the groundwater (IAEA, 1967). A small portion of the tritium is accumulated in plants as cell water or into tissue. Work conducted at the Maxey Flats Disposal Site concluded that trees could be bioindicators of tritium contamination (Rickard and Kirby, 1987). In any case, the accumulation in plants appears to be of short duration (4 to 37 days) (IAEA, 1981; Fresquez et al. 1995).

Tritium contamination of groundwater is present at the 317/319 areas at Argonne National Laboratory-East (ANL-E), as a result of past operations. Low levels of tritium, as well as VOCs, have been detected in the groundwater in this area. The contaminated plume, approximately 30 ft (10 m) deep in the glacial subsoil, is migrating toward the southern boundary of the site through a series of sand layers, into the adjacent Waterfall Glen Forest Preserve of DuPage County.

In 1999, the U.S. Department of Energy's Office of Environmental Management, through the Accelerated Site Technology Deployment (ASTD) Program, jointly funded the deployment of an innovative phytoremediation system in the 317/319 areas with the following objectives: (1) minimize water infiltration into the 317 French Drain area soils, some of which were treated previously by soil mixing, thermal desorptions and iron addition; (2) stabilize the treated soil surface in the 317 French Drain area to prevent erosion, runoff, and downstream sedimentation; (3) hydraulically contain groundwater migration and continue remediation of the residual VOCs within the source area, and (4) hydraulically contain the VOCs and tritium plume south of the 319 area landfill.

Large green plants are capable of moving significant amounts of soil solution into the plant body through the roots and evaporate this water out of the leaves as pure water vapor in the transpiration process

(Chappell, 1998; Wullschleger et al. 1998). Plants transpire water to move nutrients from the soil solution through the roots (which function as a highly dispersed, fibrous uptake system) to leaves and stems, where photosynthesis occurs, and to cool the plant. While the use of trees to hydraulically control and remediate contaminated groundwater plumes at depths in the range of five to more than 30 ft has been successfully applied at commercial installations (Nyer and Gatliff, 1996) for the remediation of VOCs and excess nutrients, its application to treat tritium contaminated groundwater has never been conducted before.

Technological Approach and Expected Results

The use of trees to remediate and contain contaminated groundwater has been successfully demonstrated in treating contaminated groundwater. Applied Natural Sciences, Inc, (ANS) demonstrated the use of phreatophytic trees (i.e., plants such as poplars and willows that do not rely on precipitation water but seek water deep in soils) with its TreeMediation® and TreeWell® systems, that use a unique and patented process to enhance the aggressive rooting ability of selected trees to clean up soil and groundwater up to 50 ft deep. Under a CRADA, ANL-E and ANS researched phytoremediation applications since 1994.

The 317 and 319 areas are located on the extreme southern end of the ANL-E site, immediately adjacent to the DuPage County Waterfall Glen Forest Preserve. The 317 area is an active hazardous and radioactive waste processing and storage area. In the late 1950s, liquid waste was placed in the unit known as the French Drain. Since that time, this waste has migrated into underlying soil and groundwater. The principal environmental concern in the 317 area is the presence of several VOCs in the soil and groundwater and low levels of tritium in the groundwater beneath and downgradient of the site. The 319 landfill and French Drain area are located immediately adjacent to the 317 area. The principal environmental concern in the 319 area is the presence of radioactive materials in the waste mound, in the leachate in the mound, and in the groundwater downgradient of the landfill. Several interim actions have already been implemented to reduce the VOC and tritium releases from these areas, as the result of the Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) conducted from December 1994 through September 1996. Currently, existing mechanical extraction wells remove approximately 20,000 m^3/yr of contaminated groundwater, which are sent to ANL's water treatment plant. While the VOC contaminants are degraded at this facility, tritium concentrations are diluted with other wastewater from the lab and discharged in accordance with regulatory limits.

The hydrogeology at the 317/319 sites is a complex framework of glacial tills interlaced with sands, gravels, and silts of varying character, thickness, and lateral extent. The subsurface is a complex arrangement of approximately 60 ft of glacial geologic deposits over Silurian dolomite bedrock. The glacial sequence is comprised of Lemont drift overlain by the Wadsworth Formation. Both units are dominated by fine-grained, low-permeability till. Permeable zones of varying character and thickness are present in each. These materials range from silty sands to sandy, clayey gravels to gravelly sands. In some locations, pure silt was encountered. If deep enough, this silt was saturated, and it is assumed to play in important role in the flow of groundwater in the study area. The permeable zones have a wide range in shape, their thicknesses range from less than one ft to roughly 15 ft and they have limited lateral extent (Quinn et al. 2000).

On the basis of a preliminary agronomic assessment, hybrid willow and hybrid poplar trees were selected for the system. In the summer of 1999, a total of approximately 800 trees were planted in three locations: the 317 French Drain area, south of the 317 French Drain area and 319 area landfill (the 317 and 319 Hydraulic Control areas), and in the waste trench south of the 319 area landfill. Approximately 160 hybrid poplars were planted in the area of interest of tritium contamination. This system is expected to prevent the further generation of contaminated groundwater in the source area by degrading the contaminants, and to prevent the further migration of these plumes by removing groundwater from saturated zones downgradient from the source area. Figure 1 shows the location of the plantings. The installed system consists of plantings of hybrid willows and special deep-rooted hybrid poplars. The willows were planted in the source area (317 French Drain area) deeper (16-20 ft) than is normal for horticultural plantings, but without some of the special modifications used with the deep-planted poplars.

In the 317 and 319 Hydraulic Control areas, poplar trees were planted in boreholes spaced 16 ft apart drilled down to the contaminated aquifer using ANS's TreeWell® system. This technology was selected, in consideration of the hydrogeological setting of the site, to target root growth in the contaminated glacial-drift permeable unit approximately 30-ft deep. The poplars were planted in two-ft diameter caisson boreholes lined with plastic sleeves in order to direct the roots exclusively to the main contaminated aquifer. These boreholes were filled with a mixture of topsoil, sand, peat, and manure to promote root growth and tree development. The capillarity of the mixture provides an added benefit of drawing water to where it is available to the young trees. All boreholes were also provided with aeration tubes to ensure a supply of air to the growing roots. Figure 2 presents a diagram of a TreeWell® installation.

Planting phreatophytic trees at the capillary fringe in the year 1999 is expected to provide full hydraulic control by the year 2003 (see below) and be self sustaining for the full-expected life of the engineered plantation. Hybrid poplar and hybrid willow trees typically have a life span of about 40 years. The Path to Closure Plan committed ANL-E to have all remedial work at the 317/319 areas completed by October 2000.

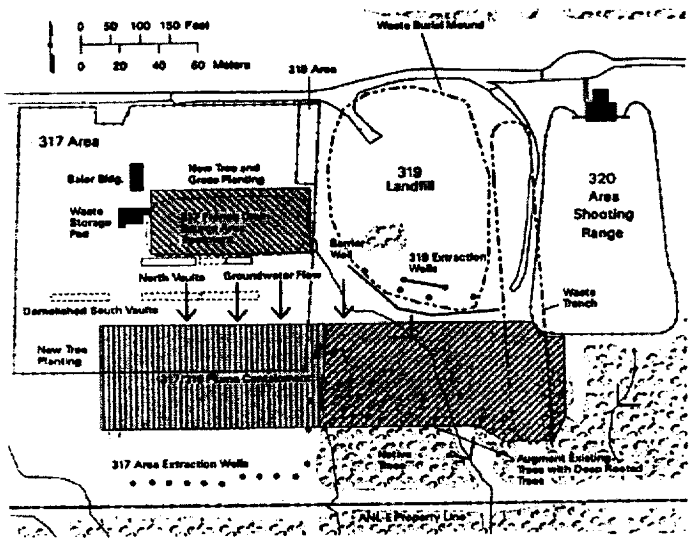

Figure 1. Planting locations at the 317/319 areas.

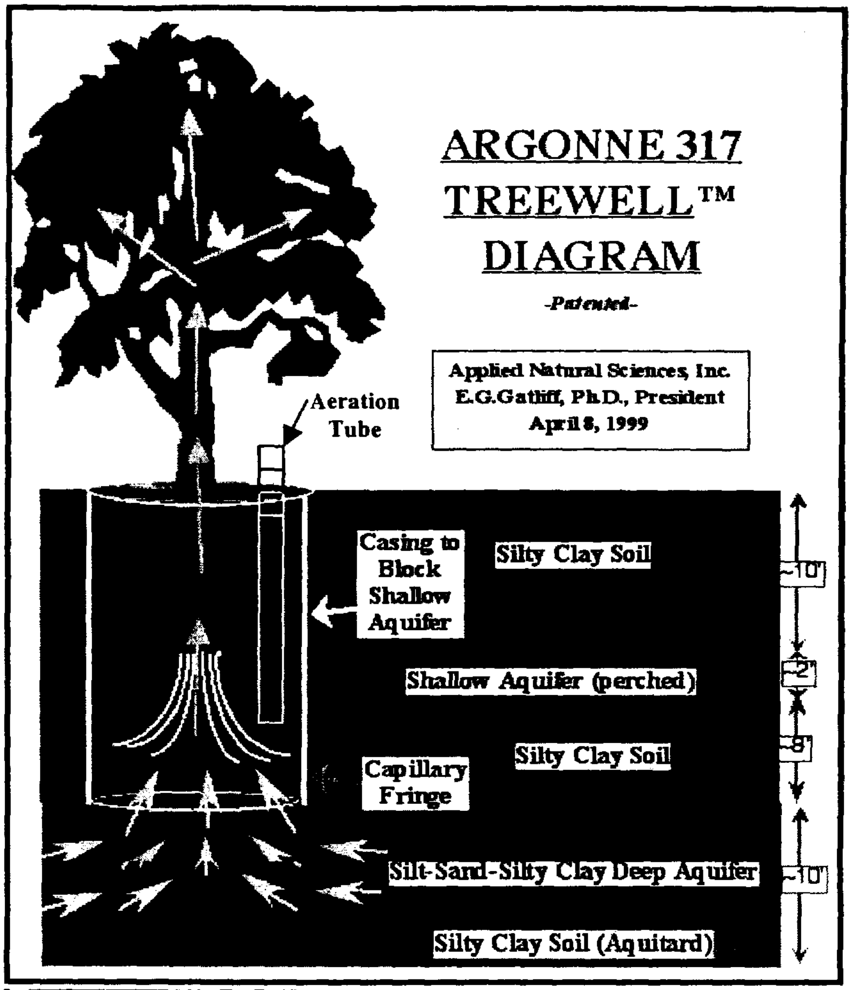

Figure 2. Diagram of a Tree Well ® installation.

ANL-E installed 48 groundwater monitoring wells on the phytoremediation project site to track the performance of the phytoremediation system. Soon after DOE funded the project, the U.S. EPA and DOE agreed to include this remediation technology deployment in the projects evaluated by the U.S. EPA Superfund Innovative Technology Evaluation (SITE) Program. Under this program, the U.S. EPA will independently monitor and evaluate the technology's performance at the ANL-E 317/319 sites in addition to the scheduled monitoring activities conducted by ANL-E. Monitoring activities have started at the completion of the construction phase. Root development will be observed through specially designed viewing ports (minirhizotrons).

At the end of the remedial process, when a final analysis will verify the absence of the contaminants in the biomass, the trees will be cut down at ground level, chipped, and air dried. The roots will be left in place to decay through natural processes and the chips will be reused on site as mulch for the planting of native prairie species, in accordance with the planned final restoration of the area.

Planning Considerations

Preliminary to the implementation of the system, a modeling study was conducted to assess potential air emission hazards, according to existing regulations (NESHAPS 40 CFR 61 Subpart H). Using maximized assumptions on tritium concentration in the groundwater and plant transpiration rates, emissions via transpiration were calculated for the four years from the time of planting to the time of canopy closure. Results are reported in Figure 3. The derived exposure rates to the nearest member of the public were calculated as required using the U.S. EPA CAP-88 PC program and resulted in values ranging between 6.32 x 10^{-6} mrem/yr in the first year to 2.58 x 10^{-5} mrem/yr during year four. As the

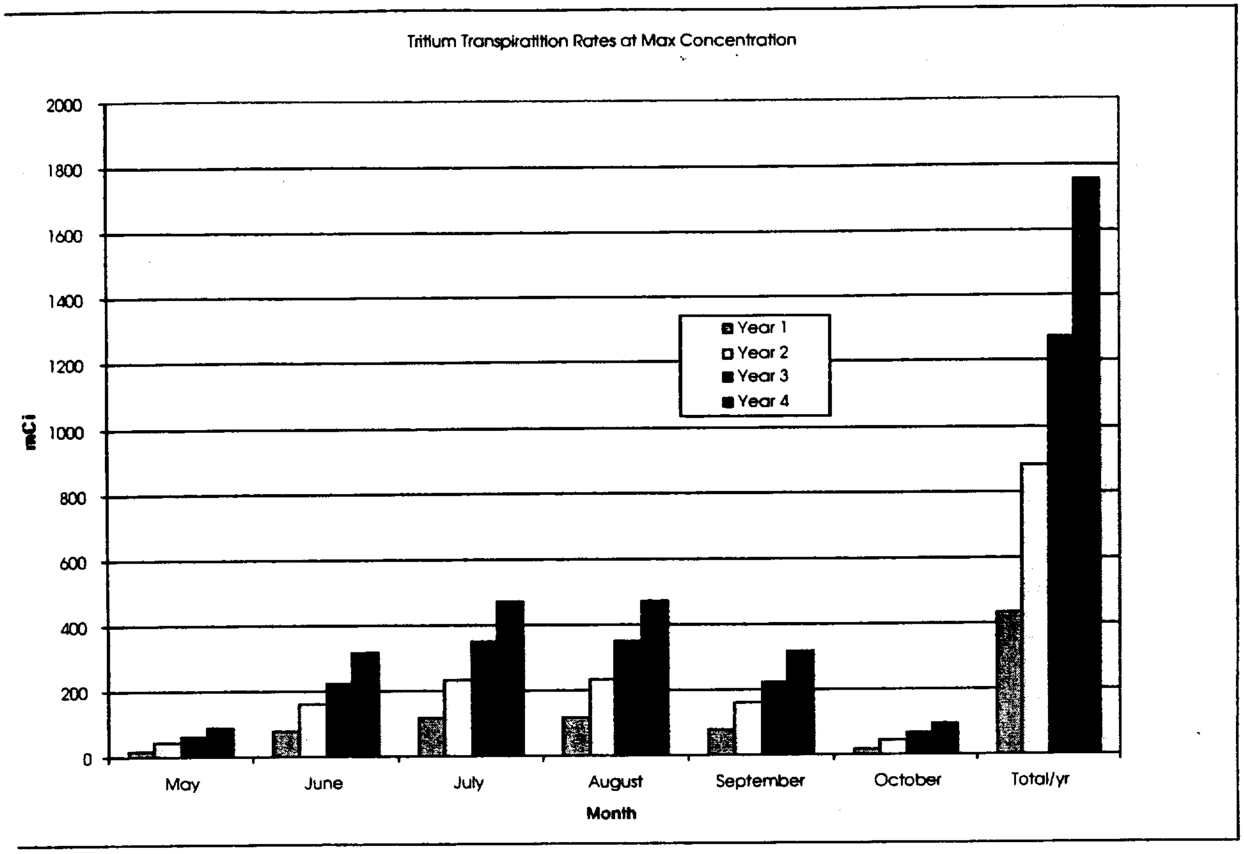

Figure 3. Tritium transpiration rates at maximum concentration.

regulatory standard is 10 mrem/yr, the added exposure was considered inconsequential. In summary, air emission models indicated that even assuming that all of the tritium (at the highest concentration ever found in the plume) were transpired by plants (at the highest transpiration rates), air emissions of tritium would be well within the National Emission Standards for Hazardous Air Pollutants (NESHAPS). At the same time, tritium in the groundwater plume would be efficiently controlled.

To support the deployment of the phytoremediation system, a groundwater flow model was also developed. Flow modeling was conducted initially to model the natural, transient changes in the flow field caused by seasonal changes in recharge to the aquifer. The model was calibrated to approximately 10 years of water level measurements from site monitoring wells. Anticipated effects of the phytoremediation system were included. The model, updated to include the as-built configuration of the phytoremediation system, indicates that the as-built plantation will provide hydraulic containment by the fourth year of growth even during the winter months when the trees are dormant (Quinn et al. 2000).

Cost Savings and Other Advantages

The conventional, baseline method of remediation of the 317/319 areas originally planned for deployment in lieu of phytoremediation included placing an asphalt cap over the VOCs source area and installing extraction wells (pump-and-treat) downgradient of the source areas, from which contaminated water would be withdrawn and discharged to a lift station, which pumps water to Argonne's waste treatment plant.

The phytoremediation installation was installed with a cost saving of 33% compared to the expected cost of the baseline approach. The plant-based system is expected to have lower operating and maintenance costs also: preliminary evaluations put the cost savings in O&M over the lifetime of the deployment at 40% compared to the baseline approach. A significant cost saving (as well as a reduction in risks of spills and worker exposure) is the avoidance of secondary waste (pumped groundwater) and related treatment. These cost savings will be demonstrated as the extraction wells are shut off, expectedly in 2003.

In addition to this actual reduction in cost, a number of technical reasons made the phytoremediation choice more advantageous versus the baseline technology. As mentioned before, the subsurface at the site may be comprised of units of widely varying lateral or vertical extent, with gradational or sharp transitions in permeability. The fibrous nature of roots allows the trees to penetrate and remediate both the relatively fast-flowing pore spaces and the less permeable zones. Fundamentally, this distinguishes phytoremediation from extraction wells, which remove water mainly from the most permeable aquifer media.

Phytoremediation was considered more acceptable than the baseline also because of the ability of trees to actively promote and assist in the degradation of the contaminants at the VOC source area, which the baseline asphalt cap would not do, with expected reduction in cleanup times. The presence of vegetation was also considered an optimal fit with the planned future land use of the contaminated site and adjacent areas, as the phytoremediation plantation will contribute to increase soil fertility to host subsequent prairie species.

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Capturing a "Mixed" Contaminant Plume: Tritium Phytoevaporation at Argonne National Laboratory

M. Cristina Negri*, Ray R. Hinchman
and James B. Wozniak
Argonne National Laboratory

presented at the
EPA Phytoremediation: State of the Science Conference
Boston, May 1-2, 2000

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Research Funded by the US. DOE
EM-50, Subsurface Contaminants Focus Area, and EM-40

What is Specific to Radionuclides?

- For practical purposes, plants do not appear to significantly discriminate between isotopes
- Added radiation hazard highlights risks to food chain and emphasizes biomass disposal issues
- Contamination levels of concern for radioactivity convert into minute amounts of mass, compared to other inorganic contaminants
- Natural radioactive decay may contribute to the selection of the remediation technology, help performance

Argonne National Laboratory, May 2000

Argonne's Activities in the Phytoremediation of Radionuclides

- Deployment of phytoremediation at the 317/319 area at Argonne-East (VOCs and tritium)
- Phytoremediation of Cesium-137 contaminated soil at Argonne-West (INEEL)

Argonne National Laboratory, May 2000

Regarding Tritium...

- A soft (low energy) beta emitter, shielded by skin, paper and 6 mm air
- Hazardous when taken internally (absorbed, ingested, inhaled)
- Half life 12.6 years, decays to Helium-3
- Shares chemical and physical properties of hydrogen [e.g., tritiated water (HTO)]
- Average biological half life in human body 7.5-9.5 days
- Has a specific activity of 9.61×10^9 μCi/g, so the drinking water standard of 20,000 pCi/L equals to 2.08×10^{-12} g/L (ppbs of a ppb)

Argonne National Laboratory, May 2000

Sources of Tritium*

SOURCE	INVENTORY
Natural (cosmic rays, steady state)	70×10^6 Ci
Nuclear test explosions, 1945-1975	8×10^9 Ci (most decayed)
Nuclear power and defense industry releases	$1\text{-}2 \times 10^6$ Ci/year
Commercial devices (radioluminescent, neutron generating)	1×10^6 Ci/year

* from: www.hfbr.bnl.gov/hfbrweb/hdbl1079a.html#ZZ5

Argonne National Laboratory, May 2000

Phytoremediation and Tritiated Groundwater

- **Tritium (^3H) is known to be directly incorporated in water and biological tissues**
- **Plants transpire tritiated water vapor, and plant biomass may serve as indicator of tritium contamination**
- **High transpiring, deep rooted plants can control contaminated groundwater in an engineered plant system**

Argonne National Laboratory, May 2000

Fate of Tritium in Engineered Phytoremediation Systems

- Plant uptake with groundwater
  - Transpiration into air with water vapor
    - Distribution in atmosphere and rapid mixing with large volumes of air , decay. Modeling needs to establish that risks of airborne radiation exposure are acceptable, largely dependent on activity concentration and site conditions
  - Accumulation in plant tissue
    - Mean residence times are 4-37 days
      - Easily exchangeable (cell water)
      - Not easily exchangeable (incorporated in tissues)
- Evaporation from soil, seeps...

Argonne National Laboratory, May 2000

Deployment of TreeMediation® at Argonne-East

Instead of an asphalt cap and extraction wells, approximately 800 trees and a herbaceous cover were planted in 1999 to:

- Achieve hydraulic control of the migrating, 20 to 30 ft deep plume
- Improve the degradation of VOCs in soil and groundwater
- Remove tritium from the subsoil
- Prevent water infiltration and soil erosion.

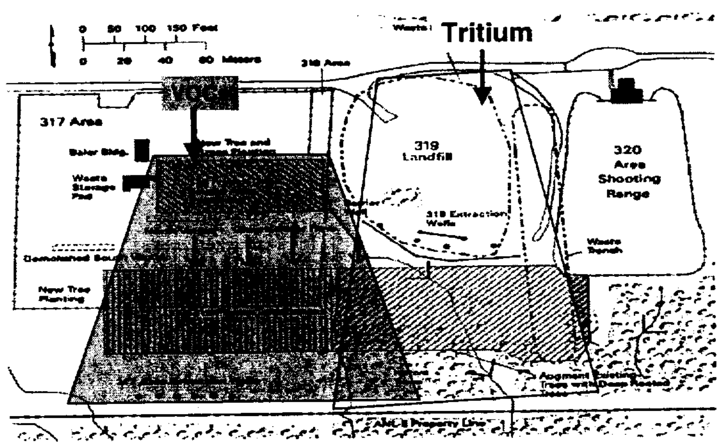
Argonne National Laboratory, May 2000

The 317/319 Area at Argonne

- Former (1940s - 1960s) laboratory waste disposal area , approx 2 ha of surface, several SWMUs in the area, currently used for waste storage
- Soil is contaminated with VOCs, and groundwater with VOCs and tritium, baseline technology (asphalt cap and extraction wells) was considered less advantages - limited predictability and zone of influence of wells in glacial subsoil, plus "perpetual" pumping
- Currently, extraction wells discharge secondary waste to Argonne's treatment plant

Argonne National Laboratory, May 2000

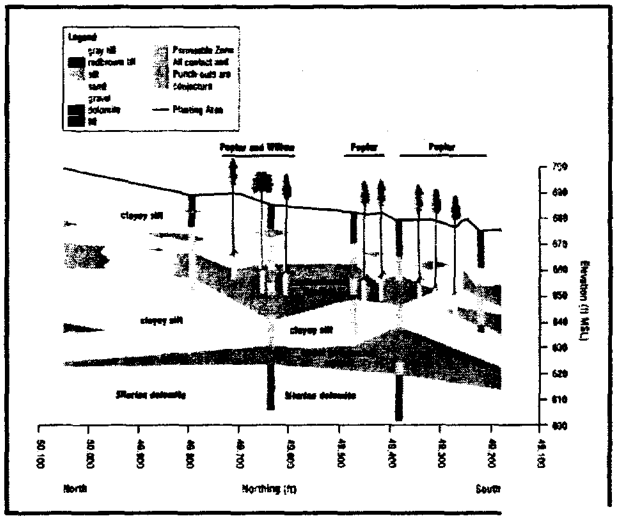
317/319 Area



Argonne National Laboratory, May 2000

The Subsoil at 317/319 Area

- Complex stratigraphy within glacial sediments forms a heterogeneous hydrologic system
- Water bearing intervals are in interconnected sand and gravel zones
- Hydrologic system is altered by perched or seasonally wet zones and by fracturing of confining clays by desiccation.



Argonne National Laboratory, May 2000

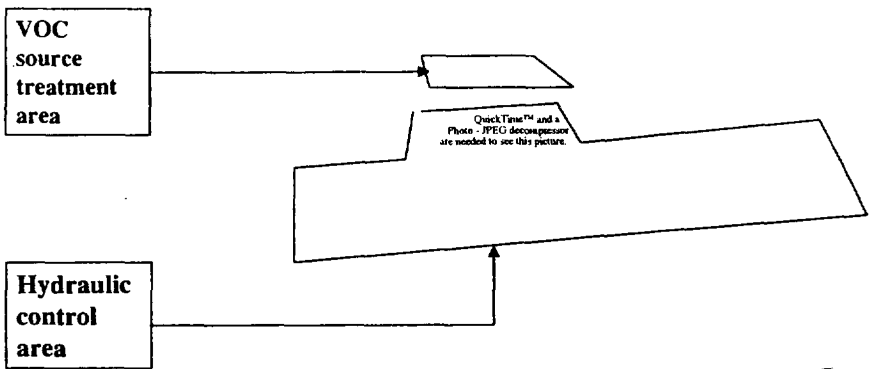
Remediation Approach

- Deep-planted, unlined TreeMediation® hybrid willows to address VOC source area
- Deep-planted, TreeWell® engineered hybrid poplars to achieve hydraulic control of groundwater
- Herbaceous cover throughout to minimize water infiltration and soil erosion
- When remediation is complete, trees will be cut down, chipped, and used as mulch on site, and native prairie vegetation established.

TreeMediation® and TreeWell® are patents of Applied Natural Sciences, Inc.

Argonne National Laboratory, May 2000

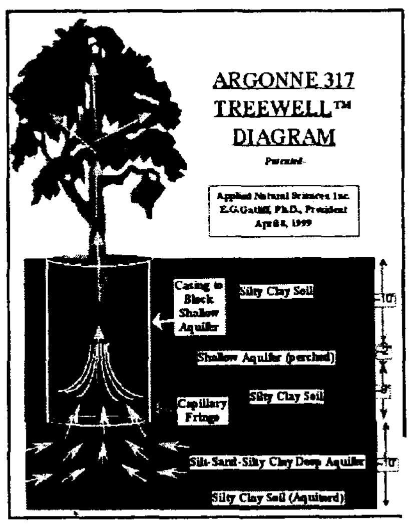
Planting Layout



Argonne National Laboratory, May 2000

TreeWell® for Groundwater
(Hydraulic Control at Depths)

- **Root-engineered plants were placed into predrilled, 30' deep boreholes**
- **Impermeable liner backfilled with plant compatible material forces growth into contaminated plume, excluding perched aquifers and precipitation water**
- **Planting design took into account plume velocity and winter dormancy**



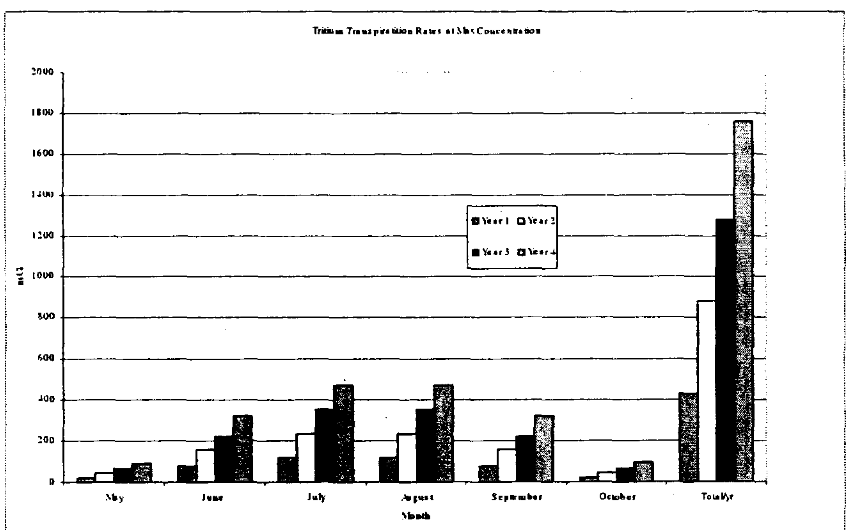
Argonne National Laboratory, May 2000

Emissions through Transpiration: Worst Case Scenario

- Use maximum concentration EVER found (500 nCi/L) -- average below 20
- All tritium is transpired
- 160 trees are planted in area of tritium contamination
- Transpiration rates 2-50 gal/day per tree, April to October
- Derived exposure calculated as required by NESHAP standard (40 CFR 61 Subpart H) using U.S. EPA CAP-88PC

Argonne National Laboratory, May 2000

Calculated Emissions via Transpiration



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Derived Exposure to Nearest Member of Public

- **Year 1 (2000): 6.32 x 10^{-6} mrem/yr**
- **Year 4 (2003) and subsequent: 2.58 x 10^{-5} mrem/yr**
- **NESHAP Standard: 10 mrem/yr**
- **ANL total for calendar year 1999: 4.3 x 10^{-3} mrem/yr**

Argonne National Laboratory, May 2000

Expected Results

- **Hydraulic control expected in four years or less**
- **Tritium is expected to be transpired without significant impact on dose to exposed population**
- **Existing extraction wells will be progressively shut off as plants grow and achieve hydraulic control**

Argonne National Laboratory, May 2000

Monitoring Performance
a combined effort:

- Argonne National Laboratory, U.S. Department of Energy (DOE)
- The U.S. EPA, National Risk Management Research Laboratory, Superfund Innovative Technologies Evaluation (SITE) Program

Argonne National Laboratory, May 2000

Cost Savings and Other Advantages

- Installation achieved 33% cost savings over baseline technology
- O&M expected >30% cost savings -- to be demonstrated at plant maturity
- Minimized handling/transportation of secondary waste
- Accelerated cleanup times
- Potential protection from unforeseen releases from other sources in the area

Argonne National Laboratory, May 2000

Application of Phytoremediation to Remove Cs-137 at Argonne National Laboratory - West

Scott Lee

Scott Lee has a B.S. in civil engineering from North Dakota State University and a M.S. in environmental engineering from North Dakota State University. He has worked as an environmental engineer for Westinghouse Electric Corporation at the Naval Reactors Facility in Idaho Falls Idaho, during the cleanup of 57 CERCLA waste sites.

Scott is currently employed by Argonne National Laboratory-West as an environmental engineer. He is in charge of all 39 CERCLA sites at Argonne National Laboratory-West being remediated under the Federal Facilities Agreement and Consent Order. He is responsible for coordinating, developing, and writing all required documents including the Sampling and Analysis Plan, Remedial Investigation Work Plan, Remedial Investigation and Feasibility Study, Record of Decision, Remedial Design Remedial Action Work Plan, and the Verification Sampling Plan. In addition, Scott is managing a two-year phytoremediation demonstration project as well as the excavation and disposal activities at these two sites. A summary of the first year of the phytoremediation demonstration project at Argonne National Laboratory-West has been written and will be published in the May/June issue of Radwaste Solutions magazine.

Phytoremediation Application for Radionuclide Removal at Argonne National Laboratory-West

Chicago Operations Office
U.S. Department of Energy

May 1, 2000

Argonne National Laboratory-West

Summary of WAG 9 CERCLA Activities

- Listed as NPL site in 1991
- Includes the investigation of 37 WAG 9 waste sites
- Includes the summary of 2 WAG 10 waste sites
- Involved collection and analysis of over 9,400 contaminant specific samples
- ROD signed 9-27-98

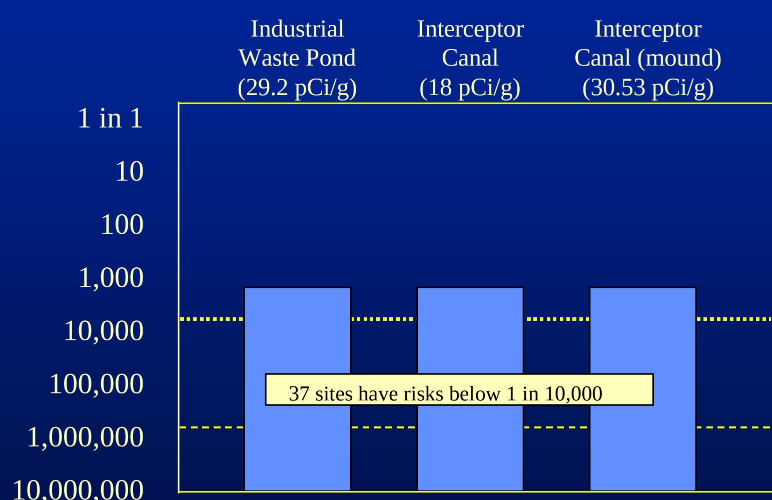
Argonne National Laboratory-West

Waste Area Group 9 Contaminants of Concern

- **Human** — *Cesium -137*
- **Ecological** — *Chromium^{+3}*, *Mercury*, *Selenium*, *Silver*, *Zinc*

Argonne National Laboratory-West

Human Health Risk Calculations
(present day occupational exposure)



Argonne National Laboratory-West

Summary of Comparative Analysis Ranking of Remedial Alternatives

Evaluation Criteria		Alternative			
	3a	4a	4a	4b	5
Overall Protection of Human Health and the Environment	meets	meets	meets	meets	meets
Compliance with Applicable and Relevant and Appropriate Requirements	good	good	good	good	best
Long-term Effectiveness and Permanence	worst	good	good	good	best
Short Term Effectiveness	worst	good	good	good	good
Reduction of Toxicity, Mobility, or Volume Through Treatment	worst	worst	worst	worst	best
Implementability	best	best	best	best	good
Cost (in millions)	7.6	5.9	5.9	13.1	2.8

Argonne National Laboratory-West

Phytoremediation Obstacles

- Ecological Receptors
- Public Concerns (Homer Simpson)
- Leaching Contaminants
- Noxious Weeds

Argonne National Laboratory-West

Ecological Concern

- Mitigate or eliminate the exposure pathway to ecological receptors.

Argonne National Laboratory-West

Contaminant Leaching

- Design and install irrigation system
- Add additional soil moisture detectors below contaminants

Argonne National Laboratory-West

Noxious Weeds

- Use of plants found in but not native to Idaho
- More harmful than beneficial
- Eradication must be economically feasible
- Adverse impact must exceed cost of control

Argonne National Laboratory-West

Special Controls for Kochia Weed

- Get State approval prior to planting to control undesirable weeds
- Harvest before flower
- Establish clear zone around site
- Seed weeds to prevent wind dispersion

Argonne National Laboratory-West

Preplanting Activities

- *Install irrigation lines, pressure regulators, risers, heads, and moisture probes*
- *Level the irregular shaped dredge piles (10x500x4 ft)*
- *Work the soil using the plow, ripper, and roto-tiller*
- *Addition of organic matter*
- *Collect real-time gamma emissions and map results*

Argonne National Laboratory-West

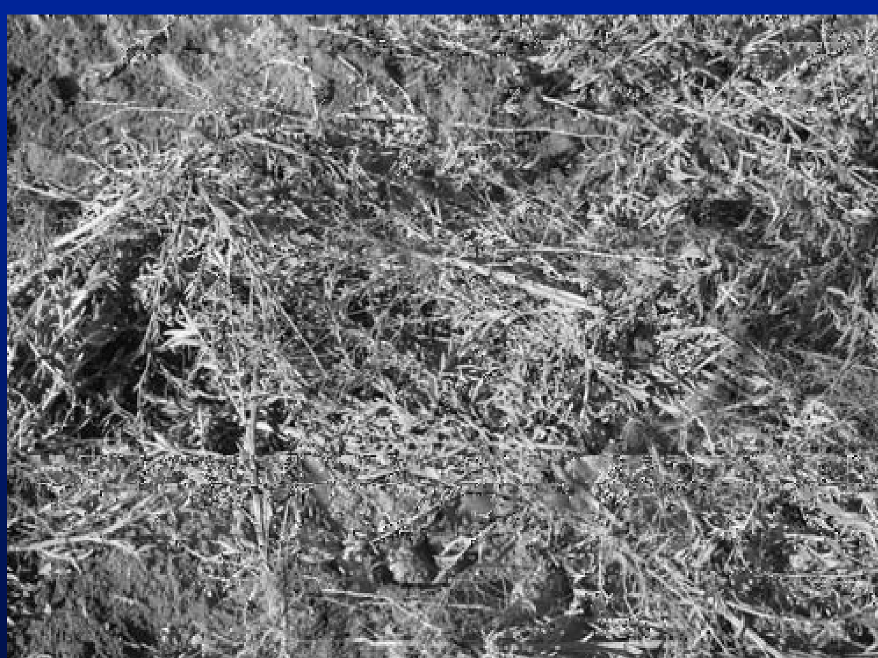
Global Positioning Radiometric Scanner (GPRS)

Argonne National Laboratory-West

Kochia with Roots

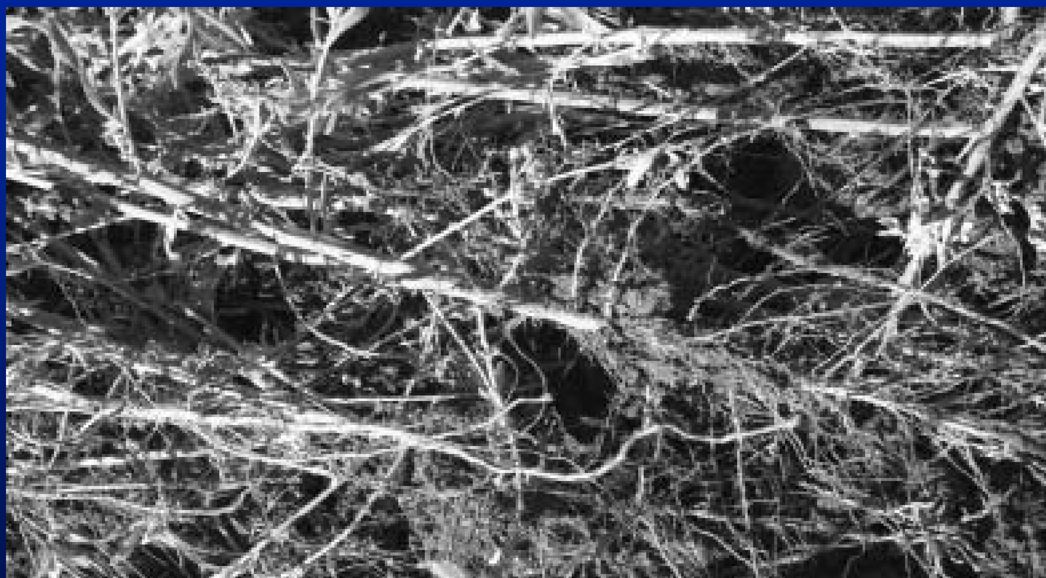
Argonne National Laboratory-West

Harvested Kochia Plants



Argonne National Laboratory-West

Kochia Roots



Argonne National Laboratory-West

Kochia Plant

Argonne National Laboratory-West

Future Activities

Establish and test three Amaranth species for comparison to Kochia *(Amaranthus: retroflexus, bicolor, and paniculatum)*

Compare the Cs-137 uptake for stress and unstressed plants prior to harvesting

Use ISSOX (directional sodium germanium detector) prior to planting, harvesting, raking, and bailing, Bale plant matter

Argonne National Laboratory-West

THE FATE OF CHLORINATED SOLVENTS THAT DISAPPEAR FROM PLANTED SYSTEMS

The Role of the Plant and the Rhizosphere in Phytoremediation

Milton P. Gordon, Sharon Doty, Paul Heilman, Lee A. Newman, Tanya Q.T. Shang, Stuart Strand, Xiaoping Wang and Angela Wilson, University of Washington

Milton P. Gordon received his Ph.D. from the University of Illinois. He then spent four years as a Post-doctoral Fellow and as a staff member in the Sloan Kettering Institute for Cancer Research. This was followed by two years at the virus laboratory and the University of California at Berkeley. In 1959 he joined the faculty at the University of Washington where he is now a Professor in Biochemistry, Join Professor in Microbiology and in Ecosystem Sciences in the College of Forest Resources. Dr. Gordon, together with his colleagues at the University of Washington, is responsible for the basic discoveries underlying the principals of plant genetic engineering using the microorganism Agrobacterium tumefaciens. He is currently interested in the use of plants to remediate toxic organic compounds in the environment, and together with his colleagues, Drs Newman and Strand, operate a field site for the testing of various species of trees to determine their ability to degrade toxic solvents.

Abstract

The metabolism of trichloroethylene in plants, animals and bacteria has been well established. Axenic poplar cells form C02, di and trichloroacetic acids, trichloroethanol, and insoluble non extractable materials. In a mass balance chamber between75 and 90% of the TCE taken up by poplar cuttings is transpired unaltered. In contrast, in an outdoor test plot only about 8% of the TCE is transpired. The majority of the remainder of the TCE (70%) is catabolized to chloride ion which can be recovered from soil. Carbon tetrachloride and perchloroethylene were similarly catabolized. The dismutation of TCE depends upon the uptake of water and TCE by trees as irrigation in excess of the ability of the trees to take up water resulted in escape of unaltered TCE. Soil samples from the planted field site did not convert TCE to C02 in amounts greater than what was seen in unplanted soils, indicating no change in the oxidative metabolism in the soil in the presence of plants.

When tobacco plants containing exogenous cytochrome P450 2E 1 were studied under hydroponic conditions in the lab, TCE was converted to trichloroethanol and its Beta-glucoside although even in this case only a small fraction (Ca 1 - 5%) of the TCE was recoverable trichloroethanol and its glucoside.

The results in our laboratory and field studies indicate a role for the plant in phytoremediation, but do not rule out participation of rhizopheric organisms on these or other sites.

Legends to go with slides

1. Metabolic pathways of TCE
2. Apparatus used to determine metabolism of axenic poplar cells
3. TCE metabolites formed in axenic poplar cells
4. Formation of CO_2 from axenic cells
5. Mass balance chamber
6. Diagram of field site
7. Field site - 1995
8. Field site - 1997
9. Field site study of TCE
10. Field site study of TCE
11. Apparatus to study transpiration of solvents
12. Chloride ion accumulation in soil of chambers treated with TCE
13. TCE in excess of uptake is not metabolized by soil rhizosphere - note recovery in late 1997
14. Remediation of CC14
15. Remediation of CC14
16. Two year recovery of CC14
17. Remediation of perchloroethylene
18. Formation of trichloroethanol and its B-glucoside in transgenic tobacco plants
19. Personnel

Amounts of TCE and metabolites found in supernatant and axenic cells exposed to TCE

	TCE	Chloral hydrate	Trichloro-ethanol	Dichloro-acetic acid	Trichloro-acetic acid
Control 1					
pellet	ND40	ND40	ND40	ND10	ND10
supernatant	ND40	ND40	ND40	ND10	ND10
Control 2					
pellet	ND40	ND40	ND40	ND10	ND10
supernatant	ND40	ND40	ND40	ND10	ND10
Exposed - batch 1					
pellet	ND40	ND40	60	12000	ND10
supernatant	2000	ND40	760	1600	ND10
Exposed - batch 2					
pellet	ND40	ND40	80	39000	130
supernatant	ND40	ND40	110	3800	30

Amounts given are nanograms of TCE or metabolite per gram of sample.
ND = not detected at stated limit.

Percent ^{14}C recovered from ^{14}C - TCE as ^{14}C - CO_2 after a four - day incubation period.

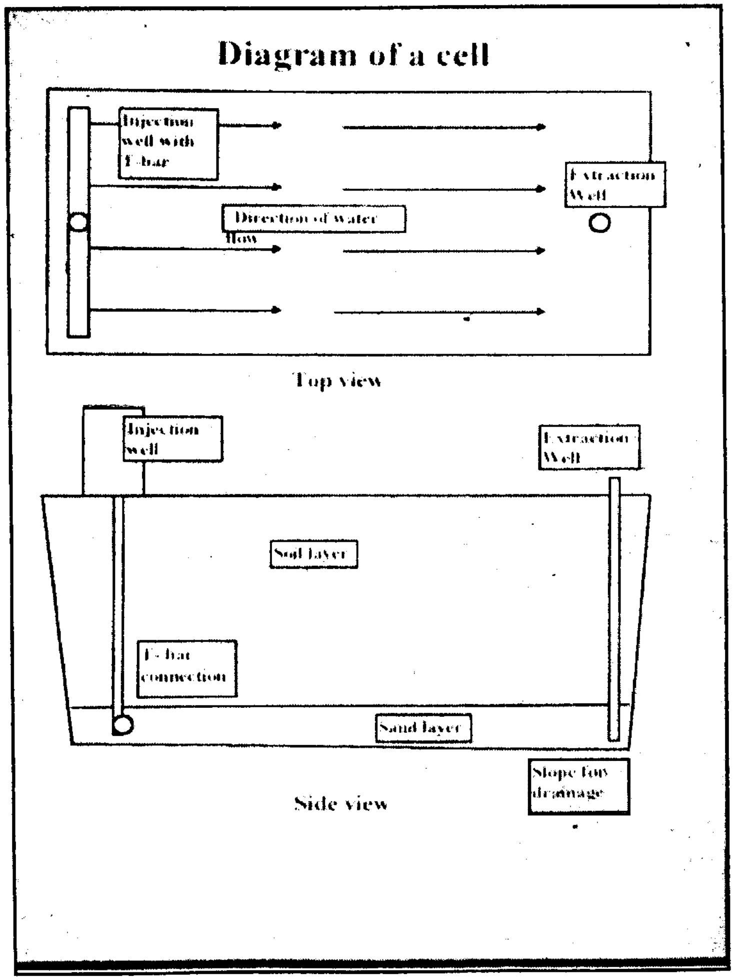
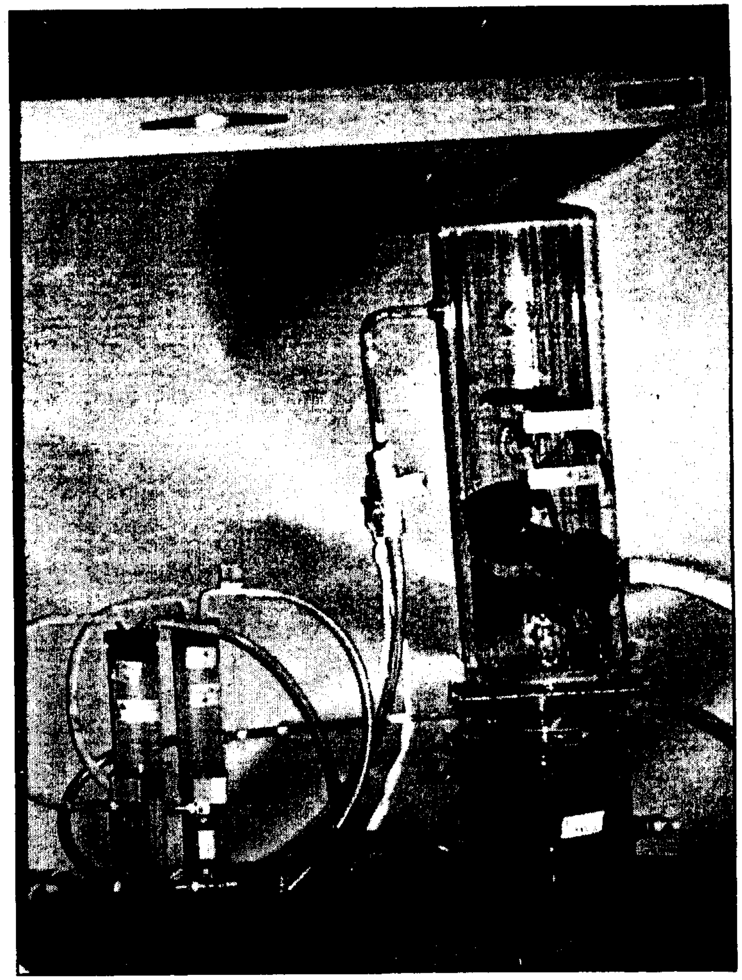
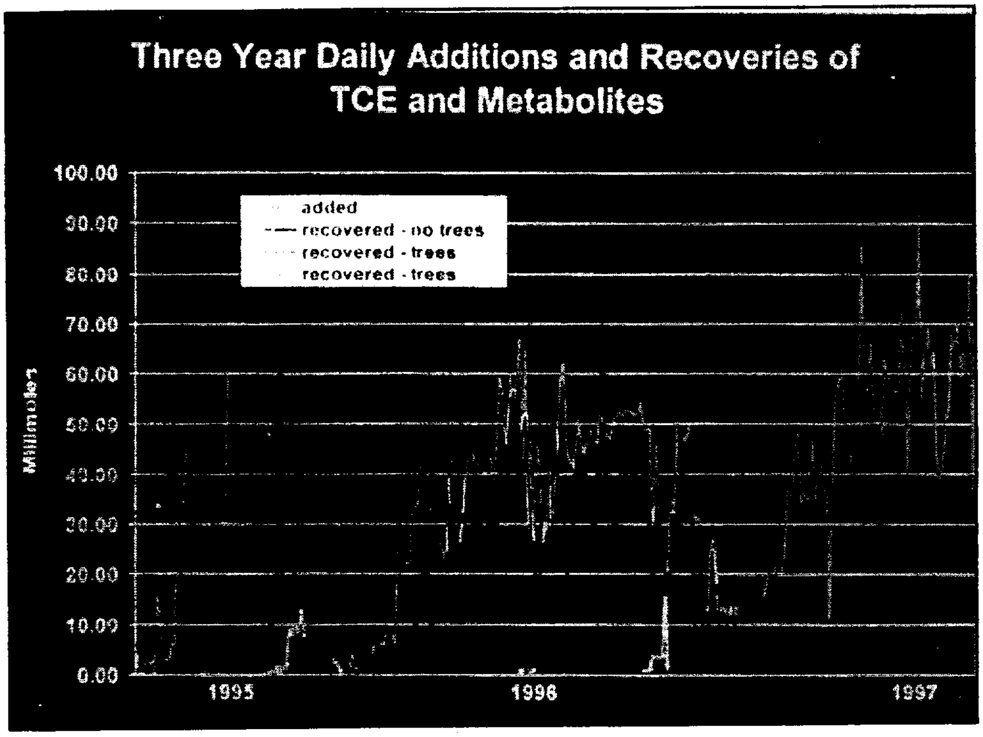
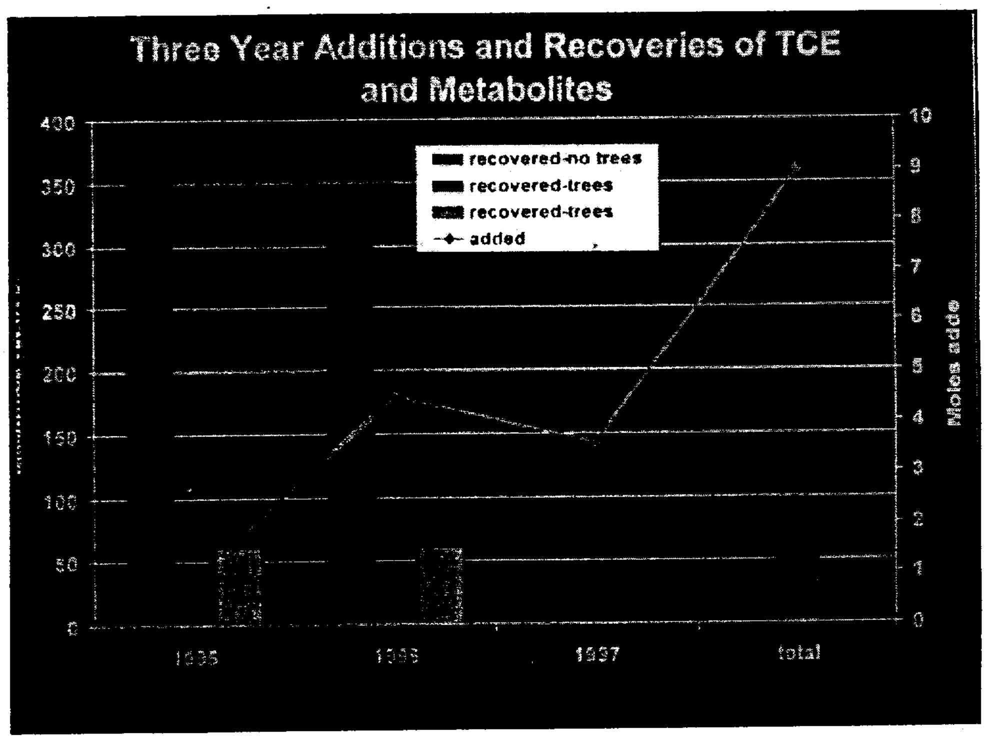


Diagram of a cell
Injection well with T-bar
Extraction Well
Direction of water flow
Top view
Injection well
Extraction Well
Soil layer
T-bar connection
Sand layer
Slope for drainage
Side view

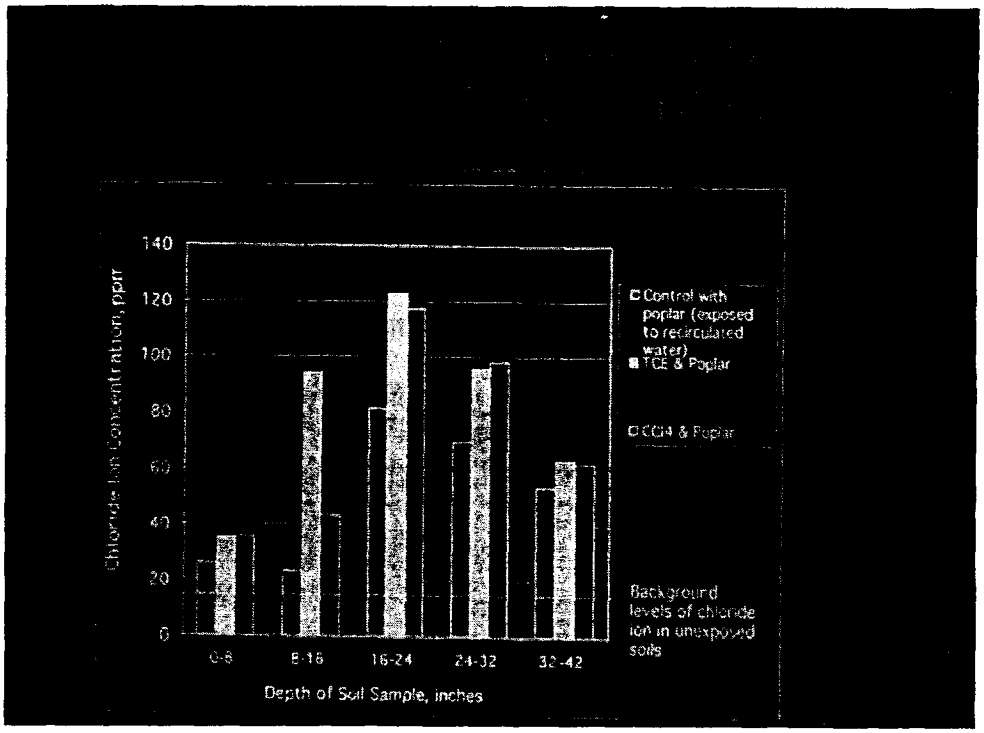




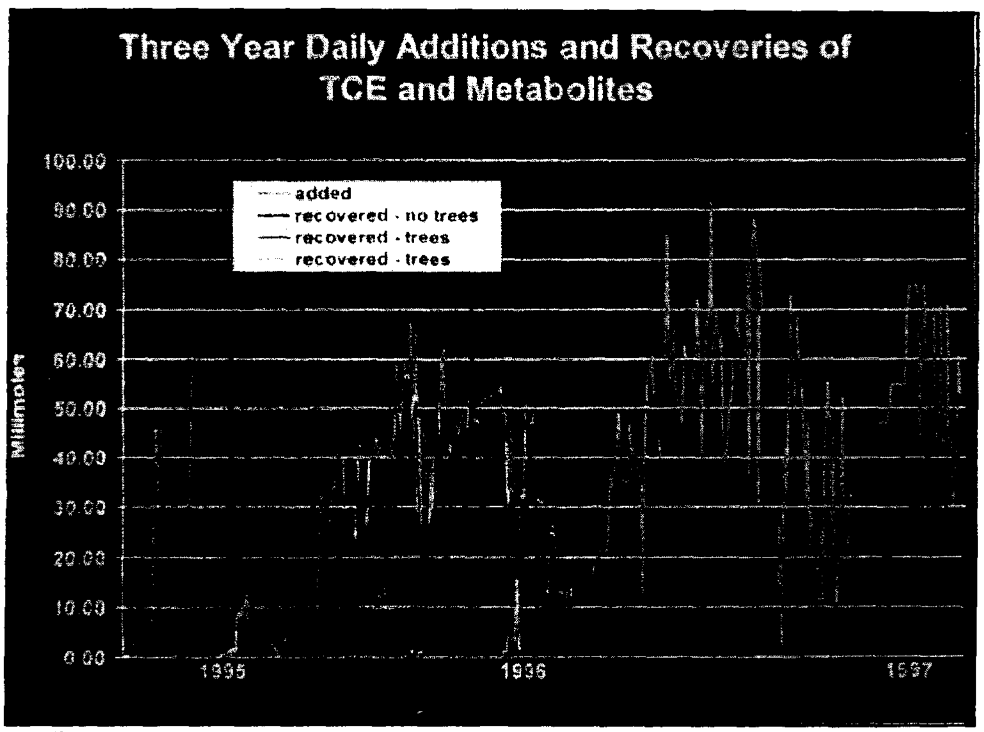
Three Year Daily Additions and Recoveries of TCE and Metabolites
Millimoles
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
added
recovered - no trees
recovered - trees
recovered - trees
1995
1996
1997



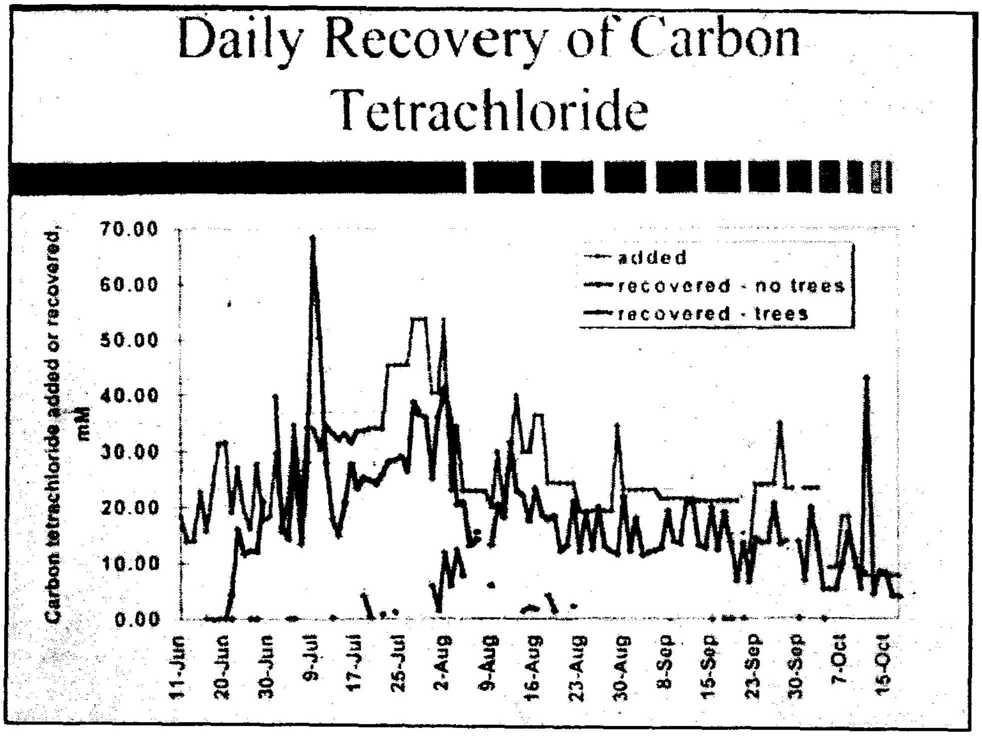
Three Year Additions and Recoveries of TCE and Metabolites
400
350
300
250
200
150
100
50
0
10
9
8
7
6
5
4
3
2
1
0
Moles adde
recovered-no trees
recovered-trees
recovered-trees
added
1997
total

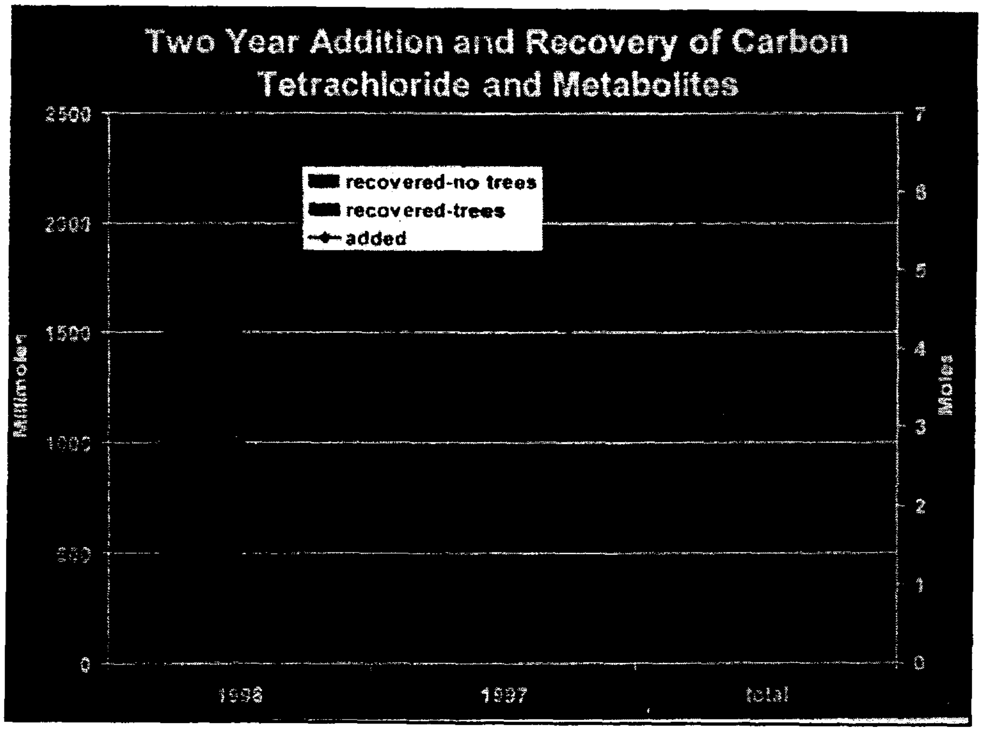


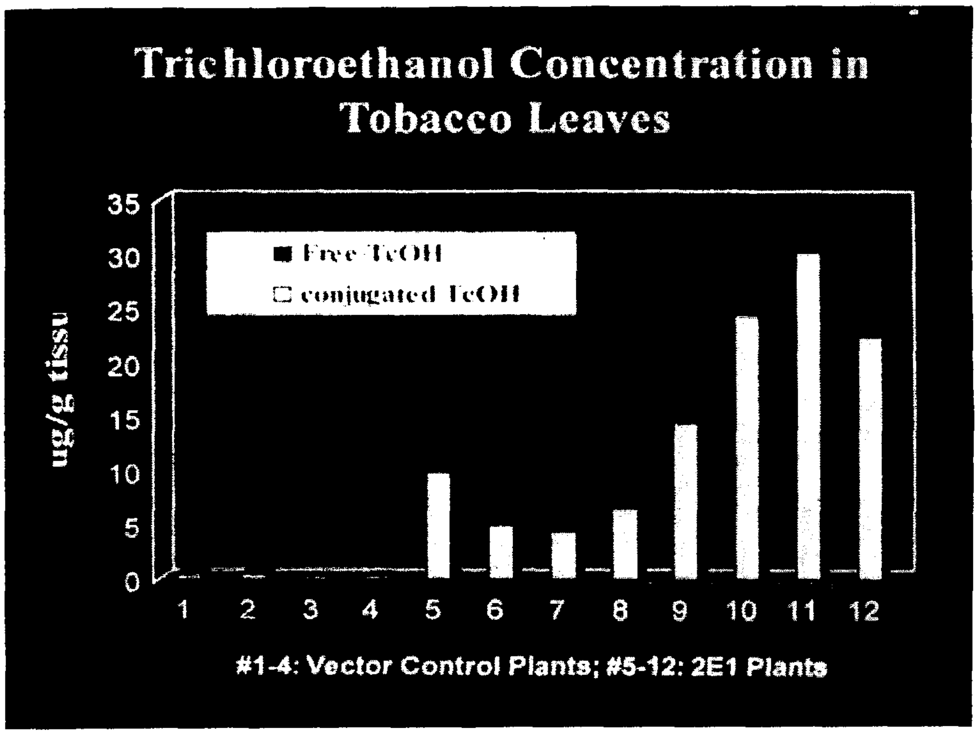
140
120
100
80
60
40
20
0
Chloride Ion Concentration, ppm
0-8
8-16
16-24
24-32
32-42
Depth of Soil Sample, inches
Control with poplar (exposed to recirculated water)
TCE & Poplar
CCl4 & Poplar
Background levels of chloride ion in unexposed soils



Three Year Daily Additions and Recoveries of TCE and Metabolites
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Millimoles
added
recovered - no trees
recovered - trees
recovered - trees
1995
1996
1997


Daily Recovery of Carbon Tetrachloride
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Carbon tetrachloride added or recovered, mM
added
recovered - no trees
recovered - trees
11-Jun
20-Jun
30-Jun
9-Jul
17-Jul
25-Jul
2-Aug
9-Aug
16-Aug
23-Aug
30-Aug
8-Sep
15-Sep
23-Sep
30-Sep
7-Oct
15-Oct


Two Year Addition and Recovery of Carbon Tetrachloride and Metabolites
recovered-no trees
recovered-trees
added
Millimoles
Moles
total



Trichloroethanol Concentration in Tobacco Leaves
Free TcOH
conjugated TcOH
ug/g tissu
0
5
10
15
20
25
30
35
1 2 3 4 5 6 7 8 9 10 11 12
#1-4: Vector Control Plants; #5-12: 2E1 Plants

The Phyto Group
Hugh Arnold
Maggie Connor
Sharon Doty
Katrina Gery
Milton Gordon
Paul Heilman
Emily Kenney
Jennifer Mears
Indulius Muiznieks
Lee Newman
Susan Paik
Tanya Shang
Marietta Sharp
Stefanie Stanley
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Angela Wilson
Rayna Wong

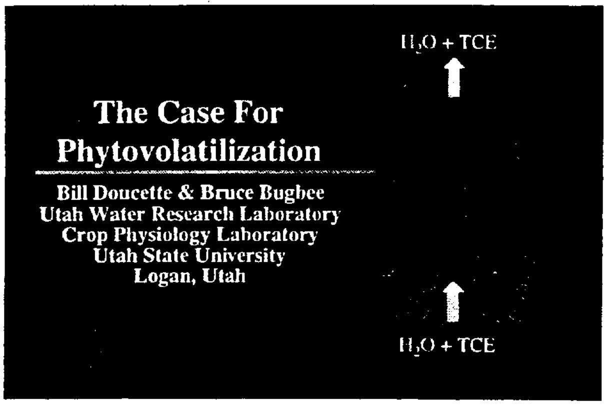
The Case for Volatilization

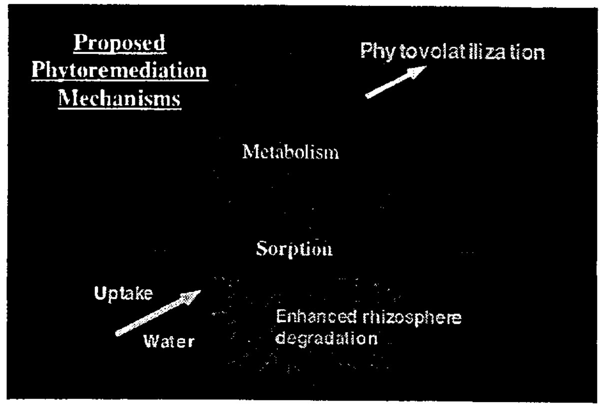
William Doucette

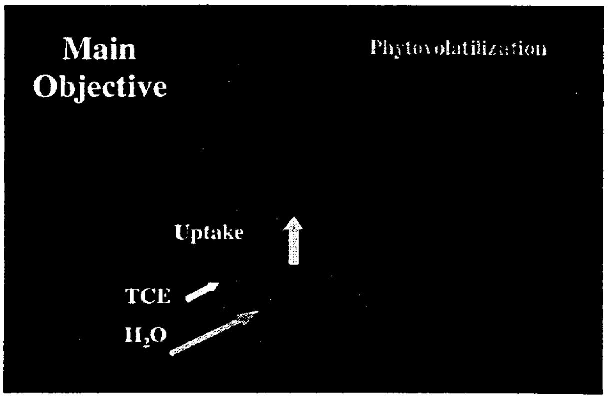
Abstract Unavailable

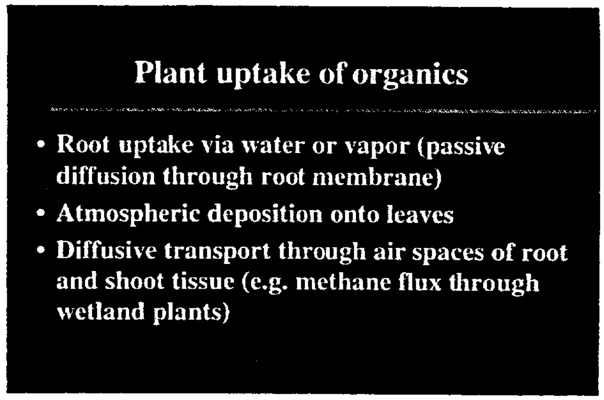
William J. Doucette has B.S. and M.S. degrees in Chemistry and a Ph.D. in Water Chemistry from the University of Wisconsin-Madison. His research focuses on the fate of organic contaminants in the environment, emphasizing the relationships between molecular structure, physical/chemical properties and environmental processes such as sorption, volatilization, biodegradation, and uptake by biota. He is currently an Associate Professor in the Department of Civil and Environmental Engineering/Utah Water Research Laboratory, at Utah State University (USU). Dr. Doucette also serves as an Environmental Chemistry Editor for the journal Environmental Toxicology and Chemistry. Prior to joining Utah State University, Dr. Doucette worked as an analytical chemist at the U.S. EPA's Environmental Research Laboratory in Duluth, MN supporting fish bioconcentration studies. Dr. Doucette was also a Senior Environmental Chemist at Lilly Research Laboratories where he directed a variety of studies evaluating the environmental fate of pharmaceuticals.

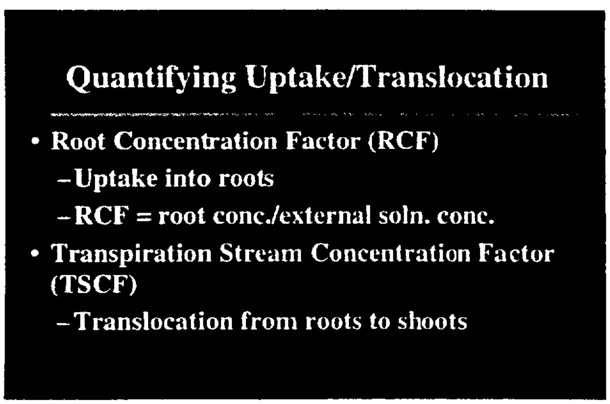
During the past six years, Dr. Doucette has teamed with crop physiologist Dr. Bruce Bugbee to investigate the impact of plants on the fate (rhizosphere degradation, uptake, translocation, and volatilization) of hydrocarbons, PAHs, pentachlorophenol and volatile chlorinated solvents in both laboratory and field studies.

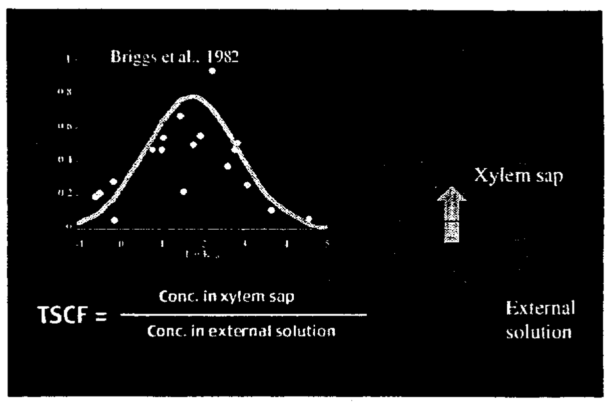




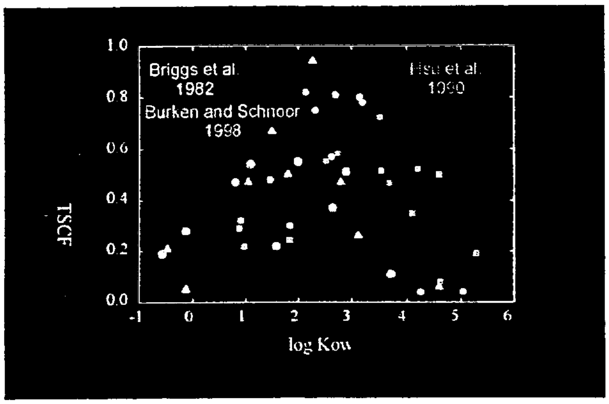








Phytoremediation State of the Science Conference, Omni Park House Hotel, Boston, MA May 1-2, 2000. (doucette@cc.usu.edu)



Uptake and Phytovolatilization of TCE-Literature review

- Schroll et al. (1994) little root uptake
- Newman et al. (1997) "Measurable" transpiration & metabolism
- Schnabel et al. (1997): 1-2%uptake shoots
- Burken & Schnoor (1998) 21% transpired, TSCF=0.75
- Davis et al., (1998) TSCFs = 0.1-0.58

Uptake and Phytovolatilization of TCE-Literature review

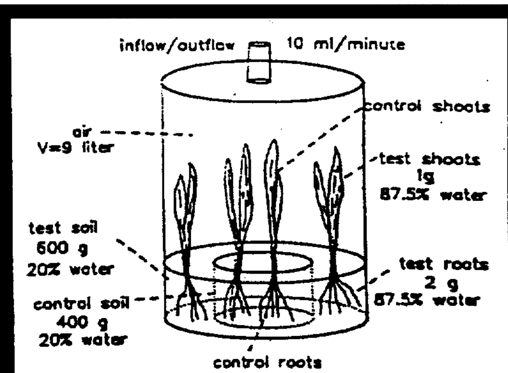
- Compton et al. (1998) TCE detected in transpiration gas samples
- Newman et al., (1999) 9% of total TCE loss attributed to phytovolatilization
- Nietch et al. (1999) transpiration & diffusive flux
- Orchard et al. (2000) TSCF = 0.02 -0.22

Possible Reasons for Differences

- Experimental approach & artifacts
- Exposure concentration & duration
- Plant growth conditions
  - –Soil vs. hydroponics
  - –Plant species and age

Laboratory approaches used to determine uptake & phytovolatilization

- Static chamber
- Flow-through chamber



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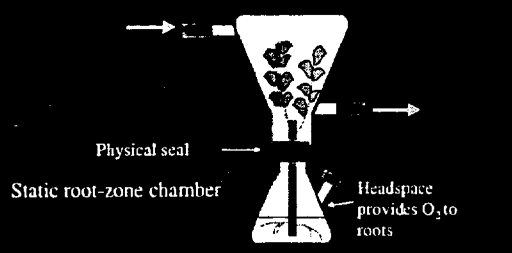
Flow-through (upper) Chamber



Burken and Schnoor (1998)

Field approaches used to measure phytovolatilization

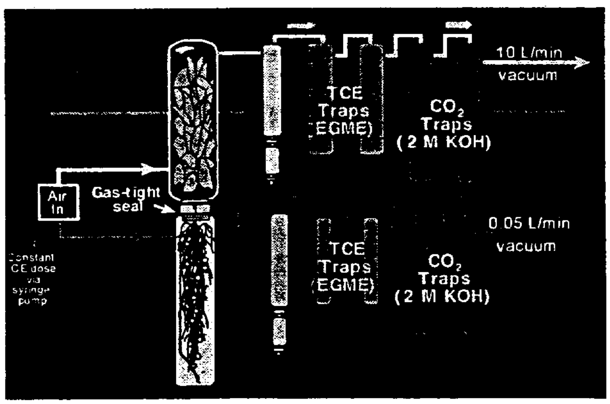
- "Open" bag
- "Sealed" bag
- Flow-through bag or chamber
- Open path FTIR

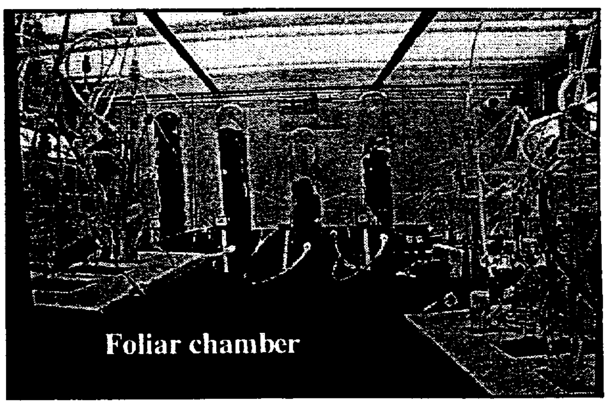
Measuring uptake and phytovolatilization: considerations

- Humidity build-up
- Temperature buildup
- Unnatural plant growth conditions
- Foliar deposition vs root uptake
- Leaks/low recovery
- Low concentrations (require trapping)

USU Laboratory study-goals

- Dual-chamber flow through system
- Natural plant environment
- High mass recovery
- Quantify phytovolatilization





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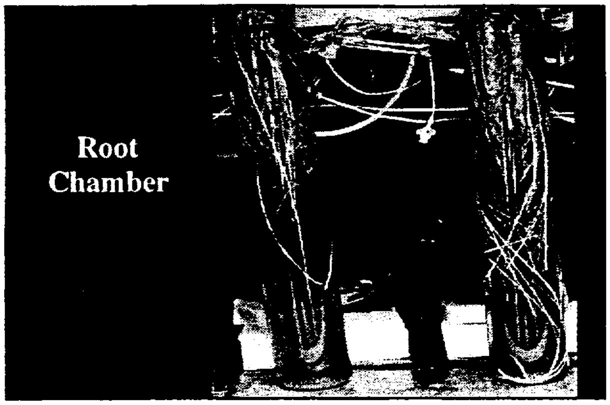
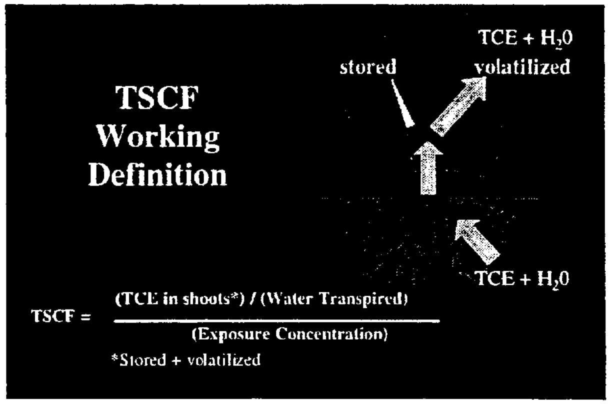
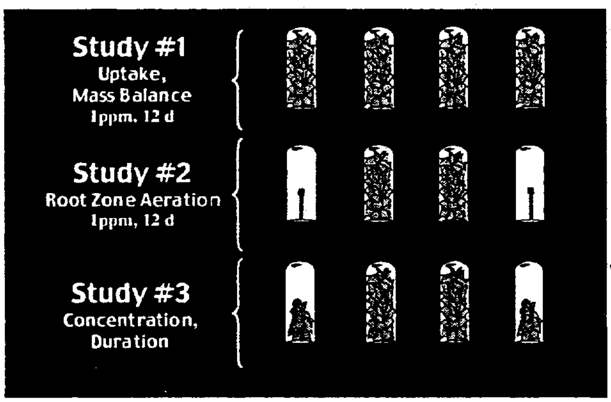
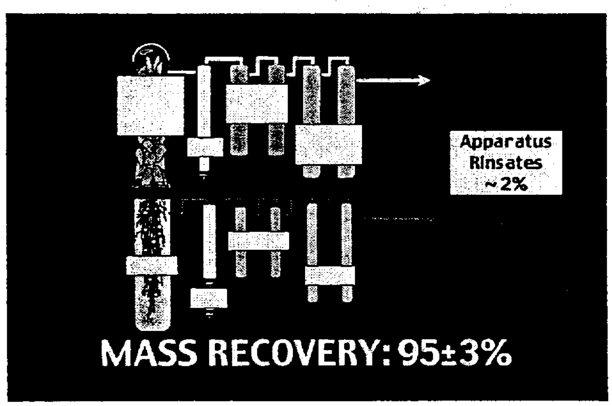


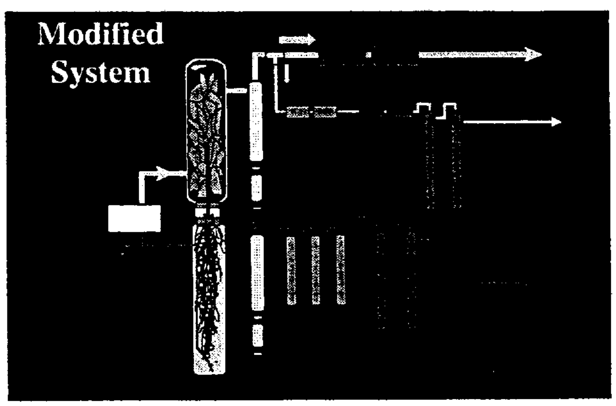






Key Results

- Mass recoveries (>92%)
- TCE, TCAA, DCAA, & TCEt identified
  - Roots > leaves > stem
- Little or no phytovolatilization
- TSCF ranging from 0.02-0.21
- TSCF independent of exposure conc. (1-70 ppm) & duration (12-26 days)



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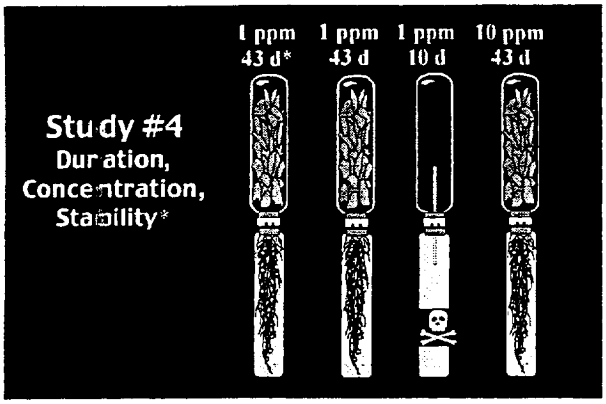
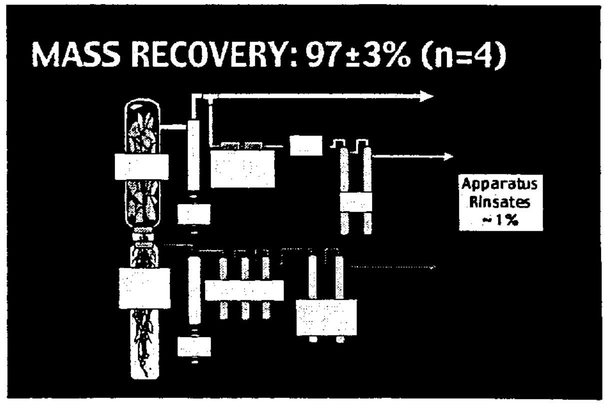
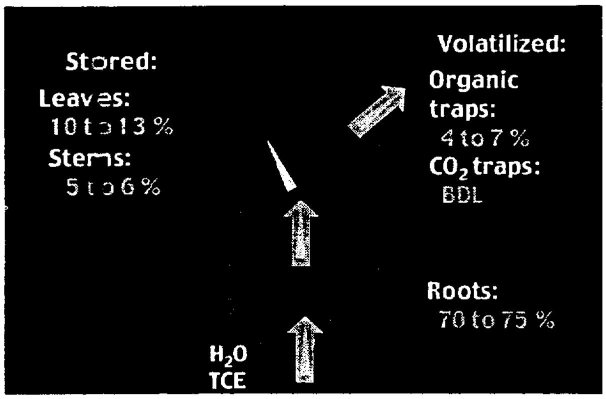




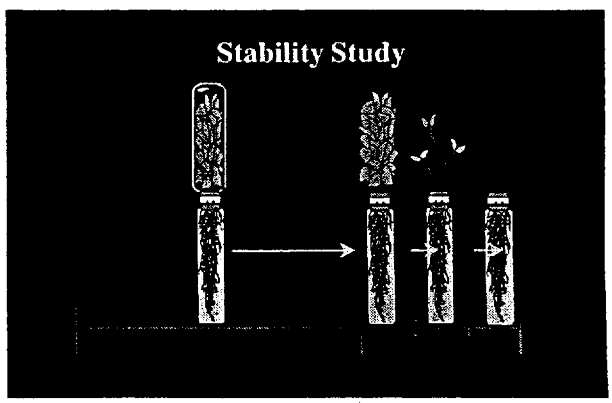


TSCF Breakdown

Dose Level	Shoot	TCE Transp'n
1 ppm	0.05	0
1 ppm	0.05	0
1 ppm	0.05	0
1 ppm	0.08	0
1 ppm	0.09	0
1 ppm	0.09	0
1 ppm	0.09	0
10 ppm	0.12	0.02
10 ppm	0.14	0
10 ppm	0.15	0
70 ppm	0.01	0.02
70 ppm	0.02	0

Tissue Analysis Results

- ^{14}C by combustion >> extractable ^{14}C.
- Short-term treatment concentrations:
  Roots > Stems > Leaves
- Long-term treatment concentrations:
  Roots > Leaves > Stems



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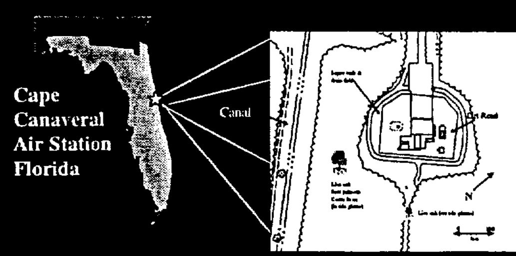
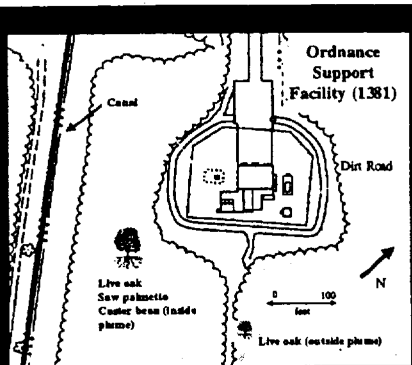
Stability Study Results

- 11% of the total shoot ^{14}C was detected in the new leaves that formed after dosing stopped.
- No detectable leakage of ^{14}C into root zone solution, even after leaf removal.

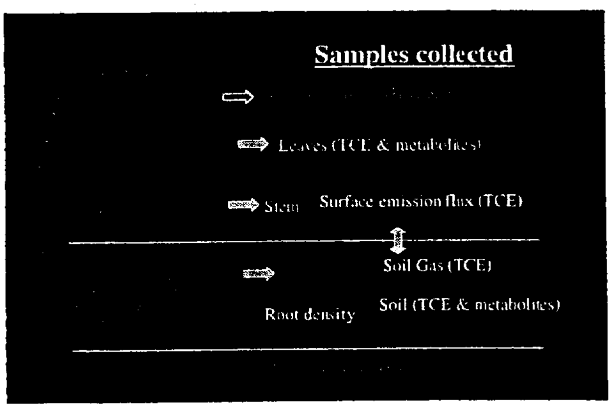
Site Location

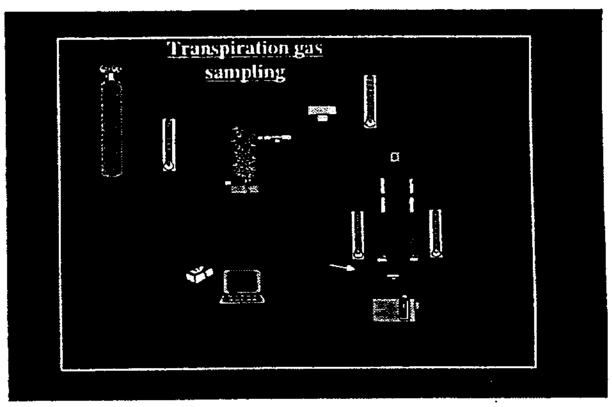




Site Description- CCAS Site 1381

- Small metals cleaning facility from 68-77
- Shallow aquifer, 2 - 4 ft bgs
- Sandy soil, little clay or silt material
- TCE (1-10 mg/L) detected in the SW corner of the site & in the southern canal
- Plume size ≈ 2200 ft x 3000 ft





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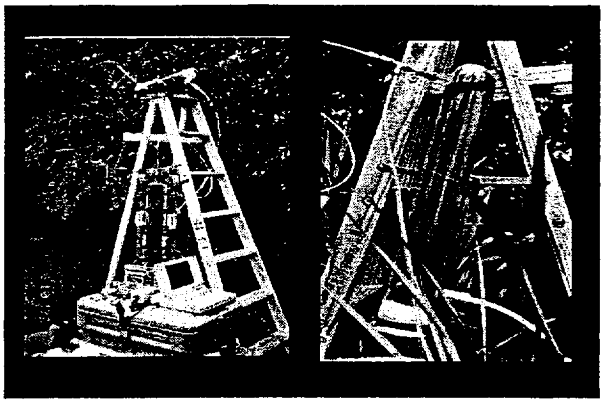

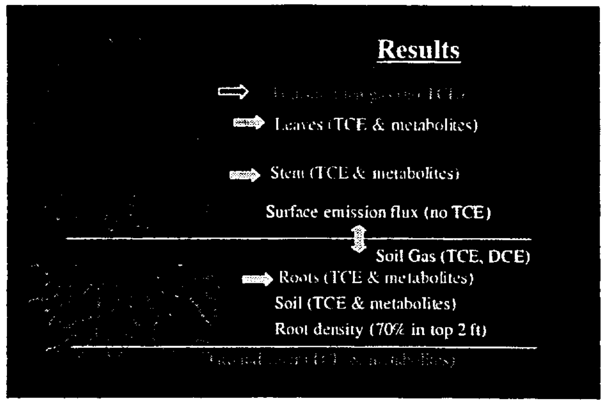

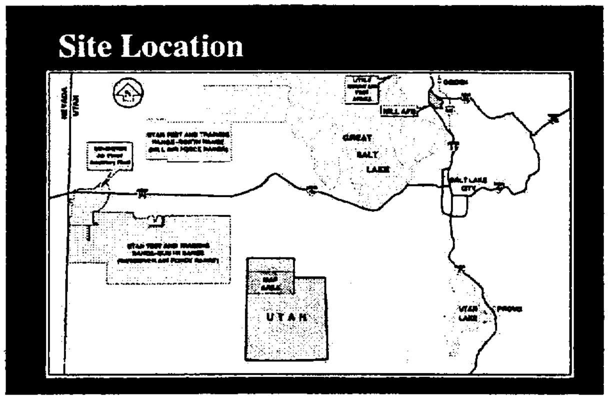

OU-2 Plant Tissue Headspace Analysis for TCE and PCE (n=3)

date sampled	location	species	tissue	range	mean mg/kg TCE	stdev
8/20 to 9/1	onsite	Poplar	leaves	0.33 to 0.46	0.364	0.124
			stem	0.25 to 36	8.14	5.780
9/17	control	Poplar	leaves	ND	0	NA
8/5 to 8/6			stem	ND	0	NA
8/20 to 9/1	onsite	Russian Olive	leaves	0.11 to 0.2	0.151	0.045
			stem	0.54 to 6.2	1.94	1.130
9/17	control	Russian Olive	leaves	ND	0	NA
9/10			stem	ND	0	NA
8/20 to 9/1	onsite	Willow	leaves	0.15 to 0.72	0.339	0.325
			stem	0.31 to 11	5.110	3.40
9/17	control	Willow	leaves	ND	0	NA
9/10			stem	ND	0	NA

date sampled	location	tree	tissue	range	mean mg/kg PCE	stdev
8/20 to 9/1	onsite	Poplar	leaves	1.53 to 1.56	1.54	0.020
			stem	ND to 7.9	2.81	1.35
9/17	control	Poplar	leaves	ND	0	NA
8/5 to 8/6			stem	ND	0	NA
8/20 to 9/1	onsite	Russian Olive	leaves	0.39 to 0.71	0.599	[illegible]
			stem	ND to 2.0	1.10	0.349
9/17	control	Russian Olive	leaves	ND	0	NA
9/10			stem	ND	0	NA
8/20 to 9/1	onsite	Willow	leaves	ND	0	NA
			stem	ND to 5.0	1.47	1.35
9/17	control	Willow	leaves	ND	0	NA
9/10			stem	ND	0	NA

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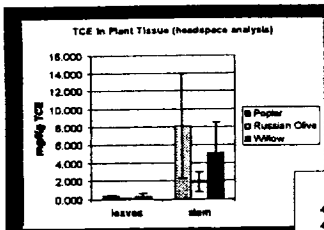

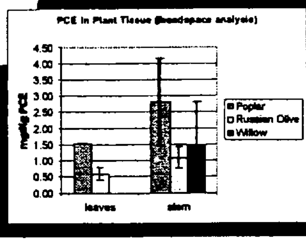

Plant tissue analysis (TCE/PCE)

Transpiration gas sampling (TCE/PCE)

tree species	TCE mg/L	stdev	PCE mg/L	stdev
on-site poplar	2.665	1.6	0.095	0.135
across canal poplar	0.365	0	0.01	0
control poplar	0	0	0.007	0
on-site russian olive	0.322	0.24	0.007	0.003
across canal russian olive	0.117	0.025	0.002	0.002
control russian olive	0.095	0.036	0	0
on-site willow	0.826	0.455	0.015	0.008
across canal willow	0.199	0.116	0	0
control willow	0.098	0.081	0	0

Comparison: CCAS and HAFB

- Groundwater TCE: similar (1 ppm)
- Plant tissue TCE: higher at HAFB
- Plant tissue metabolites: similar
- TCE highest in roots/stems, metabolites highest in leaves
- Phytovolatilization: none at CCAS, some at HAFB
- Precipitation: CCAS (50 in/yr), HAFB (15 in/yr)

Extrapolating to the Field

Plant Uptake = (TSCF)(C_{TCE})(T)(f)

TSCF and C_{TCE} are assumed constant.

T = Transpiration (200 - 1400 L/m^2-yr).

f = fraction of groundwater uptake (0.1-0.5)?

Directions/Questions for Future Research

- Improved methods for measuring phytovolatilization
- Diurnal, seasonal measurements
- Uniformity of individual trees & canopy
- Precipitation vs groundwater use
- Can lab measurements be extrapolated to field?

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Phytotransformation Pathways and Mass Balances for Chlorinated Alkanes and Alkenes

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Valentine Asongu Nzengung has a B.Sc. in geology from Georgia State University in Atlanta. Upon graduation from Georgia Tech, he worked at the United States Ecosystems Research Laboratory in Athens, GA, for two years before his appointment to a tenure-track faculty position at the University of Georgia in the fall of 1995.

Valentine Asongu Nzengung is currently an associate professor of environmental geochemistry and an affiliate member of the Advanced Ecology Laboratory. His research approach is multidisplinary and focuses on the development and evaluation of innovative environmental remediation technologies. The specific technologies his currently working on include phytoremediation, natural attenuation, *in-situ* dethionite treatment barriers for chlorinated organic solvents, preparation and determination of the effectiveness of organo-modified clays as sorbents of hydrophobic organic contaminants. His most recent discovery involves the use of selected plants and photoautotrophic microorganisms in decontamination of perchlorate-contaminated soils and groundwater. He is also involved in field demonstration and validation projects at many chlorinated solvent and perchlorate waste sites. He has published more than twenty research papers in various environmental research journals and conference proceedings.

Abstract

Phytotransformation products of chlorinated alkanes and alkenes in the rhizosphere, tissues of aquatic plants, cottonwoods and willows grown hydroponically in a greenhouse and in similar trees harvested from a phytoremediation field site were determined. Using the results of the identified products, we proposed the predominant metabolic pathways and estimated mass balances. Four mechanisms were found to be important in the removal of the chlorinated aliphatics from water by aquatic plants, namely: (1) rapid sequestration by partitioning to the lipophilic plant cuticles; (2) phytoreduction to less chlorinated VOCs; (3) phytooxidation to chloroethanols, chloroacetic acids and unidentified metabolites; and (4) assimilation into the plant tissues as non-phytotoxic products. A total mass recovery of better than 80% was obtained from the radiolabeled studies with aquatic plants. For woody plants, the predominant phytoprocesses included rhizodegradation, phytodegradation and phytovolatilization. Mineralization of chlorinated aliphatics to $^{14}CO_2$ in the tissues of aquatic plants and in the rhizosphere of woody plants was confirmed. We believe that all of the CO_2 formed could not be accurately quantified since plants utilize CO_2 during photosynthesis. The identification in the plant phase and in the root zone of metabolites formed by the oxidative and reductive transformation of the probe chemicals suggests that more than one pathway requiring different enzymes may be involved in phyto-transformation reactions. Comparison of metabolites observed in leaf extracts of mature trees growing over a TCE plume at Carswell AFB, Fort Worth, Texas; leaves harvested from younger trees at the field site; and rooted cuttings used in greenhouse studies provided evidence that phytotransformation pathways may change with the age or growth stage of vascular plants.

Introduction

The successful design and application of phytoremediation treatment systems at field sites depends on our understanding of the phytoprocess involved in the attenuation of the specific contaminants. The removal of chlorinated organic solvents (COS) from the affected environments may be influenced by many factors, such as physicochemical properties of the organic solvent, the plant characteristics, the root zone and atmospheric conditions. Due to differences in their physiology and geo-environments, the mechanisms by which aquatic, terrestrial and woody plants metabolize the same halogenated organic chemicals may vary.

We investigated the plant-mediated metabolic pathways of six halogenated aliphatics (three halogenated alkanes and three alkenes) and mass balances for three of the six compounds. The specific halogenated aliphatics included carbontetrachloride (CTC), hexachloroethane (HCA), tetrabromoethylene (PBE), tetrachloroethylene (PCE), trichloroethane (TCA), and trichloroethylene (TCE). The vascular plants used in the studies included an emergent wetland plant (*Myriophyllum aquaticum* [parrot feather]), a submergent wetland plant (*Elodea canidensis* [waterweed]), and two woody plants (cottonwoods and willows). The rooted cuttings of cottonwoods and willows were selected according to their health and maturity. Duplicate runs were made with cuttings that came from the same tree and when possible, from the same branch. This enabled consistency and very little variation. For comparisons, harvested leaves and roots from mature cottonwoods and willows growing over a shallow plume of PCE and TCE were analyzed for metabolites.

Methodology

Sorption experiments

On arrival at the laboratory, the *Elodea* to be used for sorption experiments was heat inactivated (Nzengung et al., 1999) and 7 g was weighed into 12 serum bottles and filled with nanopure water (52 mL). The vials were dosed with different concentrations of PCE or HCA (0, 0.5, 1, 2, 5, and 10 mg/L, respectively) and sealed. At the end of the equilibration period of 24 hours, 6 mL of liquid phase from each bottle were extracted into 6 mL of hexane and analyzed by GC/ECD. The equilibration time of 24 h was selected because sorption onto *Elodea* by both PCE and HCA was observed to be very rapid, with equilibrium attained in about two hours.

Static Batch Transformation Experiments

Harvested algae, parrot feather, or *Elodea* were weighed into 20 or more 60-mL serum bottles and the remaining volume was filled with deionized water. Half of the serum bottles were immediately dosed with the compound of interest and crimped with an aluminum seal and aluminum-faced silicon septa. The pH in reactors with live algae and plant samples was 5.6. Each sample vial and its corresponding control of dosed liquid without plant were hand-shaken twice a day for the duration of the experiment. Headspace was minimized in all bottles. The solution phase of dosed samples and their corresponding controls were sacrificed for analysis 15 minutes after dosing the bottles and at predetermined time intervals thereafter. The longest experiments lasted for 30 days and the shortest for 7 days. For selected samples, the entire solution phase was removed with a gas-tight syringe and the residual plant or algae tissue extracted with methanol/acetonitrile (1:1) before analyzing for metabolites. This extraction involved two steps. In the first step, the residue was first extracted by adding enough methanol-acetonitrile to fill the vial and sonicating for 10 minutes, then separating the liquid phase by centrifugation and analyzing directly by GC/ECD or LS. In the second step, the remaining pellets were then crushed and extracted as above.

Radiolabeled batch transformation studies were conducted with two different chemicals (^{14}C-PCE and CTC). The ^{14}C activity present as $^{14}CO_2$, hydrophilic, extractable and unextractable bound fractions was assayed by liquid scintillation counting. The excess solution phase was removed with a gas-tight syringe and the residual algae or plant matter extracted by sonicating three times with 20 mL of a binary solvent (methanol and acetonitrile) as described above. The unextracted bound fraction was directly quantified by combusting the remaining pellets in a Packard Model 307 sample oxidizer (Packard Instrument Co., Downers Grove, IL). The evolved $^{14}C0_2$ was trapped and quantified using a Beckman LS 6000L liquid scintillation counter.

Hydroponic Bioreactor Studies

A 2.2-liter bioreactor flask with two side ports was used in the experiment (Nzengung et al. 1999). One port was connected with a valve and a reservoir for water replenishment and the other port was equipped with a sampling-port. The growth solution was 30% of full strength Hoagland's solution and was dosed with either saturated TCE or PCE aqueous solution. Each tree was fastened into the screwed cap and sealed with dental cement and acrylic glue. All roots were completely submersed in the aqueous nutrient media and leaves were outside of the reactor. The final solution volume was 2000 - 2100 mL and the headspace was about 10 mL. The roots were shielded from direct light by shielding the medium-containing portion of the reactors with aluminum foil. All studies were conducted in a greenhouse. The volume of medium was kept constant by adding water through the replenishment port. A 1 mL aliquot was withdrawn everyday through the sampling-port and extracted into 6-18 mL of hexane. The volatile organic compounds (VOCs) in the hexane phase were measured by GC/ECD. The experiments were terminated when the PCE concentration decreased to about 25% of the starting concentration. The static headspace samples (1 mL) were taken at the beginning and at the end of the study, and analyzed on both GC/FID and GC/MS.

For radiolabeled experiments, the upper portion of the plant was encased in an inverted 5000 mL Erlenmeyer flask with 2 ports, one on top and one on bottom. The flask was secured and sealed in the same manner as the bottom flask outlined above. The top port was attached to an activated carbon trap to purify the air entering the flask. The bottom port was attached to a series of traps that were used to capture any products that the plant had transpired. The first trap was empty to catch any transpired water that built up during the duration of the experiment. The second trap contained ethylene glycol monomethyl ether, the third trap contained 1M sodium hydroxide (NaOH) and the fourth trap contained 10 g of activated carbon. The last trap was connected to a compressed air cylinder that created a continuous airflow through the entire system. Silicone grease was used to seal all joints to ensure there was no leakage at the numerous connections.

Measurement of Chloroacetic Acids

Following the hexane extraction described above, solid and aqueous samples were treated with 1M sulfuric acid and placed in an ultrasonic bath for several hours. Then, the mixture solution was extracted using MTBE. The MTBE extract (2 mL) was mixed with 150 mL diazomethane saturated MTBE solution prepared in a Wheaton Generator with 1 gram 1-methyl-3-nitro-1-

nitrosoguanidine and 5 mL of 5M NaOH. The mixture was placed in an ice bath for 5 minutes, and then at room temperature for at least 15 minutes (Hales et al., 1973). Chlorinated acetate methyl esters were measured on a Shimadzu GC-14A/ECD. The standard solutions of chloroacetic acid, dichloroacetic acid, and trichloroacetic acid were derivertized and measured under the same condition.

Headspace Measurement of VOCs

A Hewlett-Packard 5890A Gas Chromatograph with FID was used for VOCs analysis. Exactly 0.5 mL headspace was manually injected into the injection port maintained at a temperature of 200°C. A capillary column DB-VRX, 30 m X 0.25 mm I.D., 1.4 um film (J & W Scientific) was used in the separation of the different VOC components. The measurement was under helium carrier gas at the following temperature program: 30°C for 5 minutes; followed by temperature increase of 5°C/minute to 60°C and held for 2 minutes, then increased at 25°C/minute to 200°C and held for 2 minutes. Data acquisition was performed on HP 3365 ChemStation. Further VOC quantification was done on a Shimadzu GC-17A Gas Chromatograph with QP-5000 Mass Spectrometer with a DB-VRX column.

Gas Chromatography Methods

A Hewlett Packard GC-6890 with an electron capture detector (GC-ECD) was used for quantitative and qualitative analysis of the PCE, TCE, and DCE in extracted aqueous and solid phase samples. The GC-ECD configuration was a split injection of 1 µL hexane extract using a Hewlett-Parkard-7863 series automatic injector. The split injection had a split ratio of 20: 1 to maximize sensitivity. The GC-ECD configuration used was a 32 m HP-5 Cross-linked 5% methylpolysiloxane phase * 0.32 mm * .25 µm film separation column or a DB-VRX, 30 m X 0.25 mm I.D., 1.4 um film). The column temperature was programmed at 35°C and held for 2 minutes, followed by a temperature increase of 5°C/min to 85°C, and a subsequent temperature increase of 25°C/min to 160°C which was maintained for 1 minute, resulting in a total run time of 16 minutes per a sample. Nitrogen was used as the carrier gas with an in-column flow rate of 2.6 mL/min and helium was used as the makeup gas with a 60 mL/min flow rate. The inlet was held in the constant pressure mode at 11.03 Psi. The injector and detector temperatures were 250°C and 320°C, respectively. One mg/L of dichlorobenzene samples were analyzed as an external standard. To ensure accurate quantitative results, PCE, TCE, and DCE standards prepared in-house were used to construct calibration curves each week or whenever GC conditions changed as indicated by the external standard. Detection limits (GC/ECD) for TCE and PCE are 1 ppb and 20 ppb for DCE.

GC/FID methods were used in the analysis of VC and DCE with minimum detection limits of 10 and 5 ppb, respectively. The temperature program for the GC/ECD and GC/FID methods were similar and both detectors were operated simultaneously during sample analysis.

Results and Discussions

Aquatic Plants

Sorption experiments with heat-shocked *Elodea* indicated that HCA and PCE partitioned strongly to the plant matter. A partition coefficient of 8 ± 0.3 (SD) mL/g for PCE and 23 ± 0.7 (SD) mL/g for HCA was estimated. These coefficients indicate that sequestration is an important fate process that cannot be ignored. Heat-inactivated plants were used in sorption studies because viable plants transformed HCA before the end of the incubation time of 24 hrs. Since the plants were heat-treated and killed in the process, partitioning to the plant material rather than uptake was assumed.

The transformation products of the probe contaminants of concern (COCs) identified by GC/ECD and GC/FID methods (retention time) were confirmed by GC/MS. The transformation of HCA resulted in pentachloroethane (PCA) and PCE as the main dehalogenation products, while relatively small amounts (maximum <500 µg/L) of TCE and only trace amounts (<100 µg/L) of 1,1,2,2-TTCA, and 1,1,2-TCA were formed. The trace products are not included in Figure 1 as the data points were not distinguishable from zero on the plots. Shortly after the samples were dosed with HCA, the concentration of PCA and PCE increased rapidly to a maximum within the first 100 hours before slowly decreasing to below the GC/ECD detection limit of 5 to 20 ppb. The measured PCE concentration in solution was generally greater than that of PCA, but did not exceed 30% of the initial HCA concentration of 10 mg/L. The corresponding increase in TCE with decreasing PCE concentration suggests that PCE did not just accumulate, but was further reductively dehalogenated to TCE and other products not yet identified. The dehalogenation of PCE to TCE was directly confirmed by dosing algae and aquatic plants with PCE. Due to the moderate to high aqueous solubility of PCE and TCE, both chemicals should be readily taken up, transformed, and bound by oxidative enzymes in the algae and aquatic plant tissues. Neither DCE nor VC was identified as products in these experiments even though we exhaustively analyzed for them. In samples dosed with TCA, TCA appeared to have been mostly assimilated because its disappearance from solution was not followed by the appearance of reductive transformation products into solution. It has been shown elsewhere that as the number of chlorine substituents of chlorinated ethenes decreases the ability to undergo reductive dehalogenation decreases (Bradley and Chapelle, 1996).

The extractable fraction of reductive transformation products decreased with length of time into the experiment. This suggests that these metabolites were either oxidized into polar compounds or covalently bound to the spirogyra and plant tissues. Interferences from other compounds in the heterogeneous plant extract have prevented the complete identification of the hydrophilic metabolites. The identification of DCAA and TCAA in axenic *Myriophyllum* plantlets dosed with HCA is confirmation that both reductive and oxidative transformation

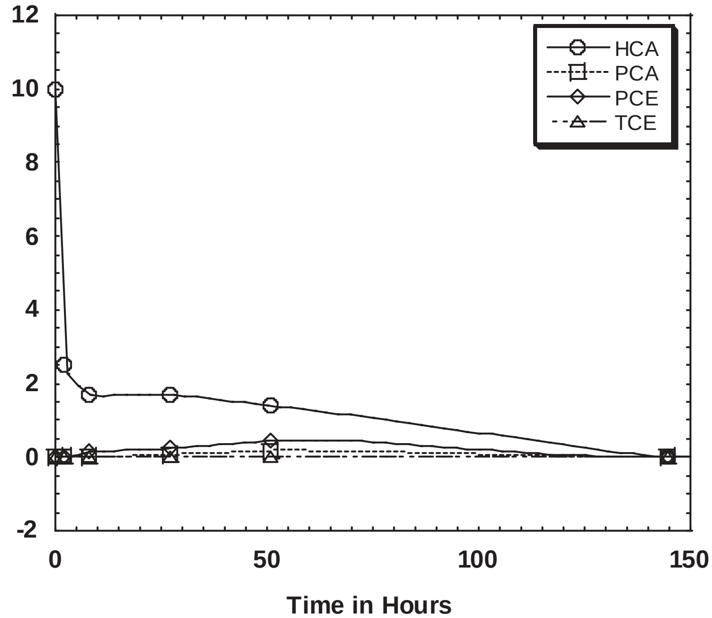

Figure1. Sorption accompanied by phytotransformation of 10 mg/L HCA by 7 g of *Elodea canadensis*, including phytoreduction products (PCA, PCE, and TCE) detected by GC/ECD and confirmed by GC/MS

pathways are involved in aquatic plant mediated transformation of HCA. The composition of the identified metabolites further suggests that the phytotransformation of COCs by aquatic plants and algae involved more than one pathway, possibly by more than one enzyme (Figures 2 and 3). Since axenic *Myriophyllum* and surface sterilized *Elodea* metabolized the same COC to the same products, we concluded that dehalogenase enzyme(s) mediated the reductive dehalogenation reactions, and oxidative enzymes (possibly cytochrome P-450 with monooxygenase activity, glutathione or laccase) mediated the bound reactions. Other studies (Lamoreaux et al., 1970) have shown that oxidative enzymes isolated from green plants were capable of binding xenobiotics to plant matter through nucleophilic addition (Kim et al., 1997).

Willows and Cottonwoods. The rate of TCE and PCE removal by rooted cuttings of cottonwood and willows grown hydroponically in a greenhouse increased with the water uptake of the tree. The highest concentration of PCE and TCE was measured in the roots and decreased progressively upward (Tables 1, 2). No PCE was measured in the leaves suggesting that the parent compound was not accumulated in the foliage because it was either completely metabolized and/or volatilized. Generally, PCE was more toxic to the rooted cuttings of cottonwoods and willows than TCE. PCE was observed to be toxic to three months old rooted cuttings at initial solution concentrations of 45 mg/L, but approximately six months old rooted cuttings of willows did not show any observable toxic effects at PCE solution concentrations of 60 mg/L.

The parent compounds and metabolites taken up by the trees are either metabolized or phytovolatilized. The suite of anaerobic degradation products identified in the headspace above the rhizosphere of our planted bioreactors (Table 3) in greenhouse studies provided direct evidence of phytoreduction of PCE and TCE in the rhizosphere of cottonwoods and willow trees. Our results are in agreement with those obtained from a field site in Carswell, Texas, where DCE, VC and higher concentrations of dissolved organic carbon have been detected in the root zone of cottonwood and willow trees growing over a shallow plume of TCE. Previous work has shown that methanogenic conditions may exist in the root zones of plants.

We observed TCAA>>DCAA>trichloroethanol in plant tissues from our greenhouse and three years old trees currently used in phytoremediation of TCE at the Carswell site. Meanwhile, DCAA made up 90% of the metabolites identified in leaf tissues of older mature trees growing over the plume for more than a decade. We hypothesize that the growth stage or age of vascular plants determines the metabolic pathway of COCs. Also, the distribution of polar metabolites appears to vary with the plant species (Tables 1 and 2). The rhizosphere and headspace gases of trees dosed with either ^{14}C-TCE or PCE (Table 4) confirmed the mineralization of these chlorinated organic solvents (COS) to $^{14}CO_2$. An accurate determination of the mineralized fraction of the parent compounds cannot be achieved because plants utilize CO_2 for photosynthesis.

A transformation pathway that couples phytoreduction in the rhizosphere, phytotransformation and assimilation in the plant tissues is proposed to account for the identified products (Figure 4). Plant enzymes such as glutathione-s-transferase and cytochrome P-450 are

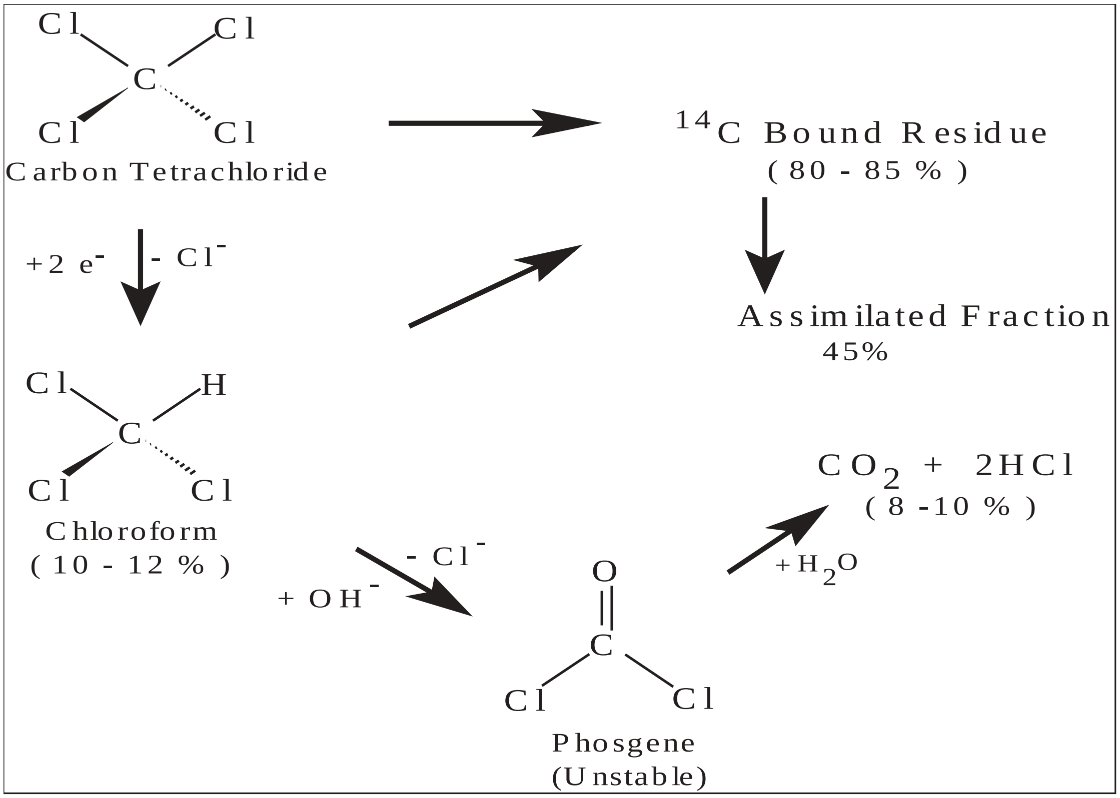

Figure 2. Proposed pathway for aquatic plants and algae mediated transformation of carbon tetrachloride.

believed to catalyze the phytoreduction and phytooxidation reactions, respectively.

Mass Balances

A mass balance based on GC/ECD quantified products of ^{12}C-COCs in solution became progressively poorer with increasing reaction time. This was attributed to the formation of metabolites not identified by the GC/ECD method and to the assimilation of the COCs by algae or aquatic plants. Mass balance estimation based on chloride in solution from reductive dehalogenation reactions was poor because of the high background chloride. As an alternative, we investigated the dehalogenation of PBE by *Elodea* and quantified the formation of bromide on a Dionex Ion Chromatograph. After 21 days, 65% of the initial 10 mg/L PBE was identified as tribromoethylene (TBE), 30% of total bromide was measured as dissolved anions in solution giving a mass balance for bromide of 95%. The mass balance for metabolism of ^{14}CTC with *spirogyra* after 10 days of incubation showed that CTC was degraded with 10 - 12% of the initial solute converted to chloroform, and 8% converted to CO_2. About 40% of the initial activity was extracted and 45% was unextracted and considered irreversibly bound to the *spirogyra*. It must be noted that the $^{14}CO_2$ measured in the solution phase in batch phytotransformation experiments with photosynthesizing algae and plants is not an accurate estimation of the amount produced in the course of metabolism of the solute because plants assimilate CO_2 during photosynthesis. The bound fraction should therefore include a fraction of the $^{14}CO_2$ assimilated by the algae or aquatic plant during photosynthesis.

In parallel batches spiked with ^{12}CTC, the extractable bound fraction analyzed by GC-ECD and GC/MS after 48 hours of incubation was identified as chloroform (CF) and CTC. The extracted fraction identified as CF and CTC decreased with increased incubation time, suggesting once more that these compounds were sequestered, transformed and assimilated, but not simply hyperaccumulated. Although greater than 80% of the ^{14}C-activity was incorporated into the plant biomass (Figure 5), not all of it was extractable with organic solvents. This suggests that the sequestered fraction may be transformed and assimilated by the plant tissue (Langebartels 1986). Kim et al. (1997) recently showed that organic chemicals can be incorporated within humic substances by oxidative enzymes and rendered nontoxic. In similar experiments involving ^{14}C-PCE and *spirogyra* the mass recovery was 95% with <5% mineralization (CO_2), 8% hydrophilic metabolites, 49-70% activity bound and the

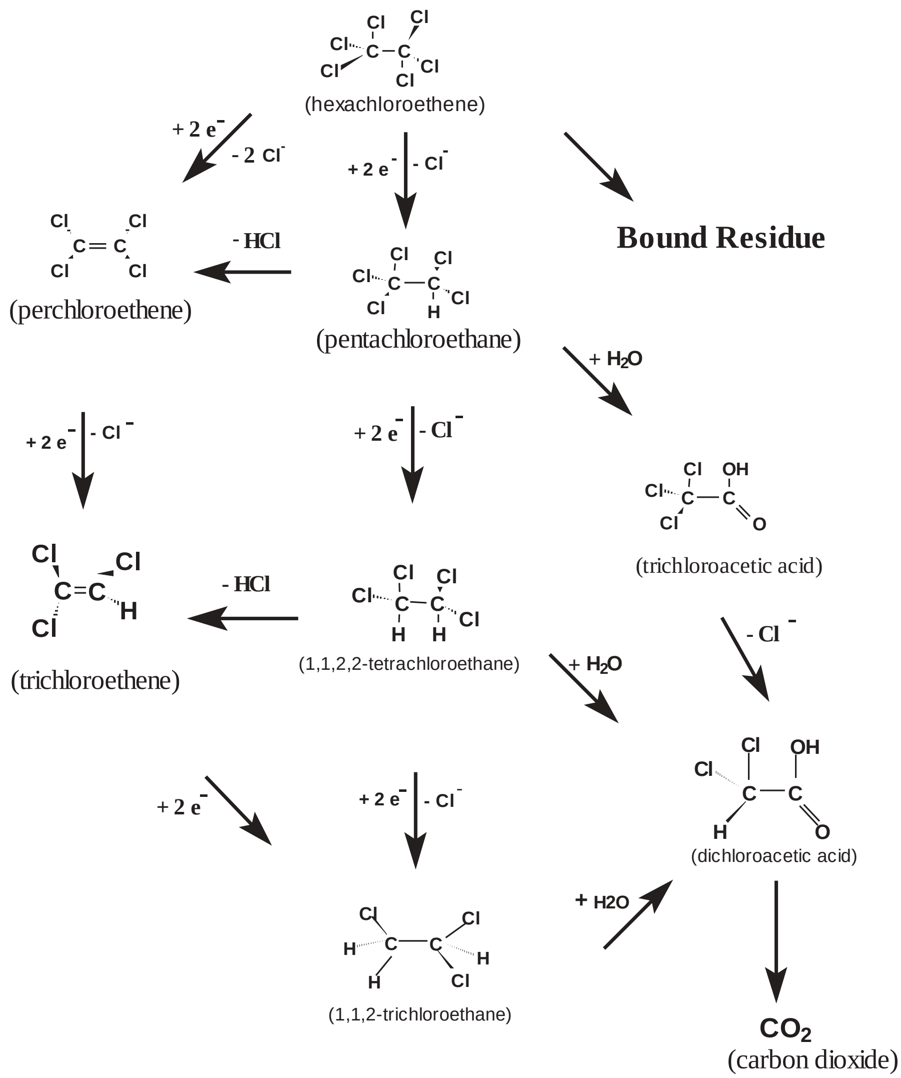

Figure 3. Proposed pathway for aquatic plants and algae mediated transformation of hexachloroethane.

Table 1. Distribution of PCE and its metabolites in the rhizosphere and in tissues of cottonwood trees

Products	Rhizosphere	Roots	Lower Stem	Upper Stem	Leaves
PCE (mg/Kg)	10	38.5	34	4.3	0
TCE (mg/Kg)	2.3	0.6	1	0.09	0
TCAA (mg/Kg)	0.01	0.59	1.42	6.41	21.7
DCAA (mg/Kg)	0	0.22	0.11	0.88	1.7
MCAA (mg/Kg)	0	0	0.27	0.67	0.24
Trichloroethanol (mKg)	trace	0	0.24	0.34	0.1

Table 2. Distribution of PCE and its metabolites in the rhizosphere and in tissues of willow trees.					
Products	Rhizosphere	Roots	Lower Stem	Upper Stem	Leaves
PCE (mg/Kg)	10.7	38.8	19.5	3.11	0
TCE (mg/Kg)	0.07	0	0	0	0
TCAA (mg/Kg)	0	1.61	0.11	0.16	2900
DCAA (mg/Kg)	0	2.64	0.82	0.50	1684
MCAA (mg/Kg)	0	trace	0	0	0
Trichloroethanol (µg/Kg)	trace	0	0.07	0.03	0.04

Table 3. Summary Results of Rhizosphere Headspace Analysis	
Experiment conducted	Metabolites Identified in Headspace above Rhizosphere Media
PCE Cottonwood	PCE, PCA, TCE, TCA, DCE, Ethene, Ethane, Methane
PCE Willow	PCE, PCA, TCA, DCE, Ethene, Ethane, Methane
TCE Willow	TCE, DCE, Ethene, Ethane, Methane

Table 4: Percent Recovery of Parent Compound and Metabolites in Solution, Plant and Air Phases		
Reactor Compartment	% Activity Recovered (^{14}TCE)	% Activity Recovered (^{14}PCE)
Plant	8.7	4.5
Solution	26 (CO_2 = 3.4)	55 (CO_2 = 3.7%)
Traps	9.4	14
Total % Recovery	~44	~74

rest as dissolved TCE (depending on the reaction time of the sacrificed sample). The radiolabeled form (^{14}[C]-HCA) of the chemical was not commercially available at the time of this study.

For planted cottonwood and willow bioreactors dosed with ^{14}C-TCE and PCE, 3.4% and 3.7% $^{14}CO_2$, respectively, was measured in the rhizosphere and little or none measured in the gases volatilized by the tree leaves (Table 4). The poor mass balance for experiments performed with woody plants is attributed to losses from the higher volatilization of CO_2 and other highly volatile less chlorinated products formed in the rhizosphere.

Conclusions

We have identified four predominant phytoprocess involved in aquatic plant mediated transformation of chlorinated alkanes and alkenes. These processes include: (1) rapid sequestration by partitioning to the lipophilic plant cuticles; (2) phytoreduction to less chlorinated VOCs; (3) phytooxidation to chloroethanols, chloroacetic acids and unidentified metabolites; and (4) assimilation into the plant tissues as non-phytotoxic products. A total mass recovery of better than 80% was obtained from the radiolabeled studies with aquatic plants. Data obtained from greenhouse studies confirmed that the mechanisms of removal of COS from water by woody plants include rhizodegradation, phytodegradation and phytovolatilization. Mineralization of halogenated aliphatics to $^{14}CO_2$ in the tissues of aquatic plants and in the rhizosphere of woody plants was confirmed. The identification of metabolites from oxidative and anaerobic transformation reactions in the plant phase and in the root zone suggests that more than one pathway re-

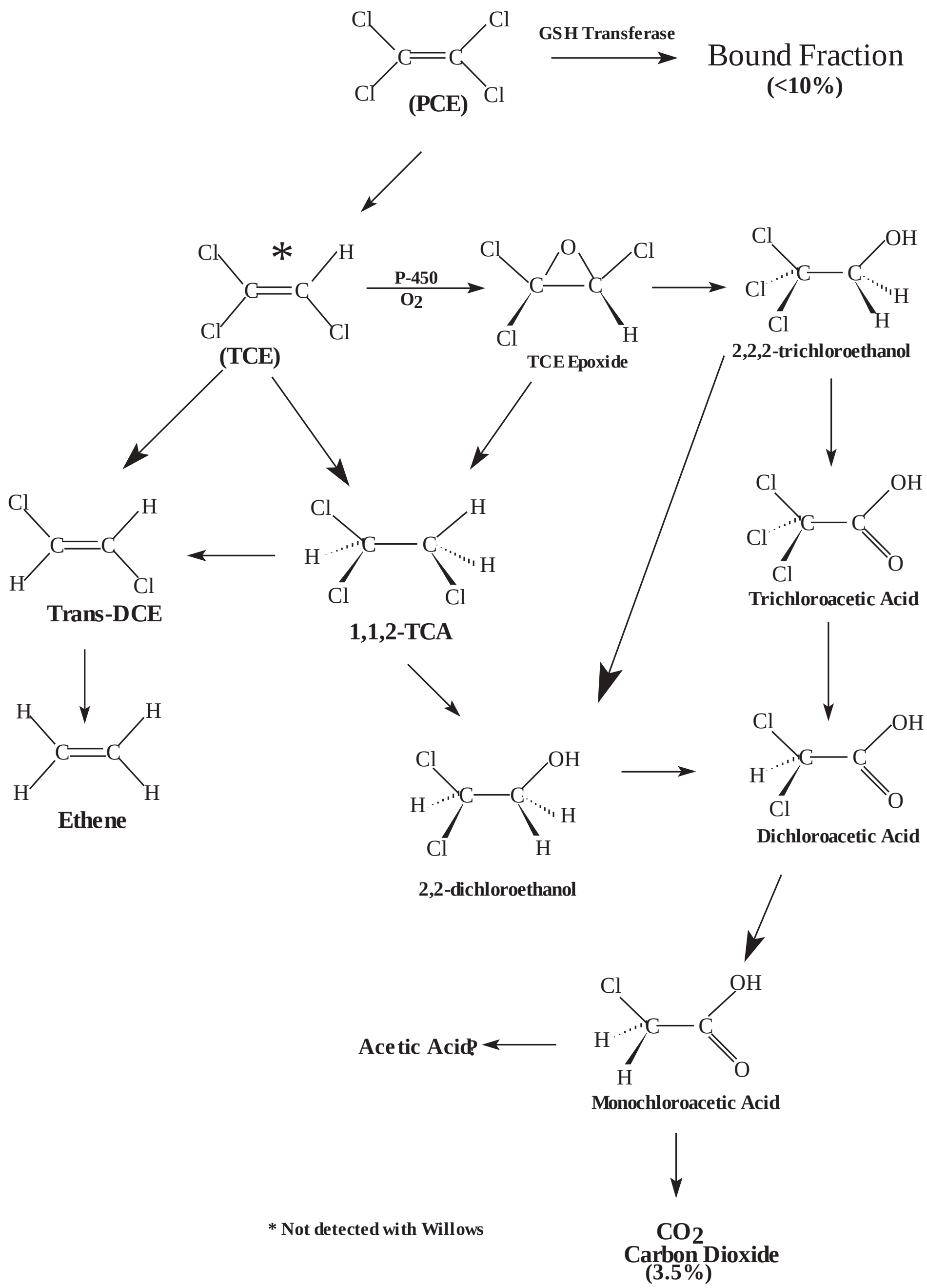

Figure 4. Proposed pathway for transformation of TCE and PCE in the root zone (rhizodegradation) and in the tissues (phytodegradation) of cottonwood and willow trees.

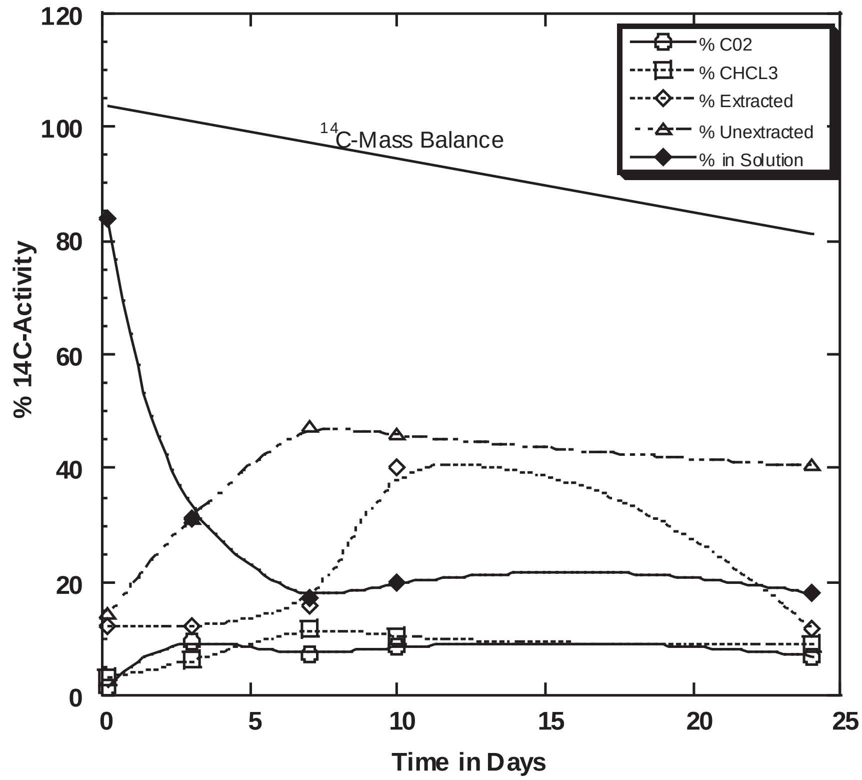

Figure 5. Distribution of transformation products of radiolabeled carbon tetrachloride (^{14}C). Mass balance is based on the quantified products.

quiring different enzymes may be involved in phytotransformation reactions. Comparison of metabolites observed in leaf extracts of mature trees growing over a TCE plume at Carswell AFB, Fort Worth, Texas, leaves harvested from younger trees at the field site and rooted cuttings used in greenhouse studies provided evidence that phytotransformation pathways may change with the age or growth stage of vascular plants.

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Phyto-transformation Pathways and Mass Balance for Chlorinated Alkanes and Alkenes

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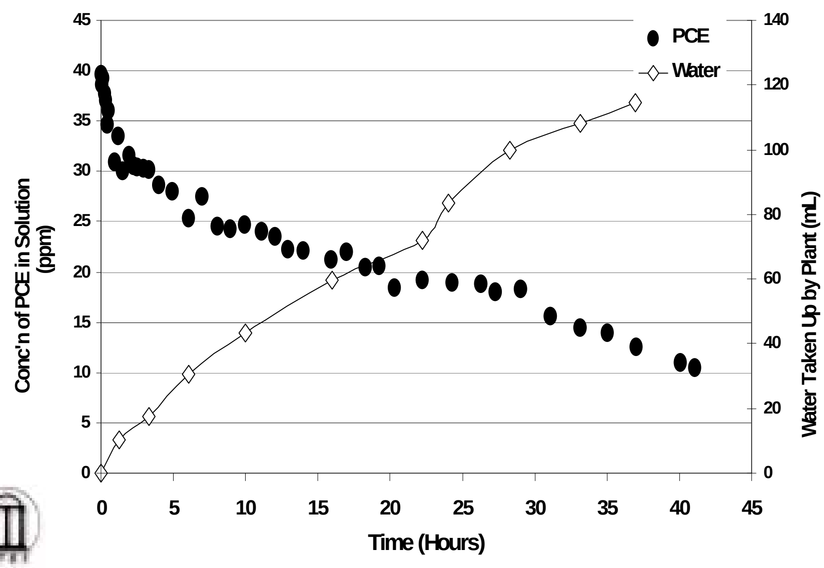
Uptake of PCE and Water by Cottonwood Tree



Distribution of PCE Metabolites in Rhizosphere and Cottonwood Tissues

Products	Rhizosphere	Roots	Lower Stem	Upper Stem	Leaves
PCE (mg/kg)	10	38.5	34	4.3	0
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TCAA (mg/kg)	0.01	0.59	1.42	6.41	21.7
DCAA (mg/kg)	0	0.22	0.11	0.88	1.7
MCAA (mg/kg)	0	0	0.27	0.67	0.24
Trichloroethanol (ug/kg)	trace	0	0.24	0.34	0.1

Percentage of Parent Compound and Metabolites Recovered in Solution, Plant and Air Phases

Reactor Compartment		% Activity Recovered (^{14}PCE)
Plant	8.7	
Solution	26 (CO2 = 3.4)	55 (CO2 = 3.7%)
Traps	9.4	
Total % Recovery	≈44	≈74

Results of Rhizosphere Headspace Analysis

PCE cottonwood: PCE, TCE, trans-DCE, ethene, ethane, methane

- PCE willow: PCE, trans-DCE, ethene, ethane, methane
- TCE willow: TCE, trans-DCE, ethene, ethane, methane
- Field site (mature trees + soil+water+TCE) TCE, DCE, VC, methane

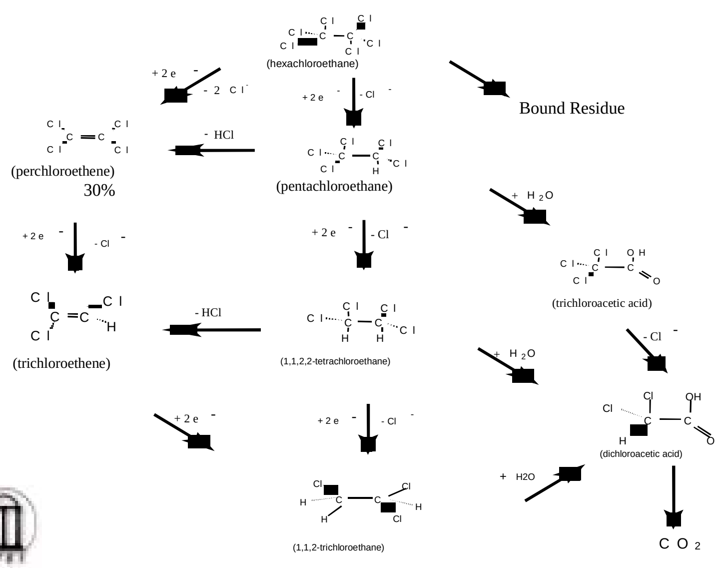
Phytodegradation Products of Trichloroethylene in Cottonwood Trees
Field Samples Collected January 1999

Type of Sample	Trichloroethanol (mg/Kg)	Trichloroacetic Acid (mg/Kg)	Trichloroethylene (mg/Kg)
Whip, Leaves on Trees	1.57 ± 0.06	0	0
Whip, Leaves on ground	0.62 ± 0.03	28.4	0
5-Gallon, Leaves on trees	0.26 ± 0.13	>30	0
5-Gallon, Leaves on ground	0.25 ± 0.07	31.3 ± 0.7	0

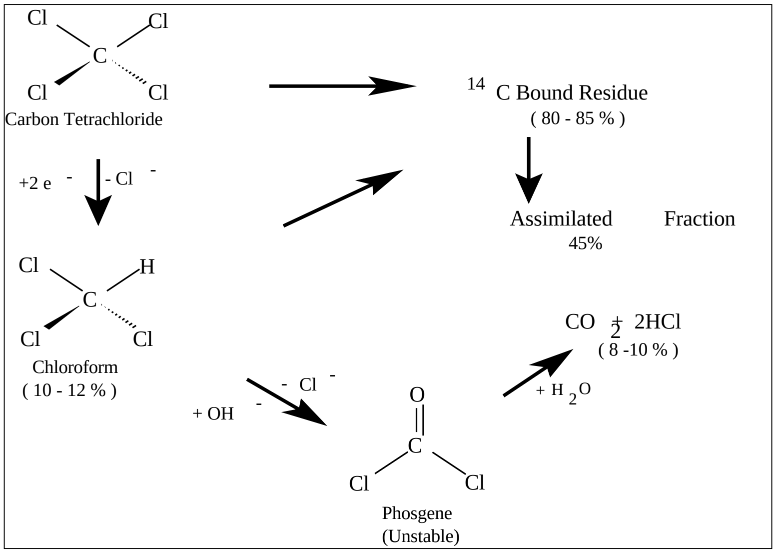
Phytodegradation Products of Trichloroethylene in Mature Willows and Cottonwood Trees at Field Site Samples Collected April 1999

Type of Sample	Trichloroethylene (mg/Kg)	Trichloroethanol (mg/Kg)	Dichloroacetic Acid (mg/Kg)
Cottonwood Leaves ¼ mile East	**0**	**0**	**1.34 ± 0.45**
Cottonwood Leaves S. end of Whips	**0.07** ± 0.01	**Trace**	**1.21 ± 0.42**
Willow	**0.17** ± 0.03	0	**2.32 ± 0.52**

Proposed Pathway for Aquatic Plants Mediated Transformation of HCA Based on Identified Metabolites in Solution and Plant Phases

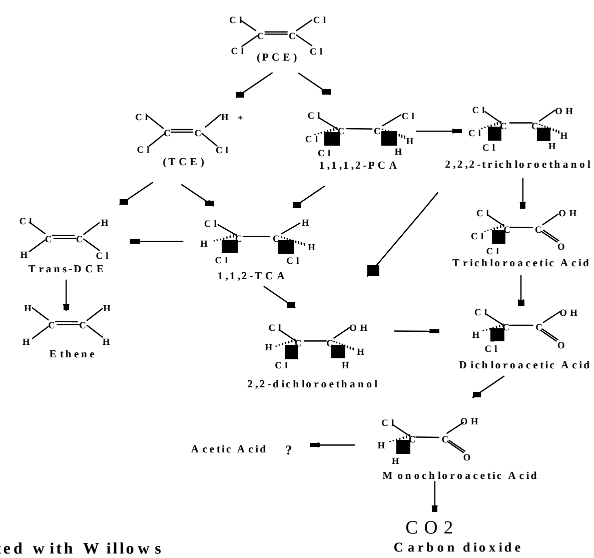


Proposed Pathways for Aquatic Plants Mediated Transformation of Carbon Tetrachloride



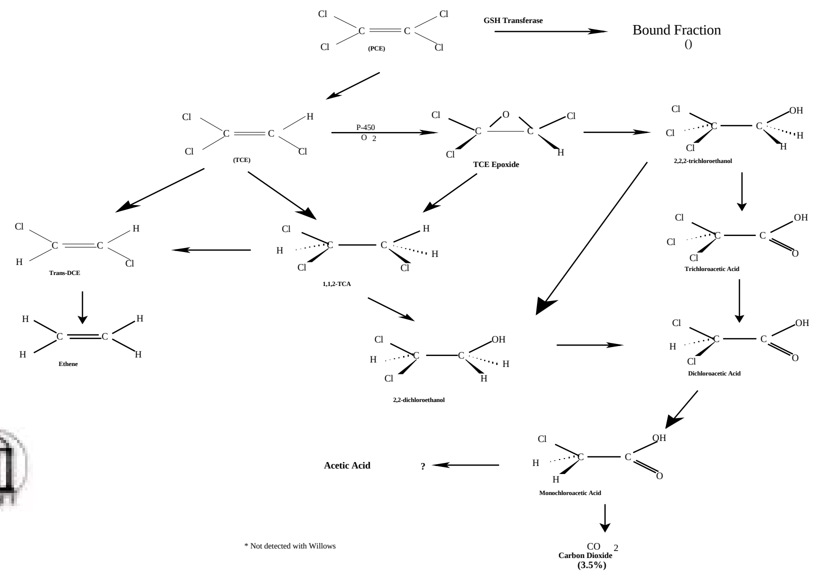
Proposed Pathways for Transformation of PCE in Root Zone (Rhizodegradation) and in Tissues (Phytodegradation) of Cottonwoods and Willows

Headspace Bioreactor and Field



* Not detected with Willows

Proposed Pathways for Transformation of PCE in Root Zone (Rhizodegradation) and in Tissues (Phytodegradation) of Cottonwoods and Willows



Conclusions

- Three primary phyto-processes are important in phytoremediation of volatile chlorinated aliphatics:

  * Phytovolatilization.

  * Phytodegradation.

  * Rhizodegradation.

- In addition, sequestration and assimilation are important processes for some plants, especially aquatic plants.

Conclusions

- Phytotransformation of volatile chlorinated aliphatics involves multiple pathways.
- Reductive dechlorination and mineralization of TCE and PCE occurs mainly in the root zone (rhizosphere) of woody plants.
- Oxidative and reductive transformation occurs in the tissues of aquatic and terrestrial plants.

Conclusions

- Trichloroethanol and trichloroacetic acid were identified at the highest concentrations in plant tissues of young trees used in phytoremediation of TCE and PCE.
- In mature or established tree plantations, dichloroacetic acid was the main metabolite identified in the plant extract.

Conclusions

- In greenhouse studies, evapotranspiration accounts for majority of the TCE, PCE and volatile metabolites taken up into the trees.
- Does the "age" or growth stage of tree plantations determine the phyto-transformation pathway(s) of chlorinated organic solvents?

INNOVATIVE SOLUTIONS FOR METALS REMOVAL

Progress in Risk Assessment for Soil Metals, and In-situ Remediation and Phytoextraction of Metals from Hazardous Contaminated Soils

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Abstract

Mining and smelting of Pb, Zn and Cd ores have caused widespread soil contamination in many countries. In locations with severe soil contamination, and strongly acidic soil or mine waste, ecosystems are devastated. Research has shown that Zn phytotoxicity, Pb-induced phosphate deficiency, Cd risk through uptake by rice or tobacco, and Pb risk to children, livestock or wildlife which ingest soil are the common adverse environmental effects at such contaminated sites. Improved understandings of soil metal risks to the environment have been developed which examine risk to all possible exposed organisms through soil, plants, animals, or water exposures. This review summarizes information about soil Cd risk to food-chains, explaining that when Cd is present at the usual 0.005-to-0.02 ratio to Zn in the contaminated soil, only rice and tobacco allow Cd to be transferred from the soil in amounts which can harm humans over their lifetime. Zn inhibits plant uptake of Cd, and inhibits intestinal absorption of Cd, protecting animals from Cd in most situations. Pb risk to children or other highly exposed organisms results from ingestion of the contaminated soil, and absorption of Pb from the soil into the blood where adverse health effects occur at 10-to-15 Fg Pb/dL blood. Soil Pb has much lower bioavailability than water Pb, and if ingested with food has even lower bioavailability. Research has shown that if high phosphate levels are added to Pb-contaminated soils, an extremely insoluble Pb compound, chloropyromorphite, is formed in soils from all known chemical species of Pb which occur in contaminated soils. It had earlier been learned that adding adsorbents such as hydrous Fe oxides and phosphate to Pb-contaminated soils inhibited Pb uptake by crops, and combined with the evidence that these materials could reduce the bioavailability of soil Pb to children, feeding tests were conducted with rats and pigs in several laboratories. A new approach to remediation of severely disturbed Pb/Zn/Cd-contaminated soils has been developed which uses mixtures of limestone equivalent from industrial byproducts such as woodash (to make soil calcareous and prevent Zn phytotoxicity), phosphate and Fe from biosolids and byproducts (to precipitate Pb and with Fe, increase Pb adsorption), organic-N from biosolids and manures and other beneficial components which correct the infertility of contaminated and eroded soils. Composting can stabilize the organic matter and slow N release to allow higher application of remediation amendments. Highly effective revegetation has resulted at four field test locations where this approach was tested, Palmerton, PA; Katowice, Poland; Bunker Hill, ID; and Leadville, CO. All plants tested were readily grown on the amended soil even with soil contained over 1% Zn and 1% Pb. Plant analysis indicates that these plants may be consumed safely by wildlife and livestock, although soil ingestion should be minimized at such sites. Although mining and smelting contamination has caused severe environmental harm in many locations, this method of soil metal remediation allows effective and persistent remediation at low cost, and should be applied to prevent further dispersal of the contaminated soil materials at many locations.

The potential use of metal hyperaccumulator plants to phytoextract soil metals is a new method of remediation under development. Combining improved cultivars of these accumulator plants, agronomic management practices to maximize yield and metal accumulation, burning the biomass to generate power, and recovery of metals from the ash appear to offer an economic technology compared to soil removal and replacement.

Introduction

Mining or smelting of Pb-Zn ores generates mine tailings rich in Pb, Zn, and Cd. Some of these tailings contain dolomitic limestone, and others contain pyrite which generates acidity when oxidized. Smelting of Pb, Zn, and Cu ores has commonly caused emission of Zn, Cd and Pb at levels which can cause adverse effects in the terrestrial environment. Strongly acidic Zn-rich mine wastes and smelter contaminated soils cause severe Zn phytotoxicity (Chaney, 1993), and can prevent all plants from surviving on the soil (e.g., Beyer, 1988). This paper is a summary of the key evidence that such mine and smelting wastes cause phytotoxicity of Zn, potential Cd risk to humans if rice or tobacco are grown on the contaminated soil, and Pb risk to children who may ingest the mine wastes or contaminated soils or housedust generated from these contaminated soil materials. Adverse environmental effects of these metals have resulted in many nations where older industrial technologies were used in mining or smelting.

On the other hand, there has been important progress in risk assessment methodology for soil metals, and research on methods to remediate Zn, Cd, and Pb-contaminated soils and sediments. New practical approaches for both *in situ* remediation by addition of amendments which reverse Zn phytotoxicity and Pb risk from soil ingestion have been demonstrated in recent years. Practical, inexpensive methods are available to revegetate such contaminated soil materials, and support vegetation which can be safely consumed by wildlife, livestock, and humans. Also, phytoextraction research has illustrated the potential of growing unusual metal hyperaccumulator crops on contaminated soils to remove some metals, and provide biomass power and an ash which can be recycled to reduce the costs of remediation.

A full discussion of present-day risk assessment and soil metal remediation methods would take a book. Thus, the goal of this paper is to give an overview of these ideas, with references to full papers and book-chapters which more fully report the science which allows the improved risk assessment and practical soil metal remediation. One of the most important advances in soil metal remediation is our development of using phosphate rich, high Fe biosolids and composts, and lime rich woodash and other lime-containing byproducts to make “Tailor-Made” Remediation Biosolids Mixtures and Composts and readily achieve effective revegetation and ecosystem restoration at such metal contaminated sites (see Chaney, Ryan and Brown, 1999; Stuczynski et al., 1997; Li and Chaney, 1998; Daniels et al., 1998; 1999; Brown et al., 1998b; Siebielec et al., 1999).

Improved Risk Assessment for Soil Metals

When present at high enough concentrations, Pb, Zn, and Cd in soils can cause adverse effects on plants, soil organisms, wildlife, livestock and humans through pathways which involve soil ingestion by children or livestock, ingestion of foods grown on the soil, ingestion of animals which ingested plants which grew on the soil, or from leaching of metals to drinking water or streams where Zn harms fish (Table 1). Extensive research and evaluation of the literature were conducted over the last decade to develop quantitative limits for metals in land-applied biosolids (municipal sewage sludge), and for characterization of the potential hazards which a soil could cause (see Chaney and Ryan, 1994; US-EPA, 1993). And research was conducted to find methods to amend or treat contaminated soils to reduce the risk of soil metals in a persistent manner such that the hazardous nature would be reversed or remediated.

The formal risk assessment method uses 14 or more Pathways to estimate the effect of soil metals on Highly Exposed Individuals (HEIs) which are humans who live on the soils, livestock pastured on the soil, crops grown on the soil, soil organisms in the soil, etc. (Table 1). For the biosolids risk assessment, it was assumed that 1000 t/ha of dry weight of biosolids would be applied over many years (centuries) of biosolids use as a fertilizer or soil conditioner. In risk assessment for hazardous soils, the contaminated soil is considered as is. One important change in the approach to risk assessment is the inclusion of valid measurements of “bioavailability” of soil metals to the HEI organism under consideration (child, adult, livestock, plant, etc.). And for the use of field-derived metal transfer coefficients from soil to plants, soil to livestock, soil to humans, etc.

The importance of using field-derived plant uptake slopes for the biosolids-amended soil is highly evident from examination of the literature. First, one needs to consider the effect of the chemical form of, and recency of metal salt additions on phytoavailability and bioavailability of metals added to soils. When metal salts are added to soil, or metal salts added to biosolids which are then mixed with soil, many errors can occur (e.g., Cunningham et al., 1975a; 1975b; 1975c). All of these errors increase plant uptake and bioavailability of added metals compared to field-contaminated soils. If pure metal salts are mixed with soil, it takes a considerable time for the added metals to reach a quasi-equilibrium with the soil (Singh and Jeng, 1993). And other constituents of a metal source (Fe and Mn oxides, phosphate, organic matter, etc.) are not applied when metal salts are used to model the risk of contaminated soils (Corey et al., 1987; Logan and Chaney, 1983; Chaney and Ryan, 1994). This has caused important confusion regarding Cd phytoavailability because Fe and Mn oxides present in biosolids can increase the selective or specific metal adsorption ability of the amended soil, but addition of metal salts cannot have this effect (Figure 1). Figure 1 shows models of the patterns of plant uptake of Cd and Zn in relation to soil Cd and Zn concentrations found in studies of long-term biosolids application compared to those for metal-salt treated soils. In Figure 1, all lines start at the linear slope usually found for added Cd-salts, and represent equal Cd additions in different forms, to one soil. Curve A represents the linear response to small additions of Cd salts found in nearly all studies in the literature. In curve B, the pattern is of increasing plant:soil slope at increasing Cd applications because Zn is also added,

Table 1. Pathways for risk assessment for potential transfer of biosolids-applied trace contaminants to humans, livestock, or the environment, and the Highly Exposed Individuals to be protected by a regulation based on the Pathway Analysis (US-EPA, 1989a, 1993; Chaney and Ryan, 1994). Each Pathway presumes 1000 t dry biosolids ha-1 and/or maximum allowed annual application of biosolids as N fertilizer.

Pathway	Highly Exposed Individuals
1. Biosolids6Soil6Plant6Human	Individuals with 2.5% of all food produced on amended soils.
2. Biosolids6Soil6Plant6Human	Home gardeners with 1000 t ha^{-1} ; 60% garden foods for lifetime.
3. Biosolids6Human	Ingested biosolids product; 200 mg d^{-1}.
4. Biosolids6Soil6Plant6Animal6Human	Farms; 1000 t/ha; 45% of “homegrown” meat.
5. Biosolids6Soil6Animal6Human	Farms; 1000 t/ha; 45% of “homegrown” meat.
6. Biosolids6Soil6Plant6Animal	Livestock feeds; 1000 t/ha; all from amended land.
7. Biosolids6Soil6Animal	Grazing Livestock; 1.5% biosolids in diet.
8. Biosolids6Soil6Plant	“Crops”; strongly acidic amended soil (1000 t/ha), but with limestone to prevent natural Al and Mn toxicity.
9. Biosolids6Soil6Soil Biota	Earthworms, microbes, in amended soil.
10. Biosolids6Soil6Soil Biota6Predator	Shrews (Sorex araneus L.); 33% earthworms diet, living on site.
11. Biosolids6Soil6Airborne Dust6Human	Tractor operator.
12. Biosolids6Soil6Surface Water6Human	Subsistence fishers.
13. Biosolids6Soil6Air6Human	Farm households.
14. Biosolids6Soil6Groundwater6Human	Well water on farms; 100% of supply.

at 100-times the Cd additions, and the added Zn competes for the stronger adsorption sites in the soil. These first two patterns have been repeatedly observed in many studies, and are illustrated well by the data in White and Chaney (1980). In contrast to patterns found when Cd salts are applied, model slope C in Figure 1 is for biosolid applied Cd, which causes decreasing slope toward a plateau with the X axis. This response is believed to result from the addition of adsorbent (Fe, Mn, Al oxides) for metals along with the metals when complex biosolids are applied to soils.

Effects of biosolids-applied Cd in the long term is the fundamental question which requires an answer. Does applied Cd remain plant available or become occluded in soils and have reduced availability? “Aging” reactions can reduce phytoavailability of applied Cd without occlusion. Several studies have shown substantial decline in Cd uptake by cereal crops after biosolids applications cease in an experiment with repeated applications (e.g., Chang et al., 1982; Bidwell and Dowdy, 1987). Such large reductions in plant Cd uptake after ceasing biosolids applications have seldom been observed for dicot crops; part of the effect is known to result from rapid biodegradation of organic matter added in the biosolids. In the studies in which cereals had much lower Cd concentrations after applications ceased, higher than N-fertilizer application rates were being applied in a research study. When applications are limited to regulated N-fertilizer supply for the crop to be grown, effects on uptake are seldom observed when high quality biosolids are utilized. Further, phytosiderophores secreted by roots of *Poaceae* species may play a role in the apparent difference between cereals and dicots in these responses.

We were able to examine the long-term effects of biosolids applications and salt-Cd additions to a soil in experiments at Beltsville. Evaluation of Cd uptake by lettuce grown on a soil amended with a Cd salt or Cd-rich biosolids in 1976 to 1979, showed that biosolids-applied Cd had low uptake slopes even when most of the organic carbon applied in the biosolid was biodegraded (Brown et al., 1998a). Even though soil pH declined over time due to application of N-fertilizers and normal acidic rainfall, uptake of Cd from the biosolids plots declined while uptake of Cd from the Cd-salt plots increased. While on plots where a high quality high Fe biosolid was applied, no increase in phytoavailability of Cd was observed.

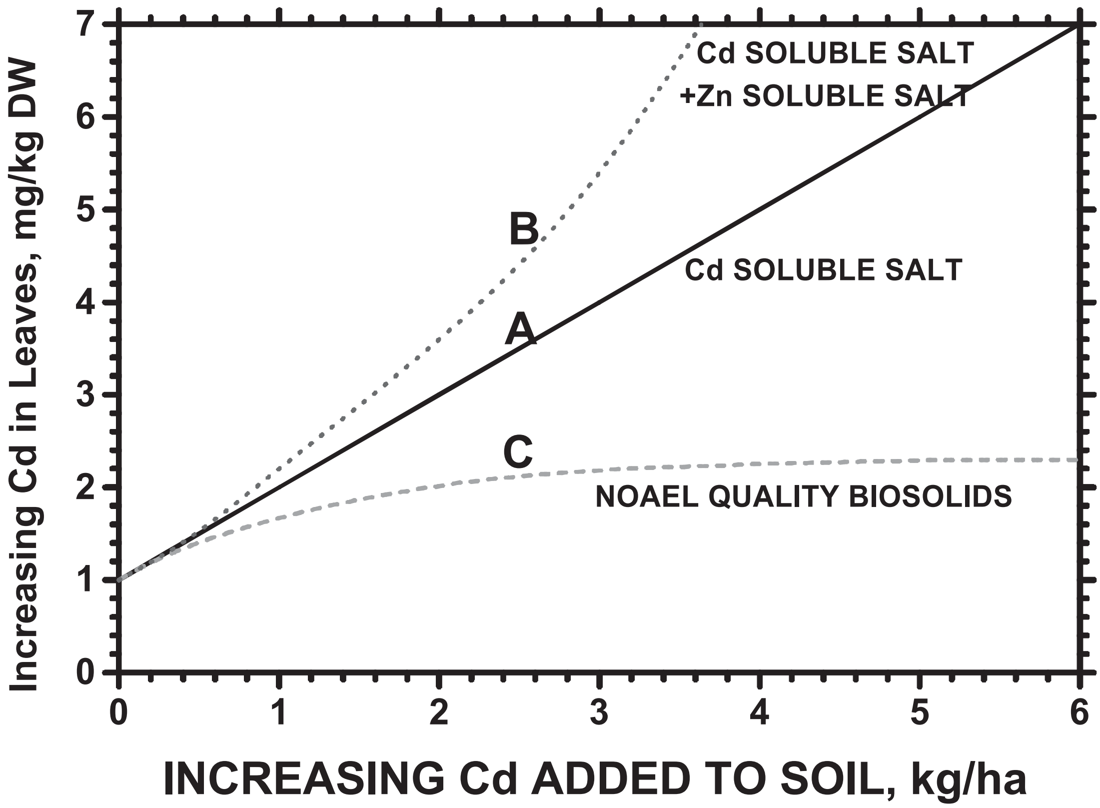

Figure 1. Hypothetical models of increasing plant Cd concentration in response to increasing total soil Cd concentration: A) From addition of a soluble Cd-salt; B) From addition of a soluble Cd-salt with 100 times more Zn as a soluble Zn-salt; and C) From addition of NOAEL quality biosolids, after organic matter stabilization to background levels.

In plots on a different soil series where high rates of high quality alkaline biosolids were applied in 1976, the high pH and low soil Mn supply allowed the alkaline biosolids to induce Mn deficiency by 1990 (Brown et al., 1997c). In this study, where the maintained calcareous pH aided sorption and occlusion of metals in the high Fe biosolids matrix, the Zn concentration in diagnostic leaves (of Mn fertilized treatments which regained crop yields) was barely adequate for plant growth. This effect, the continued control of metal phytoavailability even when added organic matter has been biodegraded, is now understood to result from the specific metal adsorption of biosolids-applied materials such as Fe and Mn oxides, and from the quasi-equilibrium reached in biosolids before application to the land. Research has repeatedly confirmed the existence of slow "aging" reactions of metals with soil surfaces and organic matter, and the increasing occlusion of metals in Fe and Mn oxides (e.g. Bruemmer et al., 1988; Corey et al., 1987). Further, study of laboratory prepared hydrous Fe oxide fails to observe the substantial increase in adsorption capacity and strength when phosphate is present along with the Fe, Zn, and Cd (Kuo, 1986). This aging response of added metals is more important for Ni and Zn than for Cd due to the selectivity of metal adsorption by soil Fe and Mn surfaces (Singh and Jeng, 1997).

Another clear evidence of biosolids-applied adsorbent was found in studies by Mahler et al. (1978) in which paired untreated and biosolids-amended soils were collected from long-term biosolids utilization farms at several locations. The researchers added 0, 5, and 10 mg Cd/kg to each soil to measure the slope of plant response to added salt-Cd as a bioassay on Cd phytoavailability, and made both soils calcareous so that simple difference in soil pH between untreated and treated soil did not confound the comparison. Figure 2 shows the results for two locations where appreciable amounts of biosolids and metals had been applied over time. The Cd uptake slope for freshly added salt-Cd by Cd accumulator crop Swiss chard on the biosolids-amended soils was lower than for the non-amended soils. In general, when unamended and biosolids-amended soils are compared at equal pH long after biosolids were applied, their ability to limit solubility and plant uptake of salt-Cd and salt-Zn applications are reduced compared to non-amended soils. In examining this sorption relationship in biosolids-remediated contaminated soils, Siebielec and Chaney (1999) reported that high Fe added with a biosolids-compost

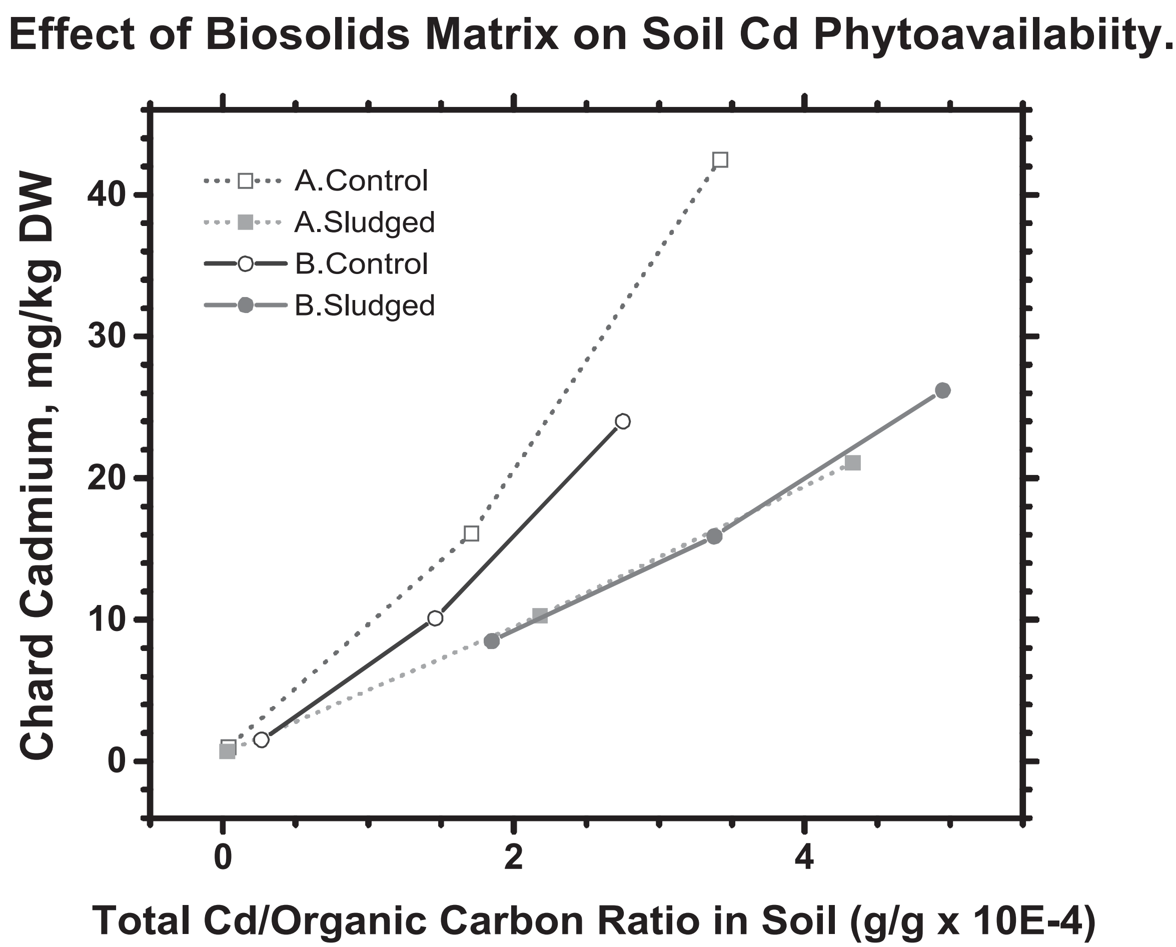

Figure 2. Linear response of chard Cd concentration to added salt-Cd on long term biosolids amended or non-amended soils. Carbon levels in the biosolid-amended soils are no longer above levels in the non-amended soils, and soil pH levels were made equivalent by making all soils calcareous (based on data from Mahler et al., 1987). Soil A was Morely, and B was Wea.

to a Zn-phytotoxic soil maintained amorphous Fe oxides at increased levels in the soil, and reduced Cd and Zn in soil solution type extractions with 0.01 M Sr(NO

One of the most insidious errors of using metal salts is the displacement of adsorbed protons from soil cation binding sites when metals are added, which lowers the pH of the amended soil; the higher the metal application, the greater the reduction in soil pH (White et al., 1978). Thus the researcher sees greater harm at higher metal concentration, the expected result, but fails to recognize that the study was confounded by pH lowering proportional to metal salt application.

Another serious error in study of biosolids Cd risk is addition of chloride in one metal salt being tested, which can substantially increase the plant uptake of Cd due to formation of chloride complexes which increase mobility of Cd in soils, and allow a complexed form of Cd to leak into roots (McLaughlin et al., 1994). Low soil pH promotes metal solubility and phytoavailability such that pH is a almost always more important factor in metal uptake and phytotoxicity than is the amount of metals added. But high chloride can overwhelm the effect of limestone in reducing phytoavailability of soil Cd (e.g., Li et al., 1997).

Another source of error in risk assessment for soil metals is the greenhouse vs. field error illustrated by the work of deVries and Tiller (1978). These researchers compared uptake of metals by lettuce and onion grown on soil-biosolids mixtures at several rates of application, when the plants were grown 1) in large pots in a greenhouse, 2) in outdoor lysimeters in which the biosolids were incorporated 10 cm deep, and 3) in growers fields in which the biosolids were incorporated 10 cm deep. As has been long known, if plants are grown in pots of contaminated soil, phytotoxicity and uptake are higher than if grown in the same soil in the field where the metal rich soil is present only in the surface soil layer. In pots, the roots cannot escape to subsurface less contaminated soils. Further, some aspect of greenhouse culture which appears related to water use or salt concentrations in the soil solution promote metal solubility and uptake by plants. The full requirement of fertilizer nutrients are usually applied to pots before starting the plants, promoting high ionic strength and hence solubility of soil metals, worse with smaller than larger pots. Other errors result from the temperature of soil in pots in a greenhouse compared to soils in the field, and water transpiration in greenhouse compared to field.

In a similar way, when the bioavailability of metals in ingested soil is measured by soil feeding studies, Pb absorption by rats declined when Pb was mixed with soil (Chaney et al., 1984; Chaney and Ryan, 1994). Similar effects of soil sorption of metals reducing bioavailability to mammals has been shown for As (Freeman et al., 1995) and Cd (Schilderman et al., 1997), and is evident in biosolids feeding tests (e.g., Decker et al., 1980). Considering the role of adsorption at the neutral pH of the small intestine where most microelement cations are absorbed by animals, it should not be a surprise that adsorption of metals on dietary soil can reduce Pb and other element uptake by animals in a manner somewhat like the reduction in absorption by plants (see Freeman et al., 1992; Chaney and Ryan, 1994).

Looking at mine wastes and smelter contamination processes in relation to these selective soil adsorption processes, what are the implications for risk assessment and soil remediation? If high Fe in biosolids can sorb metals persistently, biosolids metals can have low phytoavailability and bioavailability compared to metal salts. But smelter-emission contaminated soils will have received only the more volatile elements emitted by a smelter stack. Even here, Zn which accompanies emitted Cd can provide a persistent reduction in potential plant uptake of Cd by competition at root uptake sites, and also reduce translocation to plant shoots and storage tissues (e.g., McKenna et al., 1992b; Chaney et al., 1999a). Mine wastes may have very high Fe levels from pyrite in the ore, so Fe would accompany the metals. But if ore sulfides are allowed to oxidize, soil pH is lowered severely which greatly increases metal toxicity risk. We have measured pH of surface soil in farmer's fields which had become covered by alluvial deposits of mine waste where sulfide oxidation lowered pH to < 3. In such a case (often found in Zn-Pb ores from the Rocky Mountain area such as Butte, MT and Leadville, CO), the extreme acidity is the key feature of the contaminated site. Until this extreme acidity is neutralized, solubility of Zn will prevent plant survival.

Another important principle of soil metal risk assessment is the "Soil-Plant Barrier" to element transfer to cause food-chain risk to animals. Chaney (1980; 1983) summarized three major processes which limit risks from most elements in soils to animals through the food-chain Pathway. First, precipitation or adsorption of metals by soil particles, or in the fibrous root system hinders uptake of most elements (Pb, Cr, Sn, Ti, Fe, Hg, Ag, F, etc.). Second, phytotoxicity of the common phytotoxic elements (Zn, Cu, Ni, Mn, etc.) occurs at concentration of these elements in the plant shoots which do not comprise risk to livestock or humans chronically exposed to the metals. The third process involves interactions between elements which hinder uptake, translocation or bioavailability of soil metals. For example, Zn is normally present at 50-200 times higher concentration than Cd in Zn-Pb ores. And Zn metal products are treated to remove most Cd for separate marketing and to protect the quality of the Zn in certain industrial applications. When galvanized metal corrodes, Zn is very high and Cd low such that plant Cd is hardly increased when Zn reaches severely phytotoxic concentrations (Jones, 1983). Because Zn and Cd are commonly absorbed and translocated at about the ratio found in the soil the plant is growing on, and because Zn phytotoxicity occurs at about 400-600 mg Zn/kg dry plant shoots, co-contaminating Zn normally limits shoot Cd to less than 5-10 mg Cd/kg dry weight. Coupled with Zn inhibition of Cd absorption by animals, soil Cd risk is alleviated (see below) because Zn phytotoxicity alerts the gardener to the problem.

The Soil-Plant Barrier fails to provide complete protection for only a few elements, Se and Mo which are widely known to poison ruminant livestock, and Cd under circumstances which separate Cd from Zn (Table 2). The Soil-Plant Barrier for Co could also theoretically fail because ruminant livestock cannot tolerate the concentrations of Co (injury to ruminant livestock begins at approximately 10 mg Co/kg dry forage) which can be reached in plants when Co is phytotoxic (25 mg/kg or higher in plant shoots). Cd risks to humans is discussed below. Se is not only a risk to livestock, but can harm humans who consume only foods locally grown on contaminated soils (Yang et al., 1984).

Another case where livestock and wildlife can be harmed by metals is the case in which high emissions of Zn or other elements from a smelter cause extensive contamination on the surface of plants by deposition from the aerosol source. In this case, plants can reach much higher concentrations without phytotoxicity than possible by root uptake if the metals were in the soil. For elements which have low uptake slopes, or for which phytotoxicity protects the food-chain (e.g. Zn, Cu, Pb, As, F, Fe), deposition can cause plant metals to reach levels which can poison sensitive livestock (e.g., Chaney et al., 1988). Zn on forages has killed young horses (foals) at many Zn smelter locations because apparently healthy plants can contain over 1000 mg Zn/kg, but if the Zn had been absorbed by roots, visible signs of Zn phytotoxicity would have occurred by 500 mg Zn/kg shoots. Different livestock are sensitive to different metals, for example ruminants are sensitive to induced Cu deficiency and Pb, As and F toxicity, while young horses are especially sensitive to excessive ingested Zn.

Another aspect of soil metal risk has received much attention in recent years, the potential for soil metals to harm soil organisms. However, our experience has indicated that metal-sensitive plants such as lettuce

Table 2. Maximum tolerable levels of dietary minerals for domestic livestock in comparison with levels in forages.							
Element	"Soil-Plant Barrier"	Level in Plant Foliage[A]		Maximum Levels Chronically Tolerated[B]			
		Normal	Phytotoxic	Cattle	Sheep	Swine	Chicken
		mg/kg dry foliage		mg/kg dry diet			
As, inorg.	yes	0.01-1	3-10	50.	50.	50.	50.
B	yes	7-75	75	150.	(150.)	(150.)	(150.)
Cd[C]	Fails	0.1-1	5-700	0.5	0.5	0.5	0.5
Cr^{3+}	yes	0.1-1	20	(3000.)	(3000.)	(3000.)	3000.
Co	Fail?	0.01-0.3	25-100	10.	10.	10.	10.
Cu	yes	3-20	25-40	100.	25.	250.	300.
F	yes?	1-5	-	40.	60.	150.	200.
Fe	yes	30-300	-	1000.	500.	3000.	1000.
Mn	?	15-150	400-2000	1000.	1000.	400.	2000.
Mo	Fails	0.1-3.0	100	10.	10.	20.	100.
Ni	yes	0.1-5	50-100	50.	(50.)	(100.)	(300.)
Pb[C]	yes	2-5	-	30.	30.	30.	30.
Se	Fails	0.1-2	100	(2.)	(2.)	2.	2.
V	yes?	0.1-1	10	50.	50.	(10.)	10.
Zn	yes	15-150	500-1500	500.	300.	1000.	1000.

[A]Based on literature summarized in Chaney (1983).

[B]Based on NRC (1980). Continuous long-term feeding of minerals at the maximum tolerable levels may cause adverse effects. Levels in parentheses were estimated (by NRC) by extrapolating between animal species.

[C]Maximum levels tolerated were based on Cd or Pb in liver, kidney, and bone in foods for humans rather than simple tolerance by the animals.

and white clover are visibly harmed at soil metal concentrations below those required to harm soil microbes or earthworms, etc. (Chaney, 1993; Ibekwe et al., 1998). Further, the errors from adding metal salts are potentially much more important for soil organisms than for plants because the organisms are present at the moment when soluble metals are mixed with the soil. And many ecotoxicology studies use artificial soils with addition of metal salts, and cause much more severe toxicity to earthworms and soil microbes than found with biosolids or stack emissions cause soil contamination with Pb, Zn, and Cd (e.g., Spurgeon and Hopkins, 1996). Concerns about harm to the rhizobium for white clover from biosolids-applied Zn have been clarified by comparisons of the toxicity of Zn and Cd to the rhizobium, compared to toxicity to the plants (Ibekwe et al., 1996; 1997a; 1997b; 1998; Angle and Chaney, 1995; Angle et al., 1993). If nodules are formed before testing metal toxicity, Zn and Cd had no effect on N fixation before yield of the plant had been sharply reduced by metal phytotoxicity. And testing of microbial metal tolerance with controlled chemical activity of Zn and Cd showed that the microbes were much more tolerant of these elements than were plants. The most sensitive step appears to be the rhizobium infection of root hair process rather than survival of the microbes in soil. Even arguments about microbial genetic diversity in relation to soil metal enrichment appear to result from study of highly contaminated biosolids, or unusual soils, since Ibekwe et al. (1997b) found that low soil pH reduced survival of white clover rhizobium on both control and metal rich soils, and the rhizobium survived with good diversity when soil pH was maintained at levels needed to produce legumes. We have observed nodulated white and red clover growing on soils with very high levels of Zn (> 3000) if pH is maintained and phosphate is supplied at levels required for legume production (see below discussion of ecosystem restoration)

Soil Cd Risk Assessment

Although great concern has been expressed about Cd poisoning of humans from smelter emissions and mine wastes, research has now clarified the situations where such Cd food-chain poisoning may occur. Cd is important regarding chronic toxicity — acute toxicity is prevented by regulations to limit chronic toxicity of Cd emissions and discharges. In mammals, Cd accumulates over one's lifetime in the proximal tubules of the kidney cortex; if a toxic concentration is reached, a renal proximal tubular dysfunction will occur (this is not "kidney failure" as this term is commonly used). Ordinarily, kidney Cd accumulates in humans until about age 50, and then starts to decline over time. If one has ingested insufficient bioavailable Cd over that 50 years, no disease results. Smoking cigarettes commonly doubles kidney cortex Cd for persons who smoke one pack per day, compared to non-smokers, because Cd enters the mainstream smoke and is well absorbed in the lung (e.g., Elinder et al., 1976). Average non-smokers today have only 10-15 mg Cd/kg fresh weight of kidney cortex, far lower than the 200 mg/kg fresh weight required for the tubular dysfunction of sensitive individuals in the population.

Because soil Cd (from dispersed mine and smelter wastes) caused human disease in Japan and China (Kobayashi, 1978; Tsuchiya et al., 1978; Cai et al., 1990), and aerosol Cd in the workplace has harmed industrial workers at many factories which used pure Cd salts such as Cd-Ni battery manufacturing, much research has been conducted to improve our understanding of Cd risk to humans. In the case of soil Cd, agronomy is very important is understanding the risk to humans, not just toxicology and medicine (Chaney et al., 1999a). Although soil Cd caused human Cd disease in subsistence rice farmers, much higher soil Cd had no adverse effects on persons exposed to Zn+Cd rich soil and dust, garden foods or western grains (Shipham, UK — Strehlow and Barltrop, 1988; Stolberg, Germany — Ewers et al., 1993; Palmerton, PA, USA — Sarasua et al., 1995). Because of the chemistry of flooded soils, ZnS is formed and persists for some time after a flooded rice soil is drained, but CdS is quickly transformed to more phytoavailable forms, and pH drops making the soil Cd more phytoavailable. Rice growers drain their fields at the start of flowering to optimize yield of grain. Cd absorbed by rice during grain filling is readily translocated to grain while Zn is not increased in grain even though the soil had 100 times more Zn than Cd, similar to western soil contamination cases (e.g., Takijima and Katsumi, 1973). Further, polished rice grain contains insufficient Fe, Zn and Ca to supply the amounts needed for humans (Chaney et al., 1999a). Subsistence rice farm families are commonly Fe and Zn deficient if they do not obtain adequate Fe and Zn from other dietary sources. And deficiency in Fe, Zn, and Ca promote Cd absorption in the human intestine (Fox, 1988; Fox et al., 1984), promoting risk from Cd in rice grain. One of the first experimental findings which illustrated that rice Cd risk was qualitatively different from other foods was a study of New Zealand oyster fisherpersons who consumed up to 500 μg Cd/day in high Cd oysters, but had no evidence of renal tubular dysfunction from these high levels of Cd, as high as the Japanese rice consumers who had a high incidence of renal tubular dysfunction (Sharma et al. 1983) Further examination of these oyster consumers revealed that their kidney Cd was hardly increased by oyster-Cd, but responded strongly to smoking (Sharma et al., 1983; McKenzie-Parnell and Eynon, 1987; McKenzie-Parnell et al., 1988). Many other errors have resulted when toxicologists tried to predict Cd risk on the basis of injected Cd, or adding Cd salts to purified diets. And in interpretation of diagnostic information of secretion on low molecular weight proteins in urine by normal humans compared to persons which suffer frank tubular disease from dietary Cd (see Chaney et al., 1999a).

Wheat and vegetables have been found to have very different soil-plant-animal relationships for Cd and Zn compared to rice. These crops are grown in aerobic soils where both Cd and Zn are plant available during growth, and Zn inhibits both uptake of Cd from soil, and transport of root Cd to edible tissues of the plant. And Zn is translocated to all plant tissues where Cd accumulates so it is simultaneously present with Cd in any foods and in the intestine (Table 3) (see also McKenna et al., 1992a). Although corn is also a poor source of bioavailable Fe, when western crops are grown in soils enriched in both Zn and Cd, corn grain has increased Zn levels somewhat proportional to the increased Cd, and the Zn in the such corn grain satisfies the human Zn requirement and inhibits absorption of Cd in the intestine much more effectively than found for rice grown on such contaminated soils.

It is difficult to overstate the importance of Zn in a crop in inhibiting animal absorption of Cd from that crop. Table 3 shows the accumulation of Cd and Zn by Swiss chard (*Beta vulgaris* L. var. *cicla*) grown on soil treated with normal chemical fertilizers vs. different biosolids products used as fertilizer. For one of the biosolids, chard leaf Cd was increased by 5-fold in the strongly acidic soil, but Zn had a corresponding increase. Guinea pigs were fed the chard at a high fraction of diet for a long period, yet there was no significant increase in Cd in kidney or liver. In this situation, although the soil contains significantly increased levels of Cd, it has zero bioavailability to the guinea pigs.

When livestock are fed crops grown on Zn+Cd-contaminated soils, Cd is very poorly absorbed by cows, sheep, pigs and chickens. The usual 100 Zn:1 Cd ratio prevents accumulation of Cd in animal tissues used for food, and strongly limits accumulation in kidney and liver. For example, in the feeding study of Kienholz et al. (1979) in which 3 or 10% biosolids were mixed with cattle diets and fed for 90 days, the fraction of ingested Cd which remained in the carcass including liver and kidney was < 0.1%. Thus animal agriculture usually prevents Cd risk in humans who consume "homegrown" meat. When high quality biosolids with low Cd:Zn ratio are used on land, no increase was found in kidney or liver Cd (Decker et al., 1980). When biosolids with high Cd levels and high Cd:Zn ratios were fed to cattle, kidney and liver Cd levels were significantly increased (e.g., Johnson et al., 1981). A rare exception to this rule that Zn prevents food-chain transfer of Cd is found in Australia and New Zealand where "cape weed" selectively accumulates Cd relative to Zn on pasture soils. The soils had become somewhat Cd enriched due to use of high Cd (and high Cd:Zn ratio) phosphate-fertilizers. Capeweed could thus increase Cd transfer to sheep liver and kidney, which prevents sale of these organs in Europe for animals over 2 years of age (it is likely that even this Cd does not comprise risk because of Zn supplied in liver and kidney along with Cd; market rejection of such liver and kidney is based on Cd concentration alone, ignoring interactions which affect bioavailability of food Cd).

Soil Lead Risk From Ingested Soils.

Study of soil contamination by automotive and industrial Pb emissions clearly showed that aerosol Pb accumulated in plant leaves when air Pb was high in previous years. But high soil Pb concentrations increase Pb levels in most crops weakly. As other sources of Pb to soils were considered, an important role of house paint Pb in contaminating soils near painted walls became evident (see Chaney et al., 1984; Chaney and Ryan, 1994). We have measured up to 5% Pb in houseside soil in a remote rural home. Because of these multiple soil Pb contamination sources, a number of scientists studied uptake of Pb by garden crops which a family might grow in a home vegetable garden. A few crop types do respond to increasing soil Pb with appreciable uptake, particularly the low growing leafy vegetables such as lettuce. Potatoes and other root vegetables which can carry soil particles on their "skins" can bring higher Pb from contaminated gardens.

However, as Pb risk to children was increasingly recognized, and found to occur at lower blood Pb concentrations than previously considered toxic (Centers for Disease Control, 1985), the ingestion of soil and housedust by young children became recognized as the predominant route of soil Pb risk to children rather than plant uptake from contaminated soils. Pb risk is complex, and children become Pb poisoned from drinking water pipes with acidic water, from Pb-rich glazes on pottery, from ingestion of paint chips, from Pb in the solder which closed food cans for many decades, etc. Each of these sources can cause "undue Pb absorption" in 1-7-year-old children such that over 5% of the population exceeds 10 Fg Pb/dL whole blood. Above this level, sensitive children begin to show evidence of some Pb health effects on hearing and balance, and as Pb rises more and more above this level, populations of children show lower IQ levels (ATSDR, 1988). If housedust is enriched to high levels of Pb from paint or smelter sources, high blood Pb is commonly found, while mine wastes which cause equivalent increase in Pb ingestion cause little increase in blood Pb (e.g., Steele et al., 1990). Thus the source of Pb contamination of soil may influence the risk of this Pb. Many researchers believe this results because different sources of Pb have either different solubility or bioavailability, or physical mobility to children. One source of confusion about risk from soil Pb results from the use of fasted animals in study of Pb risk. When Pb-acetate is administered to fasted animals, it remains essentially 100% soluble and bioavailable upon ingestion. But when food in present in the stomach and intestine, humans absorb as low as 1% of diet Pb compared to 60-80% absorbed when human adults are tested in the fasted condition (e.g, James et al., 1987). Soil acts somewhat like food by buffering pH and binding Pb. Thus the risk from soil Pb may be qualitatively different from Pb in paint dust or smelter emissions where little adsorbent accompanies the Pb (see Chaney and Ryan, 1994).

High soil Pb is found at many locations in most countries. As noted above, housepaint is a very common source of high soil Pb. And leaded gasoline caused high soil Pb near heavily trafficked roads. Pb smelters, including secondary Pb smelters such as battery recycling factories, cause extensive dispersal of highly bioavailable PbO in communities if housing is near to smelter stacks. Mine wastes have often increased soil Pb, but have lower bioavailability as shown in many tests.

The first approach to protection of children from excessive soil Pb was soil removal and replacement by clean soil. For urban homes, soil removal and replacement is quite expensive. And studies have shown that in most cases soil Pb concentration is much higher near the foundation of domiciles. Paint residues fall onto the soil. And automotive and stack emission Pb in particulates are collected on the surfaces of houses by surface tension, and then washed onto the soil. Over time these Pb sources are altered to forms controlled by soil chemistry, adsorbed Pb on Fe oxides, or pyromorphite (e.g., Cotter-Howells and Thornton, 1991; Zhang, Ryan and Yang, 1998).

An important aspect of soil Pb risk was identified during a large US-EPA study evaluating removal and replacement of Pb-contaminated soil around houses. In these studies, part of the children were assigned to soil replacement immediately after characterization of population blood Pb, while other children were assigned to have their soil replacement one year later, after characterization of blood Pb in the two populations one year after the initial measurements (about 9-10 months after soil replacement). In the Boston, MA, study, the soils replaced averaged about 1950 mg Pb/kg, but blood Pb was only slightly (but significantly) reduced due to the independent effect of soil removal and replacement (Weitzman et al., 1993). Many other studies of children exposed to soil and housepaint Pb have affirmed that soil Pb has lower risk than paint Pb, which we believe

Table 3. Bioavailability of Cd in biosolids-fertilized Swiss chard fed at 28% of diet to Guinea pigs for 80 days (Chaney et al., 1978b).							
Treatment	Biosolid Rate	Soil Cd	Soil pH	Cd in Chard	Zn in Chard	Cd in Kidney	Cd in Liver
	t/ha	µg/g		µg/g dry weight			
Control	0	0.04	6.0	0.5	70	14.9 a	3.1 a‡
High Metal Biosolids	56	0.32	5.7	1.5	950	14.5 a	2.7 a
Blue Plains Digested	112	0.94	5.5	2.7	580	14.5 a	2.7 a
Blue Plains Compost	224	0.89	6.6	1.4	257	15.8 a	3.6 a

‡Means followed by different letters are significantly different at P < 0.05).

should at least partially be attributed to the adsorption of Pb by soil particles in the digestive tract. Pb in house paint is the principle Pb risk to children today, not the Pb in contaminated soils.

Guidance for Beneficial Utilization of Biosolids and Biosolids Composts.

With the development of the 40 CFR 503 Rule for land application of biosolids, a risk-based estimation of allowable cumulative biosolids element applications was provided (US-EPA, 1993; Chaney and Ryan, 1993; Ryan and Chaney, 1993). This rule included the “Alternative Pollutant Limit” (APL) which allowed marketing of higher quality products. This reflects the increasing evidence that regulation of biosolids quality would provide more protection than regulation only of the cumulative application of elements in biosolids. This pattern results from the adsorption or precipitation of these elements by the mineral constituents of the biosolid, as discussed above.

Table 4 shows the limits of the 503 Rule, the USDA “No Observed Adverse Effect Level” (NOAEL) biosolids limits, and concentrations we consider “attainable” by good pretreatment of industrial wastes, and reduction of corrosivity of drinking water. Because these lower levels of trace elements can commonly be attained by good practices, some want to require that all biosolids and composts be regulated at the lower “attainable” levels. We find this argument un-persuasive. The APL and cumulative metal application limits of the 503 Rule are protective under the very conservative risk assessment model, 1000 t/ha, for highly exposed individual with lifetime exposure at this cumulative application rate. On the other hand, we feel it appropriate to advise biosolids generators and composters that lower concentrations of these elements can be readily attained if they work at it. Higher quality products will create higher demand in the market, and bring in higher economic return for the marketed products. We view this as best practice, but not needed to achieve the protections expected by citizens which are the basis of the 503 Rule.

In the case of “yard debris” or “green wastes” composts, lower element levels can be attained than found in biosolids and biosolids composts. And composts prepared from pre-separated Municipal Solid Waste (MSW) can contain lower concentrations than found in biosolids composts (Epstein, et al., 1992). Pre-composting separation of glass, metal and plastic from other MSW constituents minimizes concentrations of elements in the compost products, but there is little evidence that this difference is so great that only pre-separation should be allowed for MSW composting. Pre-separation of MSW compostable fraction is most important for removal of glass, plastic, and metal particles which reduce acceptability to consumers.

Further, without inclusion of biosolids or manures in yard debris or MSW-composts, they are poor nutrient sources, and have little value as fertilizers or in remediation of contaminated soils. Although some individuals may believe it important to impose tight regulations on contaminants in these different kinds of composts, to require each to be as clean as possible, risk assessment should continue to be the basis of regulations (as recommended by Hornick et al., 1983). Labeling of composition, including nutrient value and trace element levels in relation to the US-EPA limits, will provide consumers the basis for choice of soil amendments. Composting or heat drying can provide the pathogen kill needed for biosolids and livestock manure, and yard debris composts, to be safely used on lawns and gardens where humans will have exposure. Perspective on risk of elements in these many compost type consumer products is needed when considering development of restrictive regulations. If the Cd and Pb in high quality biosolids composts and MSW compost products cause no increase in human or environmental risk, similar to other commercial organic amendments including yard debris composts, there is no legitimate basis for claiming such products have different Cd or Pb risk. The high Fe and phosphate of high quality

Table 4. Limits of the 40 CFR 503 biosolids Regulation (EPA, 1993) vs USDA recommended biosolid quality for long-term use on farmland, and attainable quality biosolids and composts. Deletion of Cr limits from the 503 Rule is discussed by Chaney, Ryan and Brown (1997).

Element	Ceiling 99th	Cumulative =APL, mg/kg	NOAEL (1993)	Percentile of NOAEL(1993)	Attainable Quality
	mg/kg	kg/ha	mg/kg		mg/kg
As	75	41	54	98	<25
Cd	85	39	21	91	<5-10
Cd/Zn	-	-	1.5	87	<1.0
Pb	840	300	300	90	<100
Hg	57	17	17	93	<5
Mo	75	35	54	98	<50
Se	100	36	28	98	<15
Cr	3000	1300	-	-	-
Cu	4300	1500	1500	89	<500-750
Ni	420	420	290	98	<100
Zn	7500	2800	2800	91	<1500-2000
PCBs	-	-	8.1	99	<0.5

biosolids products can provide a solution for soil Pb environmental risks as noted above, not add to Pb risk of children.

In situ Remediation or Inactivation of Soil Pb.

An alternative to soil replacement to reduce soil Pb risk to children has been developed, the use of soil amendments to precipitate soil Pb, or otherwise reduce the bioavailability of soil Pb based on animal feeding tests. These strategies are complementary, in that high phosphate can hasten formation of chloro-pyromorphite [$Pb_5(PO_4)_3Cl$] an extremely insoluble Pb mineral, and mixtures of Fe and phosphate can increase the Pb-adsorption capacity of a soil, to reduce bioavailability in the intestine by stronger binding to ingested soil particles. Some very elegant work by Ma, Ryan, Logan, and cooperators (Ma et al., 1993; Zhang et al., 1997; 1998; 1999a; 1999b) showed that pyromorphite can be formed from all chemical species of Pb found in soils, and that different Pb chemical species react at different rates. Both Pb and phosphate have limited solubility at normal soil pH, which tends to slow the reaction. But when phosphate amended soil enters the acidic stomach, the pH condition favors rapid formation of pyromorphite.

The use of biosolids to reduce soil Pb bioavailability was developed based on studies of Pb absorption by livestock which were exposed to, or fed, biosolids with different levels of Pb (e.g., Decker et al., 1980), and on the reduction in Pb uptake by lettuce when soils were amended with composted biosolids (Sterrett et al., 1996). These feeding studies were conducted to evaluate risks to livestock and wildlife of Pb in biosolids. As summarized by Chaney and Ryan (1994), until biosolids exceed 300 mg Pb/kg, there was no net retention of Pb by test animals. For some biosolids with stronger Pb adsorption ability, even higher Pb concentration in the biosolid, fed at 3-10% of dry diet, had no effect on blood or bone Pb. Both mechanisms could be at play in this case because biosolids are rich in P, and when Fe is added during wastewater treatment to improved phosphate removal, the biosolid has even higher P levels along with high Fe (up to 10% compared to typical levels of 1-2% Fe in dry digested biosolids in the absence of Fe additions during sewage processing). In a comparison of different biosolids processing technologies effect on the ability of the biosolids products to inactivate soil Pb, Brown et al. (1997b) found that all products from one treatment works could reduce Pb bioavailability, but those higher in Fe and phosphate were most effective. Any products to be used where children might be exposed to the soil must be treated to kill pathogens; and high rates of application are desired to achieve a high reduction in bioavailability with a single treatment. So composted biosolids rich in Fe are favored for remediation of soil Pb around houses. Such composted materials are also very effective in alleviating soil compaction, and Zn phytotoxicity in acidic urban soils, and improve soil physical properties and soil fertility. Thus lawn grasses usually grow very well on compost-amended urban soils, providing a physical barrier to soil ingestion by children.

Because application of composted biosolids rich in Fe and P substantially reduced Pb uptake by lettuce and other plants (Sterrett et al., 1996), and the Pb in biosolids had very low bioavailability when ingested by beef cattle (Decker et al., 1980), we tested the incorporation of different biosolids products to reduce the bioavailability of soil Pb to mammals (see Chaney and Ryan, 1994; Brown et al., 1997b). To date our cooperators have conducted 3 separate studies in which soil Pb bioavailability was reduced 50% or more (within 30 days of mixing) by incorporation of 10% biosolids in a high Pb urban soil, or smelter contaminated soil.

Remediation and Ecosystem Restoration using Tailor-Made Biosolids Mixtures and Composts.

With the finding that adding high Fe and phosphate to soils reduced Pb uptake by crops, and reduced soil Pb bioavailability to animals which ingested the soil, we considered using such biosolids plus other byproducts or "wastes" to achieve a comprehensive remediation of the usually barren soils surrounding long term Zn or Pb smelters. Such soils often contain 1% Zn, 100 mg Cd/kg, and 100-30,000 mg Pb/kg (e.g., Chaney et al., 1988; Brown et al., 1998). Smelters often emitted SO_2 in large amounts, which caused local soil acidification near the smelter as sulfuric acid was formed. In the case of mine wastes, if the mine tailings contain high levels of pyrite (FeS), when the tailings become aerobic the sulfide was oxidized generating sulfuric acid. Soil pH could be lowered below 2, causing severe phytotoxicity from many metals (Zn, Cd, Al, Mn). And when tailings or smelter emissions are rich in Pb, part of the soil Pb is converted to pyromorphite, greatly reducing the plant availability of native soil phosphate. Even if these soils are limed to pH 5.5-6, if high Zn levels are present the soil can remain severely Zn-phytotoxic. Low P availability due to the presence of Pb interacts adversely with high soil Zn because high Zn shortens roots thereby reducing P uptake ability of roots. The combination of soil acidity, high soil Zn, high soil Pb and low soil phosphate make a very difficult soil condition to remediate. One can revegetate such soils only if one remediates the P deficiency, the Zn phytotoxicity, and the potential for acid generation over time.

Considering this combination, we initially tested use of high Fe, calcareous, biosolids compost from Washington, DC, to remediate the severely Zn phytotoxic soil at Palmerton, PA (Li and Chaney, 1997; Li et al., 2000). Accumulated soil Zn made survival of Kentucky bluegrass difficult, and many homes were surrounded by barren soils; homeowners even gave up on trying to grow grasses and covered their soil with mulch. In tests we conducted, the application of limestone to reach pH 6.5 or higher, along with normal application of N, P, and K fertilizers to establish lawns, allowed grasses to germinate and start to grow. But when the plants were stressed by cold, heat, or drought, the lawn grasses died. We found that the highly Zn-resistant 'Merlin' red fescue performed well with this intermediate pH and phosphate levels, but tall fescue and bluegrass simply died on the control fertilized soil, or the limestone plus fertilizer treatment (Li et al., 2000). With the application of 224 t/ha of composted high Fe biosolids which contained 30% limestone equivalent, the soil immediately became calcareous (and had lots of pH buffering capacity), and high phosphate status (Li et al., 2000). Further investigation of these soils by Siebielec and Chaney (1999) revealed that the higher Fe in the biosolids-compost-amended soil increased metal adsorption, lowering soil solution Zn and Cd concentrations better than limestone addition alone. This same compost was highly effective in reducing soil Pb bioavailability to rats in several feeding studies (see Chaney and Ryan, 1994; Brown et al., 1997b).

Not all biosolids contain high limestone equivalent, or high Fe levels. But there are many industrial, urban, and agricultural byproducts which can provide the Fe and limestone equivalent to make a remediation product. Composts have a special value for application in cities where children would be exposed to the amended soil because composting kills pathogens in biosolids. Composts are also preferred when contaminated stream side soils are to be remediated. Chaney, Walker, Brown, et al. noted that one could combine different manures and byproducts to make a mixture which aided remediation of metal contaminated soils. The mixture needs to contain limestone equivalent, phosphate, adsorbent, and slow release organic N, as well as microbes in order to achieve effective remediation of soil Pb, Zn, and Cd. This approach has been called "Tailor-Made Remediation Biosolids Mixtures and Composts" to stress that if one searches one's region, one can find different wastes or byproducts which have little value for commercial use or are disposed in landfills at substantial cost, but which when combined and applied to metal contaminated soils, can inactivate soil Pb, prevent Zn phytotoxicity, improve soil fertility and physical properties, and supply energy, nutrients and inoculum for soil microbial populations. Limestone equivalent can come from wood ash, from lime wastes, from sugar beet waste lime, from fly ash and other alkaline byproducts if the levels of other contaminants in the byproduct would not prevent use of these materials on cropland. These materials usually contain levels of Zn, Cd, As, and some other elements higher than found in background soils, but not at levels which would cause risk through plant uptake on home gardens, or through soil ingestion.

Using such mixtures has been shown to provide a "one-shot" persistent remediation and revegetation of metal contaminated sites such as Palmerton, PA (Li and Chaney, 1998), Katowice, Poland (Stuczynski et al., 1997; Daniels et al., 1998), and Kellogg, ID (Brown et al., 1999), where mine wastes and smelter emissions killed ecosystems. Plants growing on the remediated sites contain levels of Zn and other elements which are safe for lifetime consumption by livestock or wildlife. Further, in the work to establish a demonstration experiment at Kellogg, ID, Henry, Brown et al. (1998b) found that certain biosolids spreading equipment was highly effective in applying a mixture of biosolids, wood ash, and logyard debris to strongly sloping barren soils on Bunker Hill. Non-composted mixtures are considered appropriate for such remediation because composting provides a value-added product which needs to cost more than a simple mixture of biosolids plus byproducts. Compost would be preferred to control N-mineralization so that higher cumulative rates of application can be made to improve the likelihood of full remediation of the contaminated soil, although including cellulosic byproducts in the Tailor-Made mixture can limit soil nitrate leaching potential.

Individuals need to show considerable creativity in searching for byproducts from many sources, near to the site where remediation would be conducted, to find a cost-effective combination of remediation agents and fertilizers, control the rate of N mineralization to protect groundwater and preserve the remediation, and support the growth of plants adapted to the region. When revegetation is desired "out of normal season" for planting a site, one can use large-seeded cereals, and then overseed with more expensive but more tender native grasses, legumes, etc.

Another aspect of the combination of limestone equivalent with biodegradable organic matter in the Tailor-Made Remediation Mixture is the formation of chemical forms of Ca and Mg which move down the soil profile and neutralize subsurface acidity. This effect was reported by several researchers, and confirmed for four kinds of biosolids or composts in a long term field study by Brown et al. (1997a). The less well aerobically stabilized the organic matter of the product, the more extensive was the leaching of limestone equivalent down the soil profile. In the absence of this benefit of biodegrading organic matter, surface-applied limestone slowly neutralizes soil depth by diffusion of Ca and Mg between soil particles and replacement by dissolution of the limestone material. It is possible that the high surface area of amorphous byproduct limestone materials aids in the reaction rate as well.

Although the focus of this paper is on Pb-Zn-Cd mining and smelting contamination of soils and remediation of soil metals risks, many of the same principles apply to As contamination (Chappell et al., 1997). Risk assessment for soil As must consider bioavailability, chemical speciation, etc., and high Fe additions may reduce risks of soil As.

Web Site With Photographs and Data From Studies of the Use of Tailor-made Biosolids Mixtures to Remediate Zn-Pb-Cd-Contaminated Soils.

Readers may find more details about the soil remediation research described above at a web site prepared by cooperators C.L. Henry and S.L. Brown at the University of Washington; the files contain color photographs and details of several studies in which Tailor-Made remediation methods were used to remediate severely phytotoxic soils at smelter and mine waste contaminated sites in the western US. The addresses for these sites are: http://faculty.washington.edu/clh/bunker.html (Bunker Hill, Kellogg, ID); http://faculty.washington.edu/clh/leadville.html (adjacent to Arkansas River downstream of Leadville, CO); and http://faculty.washington.edu/clh/wet.html (Page swamp wetland site near Kellogg, ID).

Phytoextraction of Soil Metals.

Phytoextraction uses plants to remove metals from soils. Several approaches have been studied. We have been working to develop the method which uses natural metal hyperaccumulator plant species. These rare plants are selected by evolution on mineralized soils where they have an advantage over plants which exclude metals because the metals can help the plant reduce the effect of chewing insects and plant disease organisms on its ability to reproduce. Table 5 lists hyperaccumulators species for several trace elements, which achieve over 1% metal in plant shoots when grown in soils where the plants evolved. Phytoextraction can be a "green" technology for soil remediation, but commercial systems are still in development.

Our research team has developed effective metal hyperaccumulator plants for Ni+Co, and for Zn+Cd (Brown et al., 1994; Li et al., 1997; Chaney et al., 1999b). Table 6 illustrates the important role of hyperaccumulation and hypertolerance of metal by these plants in the annual rate of removal of metals from the soil. Normal plant species such as corn (*Zea mays* L.) do not remove appreciable amounts of metals even when suffering phytotoxicity from the metal they accumulate from phytotoxic soils. *Thlaspi caerulescens*, on the other hand, has poorer yield than corn, but hyperaccumulated 2.5% Zn in field tests. Further, Li et al. (1997) have examined Zn and Cd accumulation from a field test plot by a number of genotypes of this species collected at different locations in Europe, and found substantial variation in Cd hyperaccumulation in the presence of the normal 1 g Cd:100 g Zn. All strains accumulated 1-2% Zn, but differed in Cd hyperaccumulation (Figure 3). These remarkable genotypes offer an effective technology for phytoextraction of Cd from soils with little Zn contamination, not possible with the 'Prayon' strain of *T. caerulescens* used in most research on *Thlaspi* (Chaney et al. 1999b). And require only the same nutrients as crop plants to achieve this remarkable metal uptake and tolerance. Because lower soil pH increases solubility of Zn and Cd, *Thlaspi caerulescens* accumulates higher Zn and Cd concentrations if soil pH is lowered by agronomic management practices. We believe that cultivars of *T. caerulescens* could be bred to combine higher yields, and the Super-Cd-accumulator trait, and be used to quickly clean up soils where rice or

Table 5. Examples of plant species which hyperaccumulate Zn, Ni, Se, Cu, Co, or Mn to over 1% of their shoot dry matter in field collected samples (about 100-times higher than levels tolerated by normal crop plants).

Element	Plant Species	Max. Metal in Leaves	Location	Reference
Zn	*Thlaspi calaminare*[1]	39,600	Germany	Reeves & Brooks, 1983b
Cd	*Thlaspi caerulescens*[1]	1,800	Pennsylvania	Li et al., 1997
Cu	*Aeollanthus biformifolius*	13,700	Zaire	Brooks et al. 1978
Ni	*Phyllanthus serpentinus*	38,100	N. Caledonia	Kersten et al., 1979
Co	*Haumaniastrum robertii*	10,200	Zaire	Brooks, 1977
Se	Astragalus racemosus	14,900	Wyoming	Beath et al., 1937
Mn	Alyxia rubricaulis	11,500	N. Caledonia	Brooks et al. 1981b

[1]Ingrouille and Smirnoff (1986) summarize consideration of names for Thlaspi species; many species and subspecies were named by collectors over many years(Reeves and Brooks, 1983a; 1983b; Reeves, 1988).

tobacco can cause human health effects. In this case, the value of Cd in the crop would not affect the need to produce the crop to decontaminate a soil; rather, phytoremediation services and the value of Zn in the crop would need to pay for the costs of crop production and processing. Phytoextraction with *T. caerulescens* cultivars would be remarkably less expensive than soil removal, and offers the only practical solution for Cd-contaminated soils which comprise risk to humans.Genetic engineering is being used to develop new plants for phytoremediation. One successful example is the transfer of microbial mercuric reduction genes to higher plants, which allows the plants to reduce soil mercuric ion to mercury metal which can be evaporated from the soil and reduce risk (Rugh et al., 1996). Methylated mercury is the dangerous form of Hg in the environment; it is lipophilic and biomagnified especially in aquatic food-chains. Plants with both the methyl mercury hydrolase and mercuric ion reductase have been developed by Rugh et al. (1996). Other fundamental aspects of developing phytoextraction technologies are summarized by Chaney et al. (1997; 1999b).

Some researchers have criticized use of hyperaccumulator plants because many have small biomass yield (e.g., *Thlaspi caerulescens* where a good yield is 5 t/ha-year). Some stress that crop plants can accumulate 1000 mg Zn/kg in some cases with little yield reduction, and compare Zn accumulation by *T. caerulescens* under the conditions which kill the crop plants. In our view, this is not a valid comparison. One must characterize how high metals can reach when each crop is managed to attain maximum levels without yield reduction. Corn, oat, and Indian mustard have only normal metal tolerance, and are greatly reduced in yield with 500 mg Zn/kg. If *Thlaspi* can accumulate 25-100 time more shoot Zn than corn under valid comparison conditions (Table 4), it seems obvious that plant species with normal metal tolerance offer little value for phytoextraction.

Unfortunately, natural plants do not accumulate concentrations of plant Pb needed to achieve significant phytoextraction of soil Pb (Chaney et al., 1999b). Some researches have shown that if one applies strong chelating agents such as EDTA, soil Pb can be dissolved, and the root membranes weakened enough to promote uptake of PbEDTA with the water moving into roots (Blaylock et al., 1997; Huang et al., 1997; Wu et al., 1999). Transpiration carries the PbEDTA from soil into plant shoots (Vassil et al., 1998). When high Pb levels are reached, the crop plants tested to date are not tolerant of the accumulated Pb, and growth ceases.

Concerns have been raised about application of EDTA to soils to achieve chelator-induced phytoextraction because of the experience the Department of Energy had with leaching of chelated radionuclides at their

Table 6. Estimated removal of Zn and Cd in crop biomass of a forage crop (corn), compared to an existing Zn+Cd hyperaccumulator or an improved Phytoextraction cultivar. Presume the soil contains 5,000 mg Zn/kg and 50 mg Cd/kg dry weight (or 10,000 kg Zn/ha@15 cm) and 50 ppm Cd (or 100 kg Cd/ha@15 cm). Crop is presumed to have 10% ash of the dry matter.

Crop	Yield	Zn in Shoots			Zn in Ash
	t/ha	mg/kg	kg/ha	% of Soil	%
Corn, Normal	20	25	0.5	0.005	0.025
Corn, Zn-Toxic	10	500	5.0	0.025	0.50
Thlaspi	5	25000	125.	0.62	25.
REMED CROP	20	25000	500.	2.5	25.
Crop	Yield	Cd in Shoots			Cd in Ash
	t/ha	mg/kg	kg/ha	% of Soil	%
Corn, Normal	20	0.5	0.010	0.005	0.0005
Corn, Zn-toxic	10	5	0.05	0.025	0.005
Thlaspi	5	250	1.25	0.62	0.40
Super-Cd *Thlaspi*	5	2500	12.5	6.2	4.0
REMED CROP	20	250	5.0	2.5	0.40
Super-Cd CROP	20	2500	50.0	25.0	4.0

facilities (Means et al., 1978). Soil-applied chelators dissolve metals based on the activity of soil metals and the selectivity of metal binding by the chelator. Non-target elements can be dissolved and leach down soil profiles if fields are irrigated, or in humid regions.

Chelator-induced phytoextraction may not work for all metals or all crops. Robinson et al. (1999) tested NTA and EDTA with *Berkheya coddii*, a South African accumulator of Ni, and found that added chelating agents actually inhibited uptake by the plants. Perhaps the special property of Indian mustard which allowed high accumulation of PbEDTA does not commonly occur in other species.

However, if such a chelate-induced phytoextraction technology were practiced with the soil over a plastic liner to prevent leaching of the EDTA chelates into the subsurface soil, it might be an effective technology. But with the need for liner and EDTA in large quantity, the method is expensive compared to the use of natural hyperaccumulators as is possible with Zn and Cd, or Ni and Co. Because of discussions about chelate-induced phytoextraction, we calculated the cost of applying EDTA at rates found to optimize Pb uptake in the work by Blaylock et al. (1977) and Huang et al. (1997), 10 mmol/kg soil. The price of technical grade EDTA ($1.95/pound) was obtained from a major US manufacturer in early 2000. Assuming 15 cm depth of soil Pb contamination, one application of EDTA at 10 mmol/kg soil costs $30,000/ha. Thus this method is very expensive as well as comprising risk to ground water contamination if liners are not used. With the highly effective *in situ* inactivation of soil Pb noted above, it seems clear that inactivation of soil Pb is the more desirable approach for remediation of soil Pb.

Some have criticized phytoextraction using hyperaccumulator plants based on presumed risk to wildlife which might ingest the crop. Because the crop is usually always high in metals which it can hyperaccumulate, the assumption was that animals would be at risk wherever this technology was practiced. However, field observation of livestock in areas where

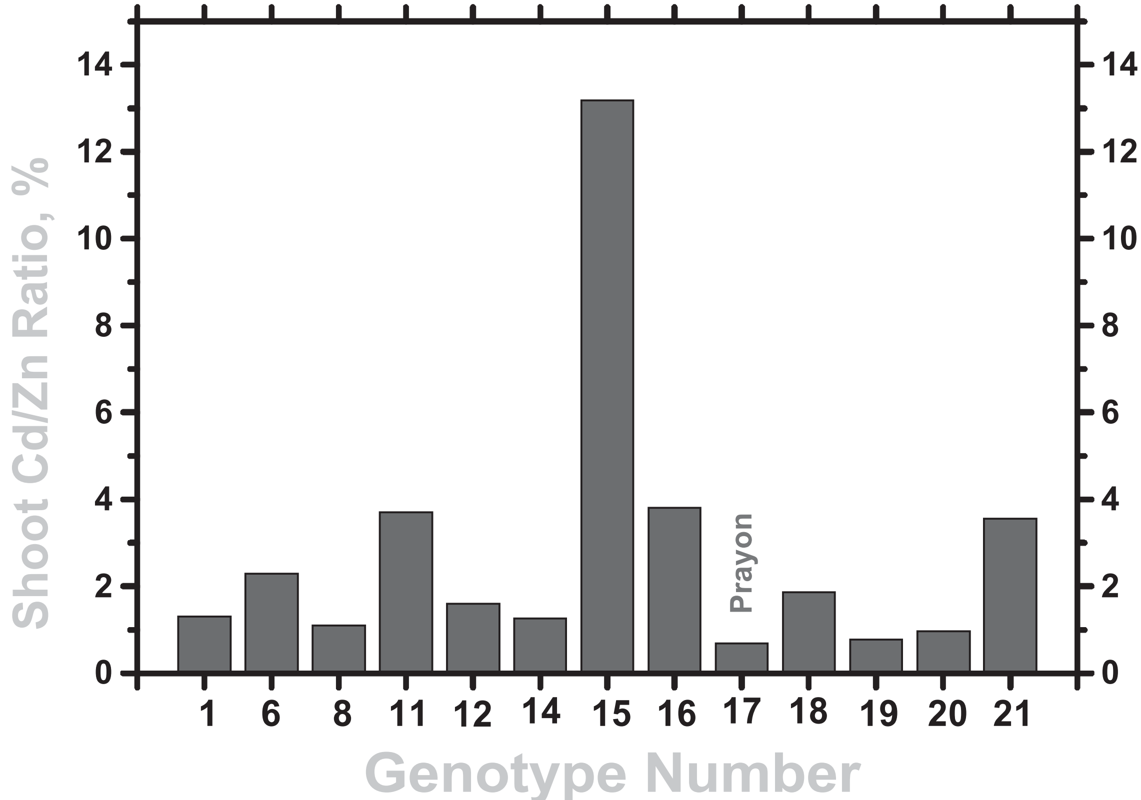

Figure 3. Variation of *Thlaspi caerulescens* genotypes in shoot Cd:Zn ratio; all accumulated 10,000-20,000 mg Zn/kg, but Cd transported to shoots reach very high levels in selected genotypes (Li et al., 1996).

hyperaccumulators occur naturally indicates that sheep, goats and cattle avoid the *Alyssum* and *Thlaspi* metal hyperaccumulators. The seeds of these species are small, and comprise little feed value. Further, it is very unlikely such animals will choose to ingest only a diet of hyperaccumulator plants considering the avoidance of metal rich leaves in the studies of Boyd and Martens (1994) and Boyd and Moar (1999). Chronic exposure to intrinsic plant metals has never been reported, and would be a valuable topic of study to settle whether wildlife or livestock may be at risk from fields of farmed hyperaccumulator crops. In general, birds and large mammals have large ranges, and would be unlikely to consume much hyperaccumulator plant biomass unless it were attractive (not found in practice). Small mammals such as field mice or other herbivore wildlife with a small range could live within a phytoextraction field, and would be expected to be harmed by the plant metals if they consumed only those plant tissues. Whether field mice would avoid these plants as found for sheep and goats is unknown at this time.

Mechanisms Used by Natural Hyperaccumulators or Metal-Tolerant Plants in Storage and Tolerance of Metals

Research on both natural metal hyperaccumulators, and evolved metal tolerant plant species or ecotypes has shown that tolerance relies on vacuolar storage of metals rather than formation of chelates with soluble ligands, especially those containing P (phytate) or S (phytochelatins, or metallothioneins). The work on *Silene vulgaris* by Verkleij, Schat, Ernst, et al., has illustrated this relationship very strongly (Schat and Kalff, 1992; Harmens et al., 1993; Chardonnens et al., 1999). And studies on hyperaccumulators have shown this vacuolar storage to play a very significant role in natural hyperaccumulators (Lasat et al., 1998; Küpper et al. 1999; Verkleij et al., 1998). Also, attempts to use protoplast fusion to build plants with higher biomass but natural hyperaccumulation ability have proved unsuccessful (Brewer et al., 1999)

Phytoextraction With Hyperaccumulator Offers Great Promise for Soil Remediation

Metal hyperaccumulation by plants offers a new cost effective approach for soil remediation. Further, the crop can be harvested as a biomass crop, air dried like “hay”, and burned in a biomass power generator. For metals which have commercial value, the ash is a high grade ore, very different from the traditional metal ores of commerce. For Zn and Cd, the value of biomass energy and metals for recycling appears to be a profitable opportunity (MacDougall et al., 1997), and for more valuable metals, hyperaccumulation may be more cost effective than mining technologies. Phytoextraction and phytomining technologies require extensive research and development. One is essentially domesticating a new crop, a difficult task. Cost effective metal phytoextraction is sufficiently promising that several research teams are working to develop practical phytoextraction systems (improved plant cultivars, and agronomic management practices needed for cost effective metal hyperaccumulation) (see Chaney et al., 1999b).

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Phytoextraction: Commercial Considerations

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Dr. Michael J. Blaylock holds a Ph.D. in soil chemistry from the University of Maryland and BS and MS degrees in agronomy from Brigham Young University. His research activities have focused on rhizosphere processes affecting trace element and heavy metal uptake by plants. Dr. Blaylock has worked for the past eight years evaluating and developing strategies to address heavy metal and radionuclide contamination of soils. Dr. Blaylock is an internationally recognized expert in the development of phytoextraction of metal-contaminated soils.

Dr. Blaylock is currently the Director of Ag Research and Development at Edenspace Systems Corporation where he leads Edenspace's research, analysis and development team. He has conducted or managed numerous phytoremediation projects at government and industrial sites including brownfields, the EPA SITE program, firing ranges within the Department of Defense, RCRA Corrective Action sites, former nuclear weapons development complexes within the Department of Energy, and a "Big Three" auto manufacturer. His research has led to five company-filed patents and more than sixteen peer-reviewed publications.

Abstract

Phytoextraction of metal-contaminated soils has emerged as an attractive alternative to traditional soil remediation methods such as excavation and disposal. The ability to use phytoextraction as a remediation tool requires plants capable of accumulating sufficient metal concentrations in their harvestable biomass coupled with biomass yield rates that facilitate a significant quantity of metal removal from the soil to achieve site goals. The successful application of this technology, however, requires an understanding of site-specific conditions and key parameters that influence performance. The site assessment process routinely includes an evaluation of soil conditions, contaminant distribution and bioavailability, remediation goals, and agronomic and phytometric analyses that allow a determination of appropriate practices (crop selection, soil amendments and conditioners, and agronomic practices) to ensure success.

To improve the performance and applicability of the technology, phytoextraction of metal-contaminated soils can be integrated with compatible ex situ and in situ technologies such as particle size separation and electrokinetic processes. Recent advances in the technology have expanded the applicability to soils with particulate contaminants, contamination below the root zone of plants, and the use of perennial crop plants and grasses. Current applications of the technology at firing ranges and RCRA Corrective Action sites will be presented and discussed to demonstrate the versatility of phytoremediation to address metal-contaminated soils.

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Phytoextraction: Commercial Considerations

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PHYTOREMEDIATION: Using plants to remove pollutants from the environment.

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Technologies

- **PHYTOREMEDIATION:** Removal of pollutants from the environment
- **PHYTOEXTRACTION:** Metal accumulating plants to remove toxic metals from soil
- **RHIZOFILTRATION:** Hydroponic plants to remove toxic metals from polluted waters
- **PHYTOSTABLIZATION:** Contaminant-tolerant plants to reduce mobility and prevent further contamination

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Site Challenges for Phytoextraction

- High total metal concentrations
- Mixed contaminants
- Contaminants below the effective root zone
- Unfavorable water table or drainage conditions
- Particulate/insoluble contaminant sources

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Phytoextraction's Place in the Remediation Tool Box

- **Many sites contain inorganic contaminants that are only treated through a combination of technologies.**
- **The combination of phytoextraction with soil washing (particle size separation) and stabilization increases the number of sites amenable to treatment.**

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Approach

- **Integrate conventional remediation with innovative technologies**
- **Use strengths of compatible technologies to overcome site challenges**

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Compatible Technologies

- Soil washing/particle size separation
- Excavation - ex situ treatment
- Electrokinetics
- Stabilization

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Phytoextraction Process

- Site investigation and assessment
- Site applicability or treatability study
- Development of agronomic practices
- Irrigation and water management
- Implementation (planting, cultivation, and harvesting)
- Monitoring and analysis
- Biomass treatment

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Treatability Study

- Soil characterization
  - Physical
  - Chemical
- Contaminant bioavailability and partitioning

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Case Study: Simsbury CT

- Surface soil lead
- Groundwater concerns
- Address leachable lead as well as total lead concentrations
- On-going site use and activities

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Summary of Results - Simsbury

- **Areas exceeding total lead concentration goals were reduced.**
- **Average lead concentrations from all crops of Brassica juncea exceeded 1000 mg/kg.**
- **SPLP leachable lead decreased from an average of 0.85 in April 1998 to 0.08 mg/L in October 1999.**

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Case Study - DaimlerChrysler

- **Three-acre ex situ site remediation**
- **Elevated lead concentrations below the root zone**
- **One year clean-up target**

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DaimlerChrysler Approach

- **Excavate subsurface soils for ex situ placement**
- **Two crops (Brassica juncea, sunflower)**
- **Dispose of soil exceeding total lead regulatory goal at the conclusion of one season**

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Commercial Success

- **September 21, 1999 - DaimlerChrysler presented a 1999 Environmental Excellence award to the Detroit Forge Phytoremediation Project Team**
- **Attended by more than 150 DaimlerChrysler environmental professionals from throughout the world, the annual meeting recognized seven top environmental projects**
- **The award recognized that the team's innovative use of phytoremediation saved DaimlerChrysler more than $1,000,000 compared to alternative remediation techniques**

Zinc Hyperaccumulation in *Thlaspi caerulescens*

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Abstract

Research presented here is aimed at elucidating the mechanisms that underlie the accumulation of extraordinarily high levels of Zn in *Thlaspi caerulescens* leaves (up to 3% of the dry weight). Physiological studies focused on the use of radiotracer flux techniques (^{65}Zn) to characterize zinc transport and compartmentation in the root, and Zn translocation and accumulation in the shoot of T. *caerulescens* in comparison with a related Zn nonaccumulator, *T. arvense.* Results indicated that Zn transport was stimulated at a number of sites in *T. caerulescens* including Zn influx into root and leaf cells and Zn loading into vascular tissues. Stimulation of Zn influx into the root cells of *T. caerulescens* was hypothesized to be due to an increased abundance of Zn transporters at the root cell plasma membrane. In addition, a compartmentation analysis showed that Zn was sequestered in the vacuole of *T. arvense* root cells, and this mechanism retarded Zn translocation to the shoot in this nonaccumulator species. Molecular studies focused on the cloning and characterization of Zn transporter genes in *T. caerulescens.* Complementation of a yeast Zn transport defective mutant with a *T. caerulescens* cDNA library resulted in the recovery of a cDNA, ZNTI, that encodes a Zn transporter. Sequence analysis of *ZNTI* indicated that it is a member of a recently discovered micronutrient transport gene family which includes Fe transporter, IRTI and ZIP Zn transporters. Northern analysis of *ZNTI* indicated that enhanced Zn transport in *T. caerulescens* results from a constitutively high expression of the *ZNTI* gene in roots and shoots. In *T. arvense, ZNTI* is expressed at far lower levels and this expression is stimulated by the imposition of Zn deficiency.

Introduction

A recent EPA analysis of approximately 1,000 superfund sites with RODs indicated that more than 600 were contaminated with toxic metals. A similar study indicated that more than 70% of investigated Brownfields were contaminated with toxic metals. These results indicate that soil contamination with toxic metals is a significant environmental problem.

Metal-contaminated soils are notoriously hard to clean. Current technologies resort to soil excavation and landfilling, or separation of contaminants by chemical, physical or electrochemical methods. However, at many sites, the high cost associated with the use of conventional engineering methods can be prohibitive. It has been estimated that cleanup of U.S. sites contaminated with heavy metals alone can cost up to $1.7 billion, while the cost of cleaning mixtures of heavy metals and organics was estimated at $35.4 billion (Salt et al. 1995). Because of the high cost, there is a need for less-expensive remediative technologies. Phytoremediation is emerging as a cost-effective alternative. Several analyses have demonstrated that the cost of phytoextraction is only a fraction of that associated with conventional engineering approaches (Glass, 1999). Furthermore, because it remediates the soil *in situ* phytoextraction avoids dramatic landscape disruption, and preserves the ecosystem.

The concept of using plants to clean up contaminated environments is not new. About 300 years ago, plants were proposed to be used in the treatment of wastewater (Hartman, 1975). Subsequent research has led to the identification of plants capable of removing a variety of toxic metals. Thus, at the end of the XIX century, *Thlaspi caerulescens* and *Viola calaminaria* were documented to accumulate high levels of metals in the leaves (Baumann, 1885). In 1935, Byers reported that plants of the genus *Astragalus* were capable of accumulating up to 0.6 % selenium in shoot biomass. One decade later, Minguzzi and Vergnano (1948) identified plants capable of accumulating up to 1% Ni in shoots. More recently, tolerance and high Zn accumulation in *Thlaspi caerulescens* has been reported (Rascio, 1977).

The idea of using plants to extract metals from contaminated soil was reintroduced and developed by Utsunamyia (1980) and Chaney (1983), and the first field trial on Zn and Cd phytoextraction was conducted in 1991 (Baker et al.). Identification of hyperaccumulators, species capable of accumulating extraordinarily high metal levels, demonstrates that plants have the genetic potential to extract metals from the rhizosphere. Unfortunately, the use of hyperaccumulator species for metal extraction is limited by plants' small size and slow growth (Ebbs et al., 1997). In an effort to make metal phytoremediation a commercial reality, Brown et al. (1995) proposed the transfer of genes that confer the hyperaccumulating phenotype to plants with higher potential for shoot biomass production. Progress toward this goal, however, is hindered by a lack of understanding of the basic physiological, biochemical and molecular mechanisms involved in metal hyperaccumulation.

In this paper, we present and discuss results of a recent investigation into fundamental aspects of the physiology and molecular biology of Zn hyperaccumulation in *Thlaspi caerulescens*. This species is a Zn hyperaccumulator, capable of accumulating up to 40,000 ppm Zn in shoots without showing toxicity symptoms (Chaney et al., 1999). This is remarkable considering that for most common nonaccumulator plants optimal Zn concentration is < 100 ppm (Mengel and Kirkby, 1987). Thus, *T. caerulescens* represents a very interesting experimental system for studying the mechanisms of metal hyperaccumulation as they relate to phytoremediation. As a reference, we used *T. arvense,* a related Zn nonaccumulator species.

Results

To test whether *T. caerulescens* has a greater potential for Zn accumulation compared to its nonaccumulator relative, *T. arvense*, we grew the two species in the same solution and analyzed Zn content of roots and shoots. Results shown in Table 1 indicate different patterns of Zn accumulation in the two *Thlaspi* species; whereas most Zn was accumulated in roots of *T. arvense*, the metal was preferentially accumulated in the shoots of the hyperaccumulator *T. caerulescens*. Interestingly, *T. caerulescens* showed no injury even at Zn levels as high as 100 µM. However, severe chlorosis was measured in leaves of *T. arvense* grown in 25 µM Zn. To investigate in more details the difference in Zn accumulation between the two *Thlaspi* species, we conducted short-, and long-term radiotracer (^{65}Zn) flux experiments. In short-term (3 hours) uptake studies, we measured unidirectional Zn influx into roots. In long-term (96 hours) experiments, we measured the net Zn accumulation in roots, which is the result of Zn influx and other Zn transport processes such as translocation to shoot, and efflux from the root back into the external solution. In short-term uptake studies, approximately twice as much Zn was accumulated in roots of *T. caerulescens* compared with *T. arvense*. These results indicate that *T. caerulescens* has a greater capacity for unidirectional Zn transport into the root cells. To our surprise, however, in long-term uptake studies, more Zn was accumulated in the roots of *T. arvense* compared with *T. caerulescens*. As expected, at the end of the 96-h-long uptake experiment, significantly more Zn was accumulated (translocated) in the shoots of *T. caerulescens* compared with *T. arvense* confirming findings shown in Table 1. Alteration of Zn transport at several sites may be responsible for the inhibition of Zn translocation from roots to shoots of *T. arvense.* Measurements of Zn concentration in the root sap indicated that significantly more Zn was loaded in the vascular tissues of *T. caerulescens*, suggesting that in *T. arvense* Zn is prevented from reaching roots vascular tissues (Lasat et al., 1998). To investigate the mechanism of Zn sequestration in *T. arvense* roots, we conducted an efflux (compartmentation) experiment. In this experiment, roots were loaded to a quasi-equilibrium state with ^{65}Zn, and subsequently, the rate of ^{65}Zn movement from roots

Table I. Zn accumulation and relative chlorophyll content in *T. arvense* and *T. caerulescens* seedlings exposed for 10 days to different Zn levels.
Tubs containing 22-day-old seedlings grown on nutrient solution containing 1µ M Zn^{2+} were refilled with nutrient solution containing 1, 25, 50, or 100 µM Zn. After 20 days, Zn concentration in roots and shoots was determined by emission spectroscopy. Relative chlorophyll content was determined with a chlorophyll meter (SPAD-502). Results are presented as means ± SE.

	T. arvense			*T. caerulescens*		
Zn conc µM	Roots ppm	Shoots ppm	Chl[a] %[a]	Roots ppm	Shoots ppm	Chl[a] %[a]
1	-	205	100	-	630	100
25	3500±368	789±102	53±8	1206± 89	1296±208	98±12
50	3481±502	940±108	32±5	1656±172	2616±306	102± 8
100	5870±702	986±169	18±4	3093±515	4522±202	104± 8

[a]Chlorophyll content

Table 2. Intracellular ^{65}Zn compartmentation and half-times for ^{65}Zn efflux from different root compartments ($t_{1/2}$) for *T. arvense* and *T. caerulescens* seedlings.
DPM and t1/2 values were calculated as described by Lasat et al. (1998).

	T. arvense			*T. caerulescens*		
	$^{65}Zn^{2+}$		$t_{1/2}$	$^{65}Zn^{2+}$		$t_{1/2}$
	DPM	%	min	DPM	%	min
Cell wall	87,100	61	6	87,100	66	6
Cytoplasm	39,800	27	30	38,300	29	38
Vacuole	17,000	12	260	7,100	5	150

into an unlabeled (^{65}Zn free) external solution was measured. The ^{65}Zn efflux curve could be dissected into three linear components which were interpreted to represent efflux from three root compartments: cell wall, cytoplasm and vacuole (Lasat et al., 1998). Two important results were obtained in this study: a semi-quantitative estimation of ^{65}Zn accumulation in root compartments, and estimates of rate constants for Zn efflux from these compartments. Data shown in Table 2 indicate that approximately 2.5-fold more Zn was accumulated in the root vacuole of *T. arvense* compared with *T. caerulescens*. In addition, the mobility of vacuolar Zn was significantly lower (higher $t_{1/2}$ value) in *T. arvense.* These results indicate that Zn is sequestered in the root vacuole of *T. arvense* and made unavailable for translocation to the shoot. In summary, results obtained in radiotracer flux studies conducted with roots documented two major differences between the two *Thlaspi* species: 1) higher capacity for Zn transport into root cells of *T. caerulescens*, and 2) inhibition of Zn translocation to the shoots of *T. arvense* due to Zn sequestration in the root.

A set of uptake experiments was conducted to investigate Zn transport and accumulation in leaves of the two *Thlaspi* species. In radio tracer flux studies, significantly more Zn was accumulated in the leaf sections of *T. caerulescens* compared with *T. arvense*.

Results obtained in uptake experiments with leaves and roots point to a genetic modification of Zn transport in the hyperaccumulator *Thlaspi* species. To isolate and characterize Zn transporters, a research strategy based on functional complementation of a yeast mutant defective in Zn transport (*zhy3*) was employed. This strategy relied on the construction of a *T. caerulescens* cDNA library in a yeast expression vector. After transformation of *zhy3* with this library, cDNAs of interest (encoding Zn transporters) were identified as those that permitted growth of the yeast colonies on a Zn-restrictive medium. To construct the library, a commonly used yeast expression vector, pFL61, was employed. This vector has been successfully used to isolate other plant genes, including genes involved in amino acid biosynthesis, and genes encoding nutrient transporters. cDNA from *T. caerulescens* mRNA was synthesized and subsequently size-selected for products that were greater than 1 kb in length. This cDNA was ligated into pFL61, and a primary library consisting of 3 x 10^5 independent clones with an average insert size of 1.3 kb was generated.

To identify genes involved in Zn transport, we isolated *zhy3* transformed clones capable of growing on a screening medium containing restrictive Zn level (Lasat et al., 2000). Screening of yeast transformants resulted in the identification of 20 colonies capable of growing on Zn limiting medium. DNA sequencing analysis revealed that five of the seven clones represent the same gene which was designated *ZNT1*. The ability of *ZNT1* to mediate Zn transport was independently confirmed in a radiotracer experiment. Expression of *ZNT1* in yeast mutant, *zhy3,* greatly enhanced cells' ability to accumulate Zn over a wide concentration range.

To compare the abundance of *ZNT1* in *T. caerulescens* (Zn hyperaccumulator) and *T. arvense* (Zn nonaccumulator), a Northern analysis was conducted. *ZNT1* mRNA abundance is greater in both roots and shoots of *T. caerulescens* compared with *T. arvense*. This pattern was obtained regardless whether Northern analysis was conducted with *T. caerulescens ZNT1* cDNA, or a probe representing a *ZNT1* homologue from *T. arvense* (data nor shown). In addition, in the normal (nonaccumulator) plant (*T. arvense*), *ZNT1* gene is expressed at very low levels in Zn sufficient plants. Imposition of Zn deficiency induced the expression of *ZNT1* in this species. In the Zn hyperaccumulator, *T. caerulescens*, *ZNT1* was expressed at high levels and was less dependent on plant Zn status.

Discussion

Maturation of phytoremediation into a commercial technology requires the understanding of the basic plant mechanisms that allow plants to absorb and accumulate metals in roots and shoot. These mechanisms are likely to involve metal transport regulation at several sites, including influx across root-cell plasma membrane, transport within root cells, unloading into the root vascular tissues, translocation to the shoot, reabsorption from the sap into leaf cells, and storage into leaves. In this study, we characterize the molecular physiology of Zn accumulation and translocation in the Zn hyperaccumulator *T. caerulescens* compared with *T. arvense*, a related nonaccumulator.

Zn accumulation exhibited different patterns in the two *Thlaspi* species. Thus, Zn was preferentially accumulated in the shoot of *T. caerulescens*, whereas most Zn remained in the root of *T. arvense* (Table 1). In addition, *T. caerulescens* showed greater Zn tolerance. Thus, this species showed no injury at Zn concentrations as high as 100 μM. In *T. arvense*, however, with the exception of the solution supplemented with 1 μM Zn^{2+}, all other Zn additions were phytotoxic. Therefore it is possible that high Zn levels measured in *T. arvense* roots were caused by a loss of regulatory mechanisms or other physiological properties due to Zn phytotoxicity as indicated in Table 1. Results shown in Table 1 demonstrate the existence of significant differences in Zn transport and accumulation between the two *Thlaspi* species. To further investigate Zn transport in the two species, we conducted a set of radiotracer flux studies. For this purpose, we developed a protocol to measure unidirectional Zn influx into root cells (Lasat et al., 1996). Zn influx into root cells was significantly greater in *T. caerulescens*. We have subsequently demonstrated that Zn transport in the root cells of the two *Thlaspi* species is via similar protein-mediated systems that exhibit saturated uptake kinetics. However, capacity for Zn transport was significantly higher in *T. caerulescens*, and we suggested that this was caused by greater deployment of Zn transporters at the root cell plasma membrane of this species (Lasat et al., 1998). In long-term uptake experiments, we observed that significantly more Zn accumulated in roots of *T. arvense*. This result was somewhat surprising because Zn influx was shown to be higher in *T. caerulescens*. However, Zn translocation from roots to shoot was 8-fold greater in *T. caerulescens* indicating that in *T. arvense* Zn transport to the shoot was inhibited possibly due to sequestration in the root. To investigate this hypothesis, we conducted an efflux (compartmentation) study. Advantages and limitations associated with this technique were discussed earlier (Lasat et al., 1998). Results shown in Table 2 indicate that Zn was sequestered in the root vacuole of *T. arvense*. In *T. caerulescens*, this mechanism is disabled allowing more Zn to be translocated to the shoot. In addition, leaves of *T. caerulescens* were shown to have a greater capacity for Zn uptake than *T. arvense*. These results have been confirmed in radiotracer experiments with leaf proptoplasts (Lasat et al., 1998).

Results obtained in radiotracer flux experiments with both roots and leaves point to a genetic alteration of Zn transport in *T. caerulescens*. To identify Zn transport genes, we employed an experimental strategy based on functional complementation of a yeast mutant deficient of Zn transport with a *T. caerulescens* cDNA library. This study resulted in the cloning of a Zn transport gene, *ZNT1* from *T. caerulescens*. Sequence analysis of *ZNT1* indicated it is a member of a recently discovered micronutrient transport gene family (Eide et al., 1996; Grotz et al., 1998). Following identification of the gene responsible for Zn transport, we analyzed its expression in the two *Thlaspi* species. The abundance of *ZNT1* was significantly greater in *T. caerulescens* compared with *T. arvense*. In addition, in *T. caerulescens* the expression of *ZNT1* was less dependent on plant Zn status, whereas in *T. arvense* Zn deficiency induced the expression of *ZNT1*. These results suggest a constitutively higher expression of Zn transporters in Zn hyperaccumulator *T. caerulescens*. Clearly, there is an alteration of the signal transduction pathway linking Zn status to expression of Zn transporter genes in *T. caerulescens*. It is likely that this alteration is linked to the tolerance mechanism(s) employed in this species.

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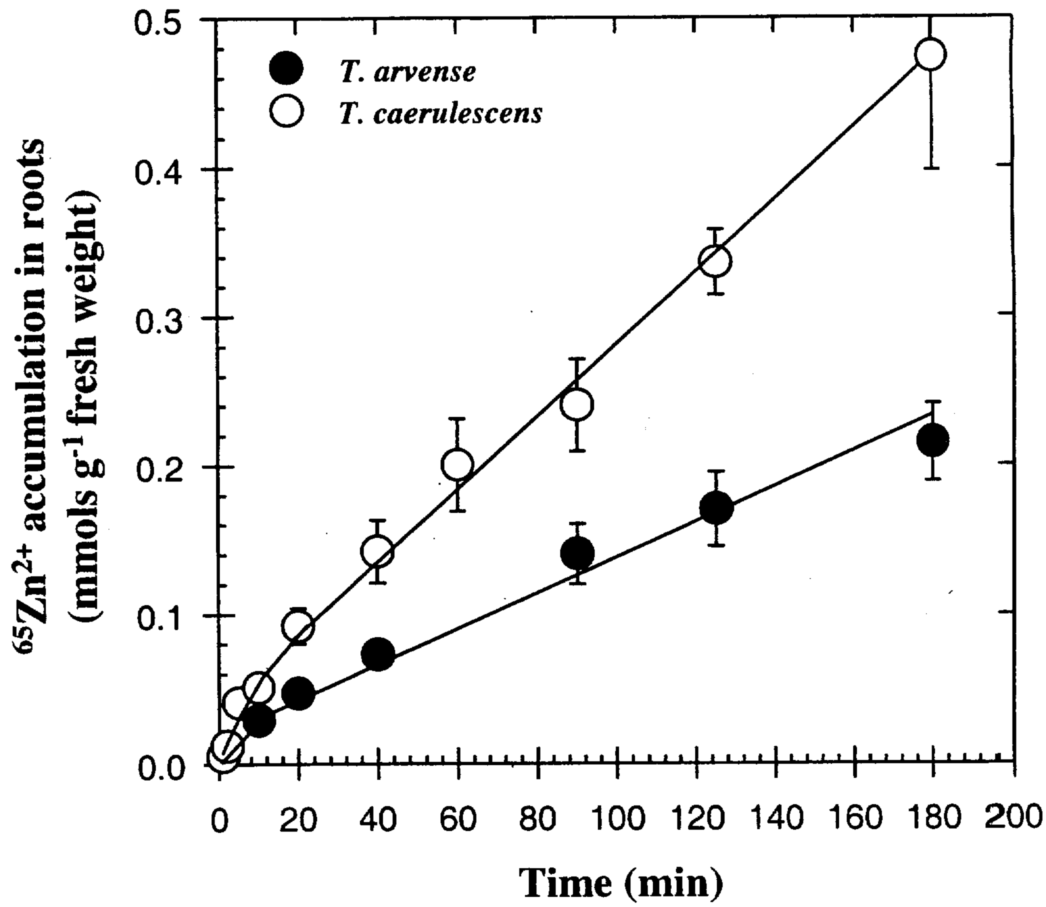

Figure 1. Short-term time-course of ^{65}Zn accumulation in roots. Roots of intact *T. arvense* and *T. caerulescens* seedlings were immersed in an uptake solution containing 10 μM ^{65}Zn. At the end of the time intervals shown, roots were desorbed for 15 min to remove cell wall bound Zn. Following desorption, roots were separated from shoots, blotted, weighed and gamma activity (^{65}Zn) measured.

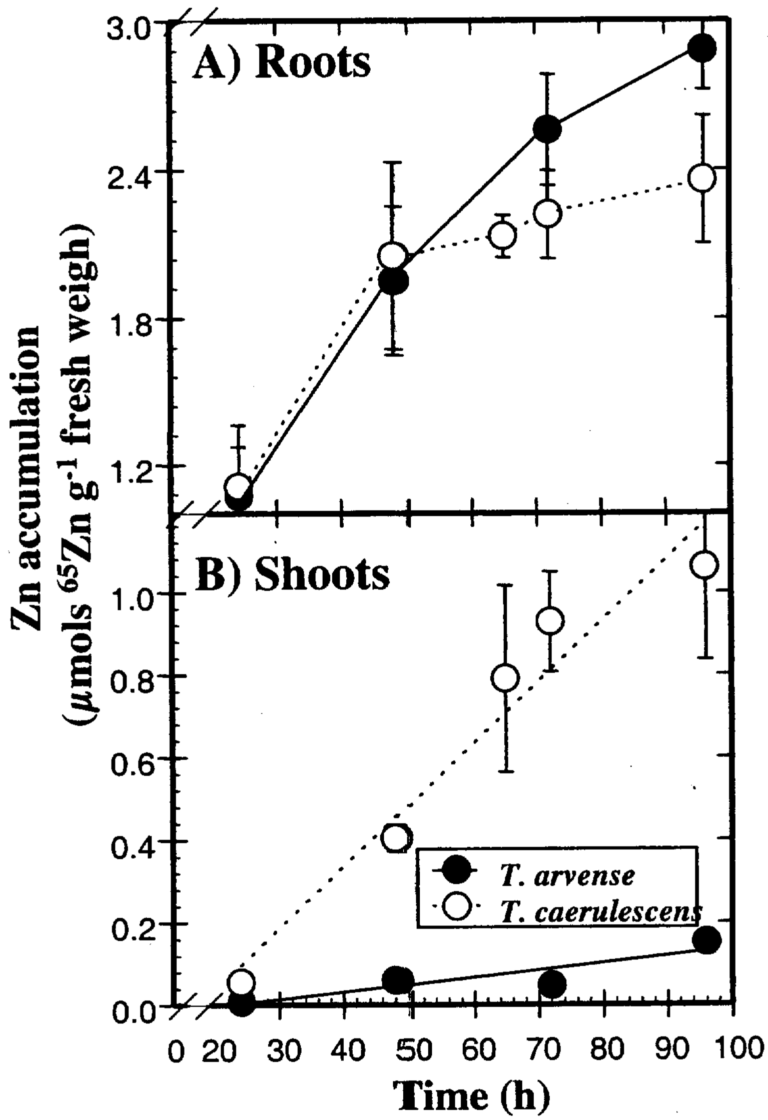

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Figure 2. Long-term time-course of ^{65}Zn accumulation in: A) roots and B) shoots of *T. arvense* and *T. caerulescens*. Roots of intact seedlings were immersed in a radioactive uptake solution containing 10 $\mu M\ ^{65}Zn$. Following incubation periods shown, roots were desorbed for 15 min. Roots were then excised, blotted, and both roots and shoots weighed and gamma activity measured.

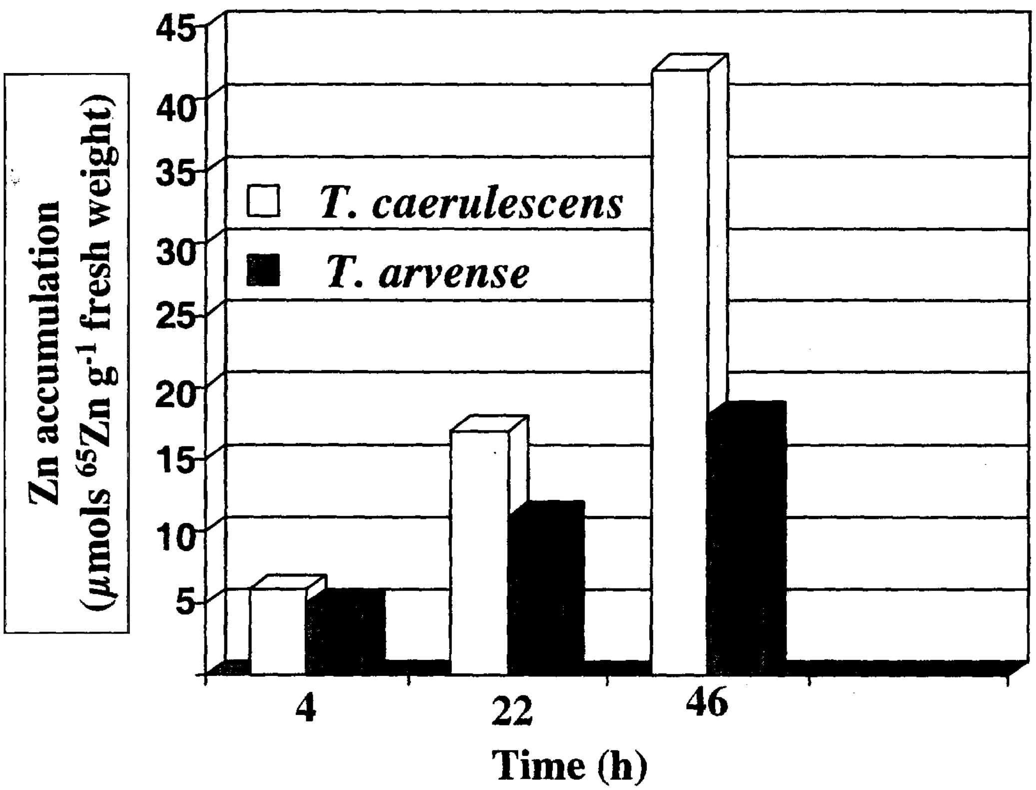
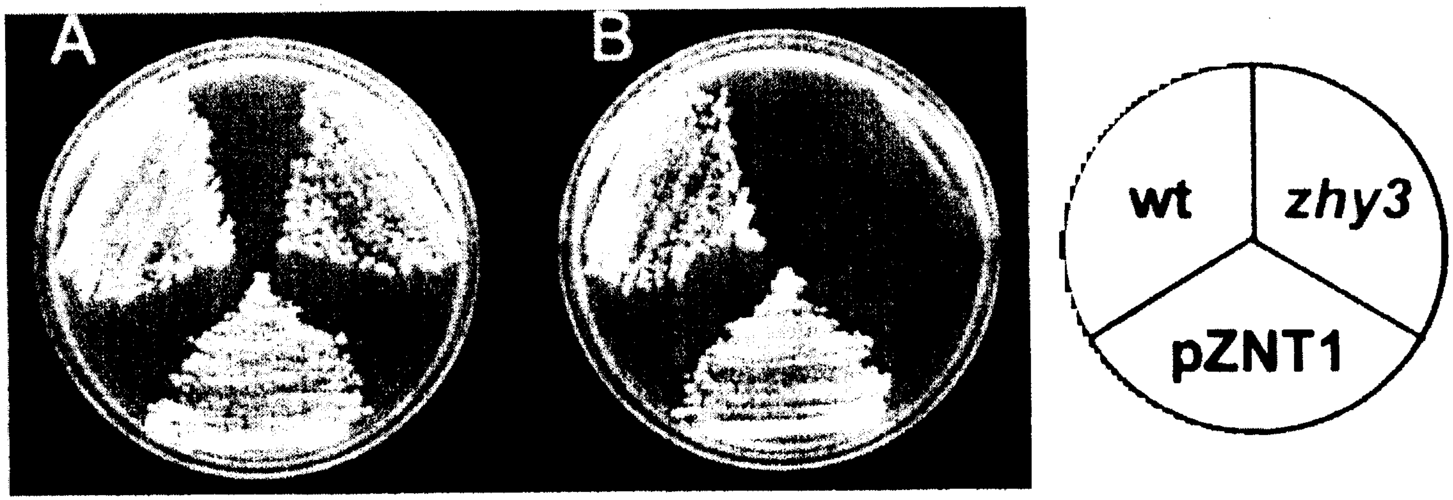


Figure 3. Time course of ^{65}Zn accumulation in leaf sections of the two *Thlaspi* species. Leaves of *T. arvense* and *T. caerulescens* seedlings were cut into 10 to 20 mm^2 sections and immersed in an uptake solution containing 1,000 µM ^{65}Zn. Following exposure times shown, leaf sections were desorbed for 15 minutes. Leaf sections were then harvested, blotted, weighed, and gamma activity measured.



Zn adequate medium

Zn restrictive medium

Figure 4. Functional complementation of yeast Zn transport deficient mutant, *zhy3*, with *T. caerulescens* Zn transporter gene, *ZNT1*. In A, growth medium contained adequate Zn levels. In B, growth medium was supplemented with EDTA to maintain low Zn activity. Wild type yeast, wt, grew in both media. However, the growth of Zn transport deficient yeast mutant, *zhy3*, was precluded on Zn restrictive medium due to mutant inability to acquire Zn from low external supply. Transformation of *zhy3* with *ZNT1* restored the growth of yeast mutant on the medium containing low Zn level (B).

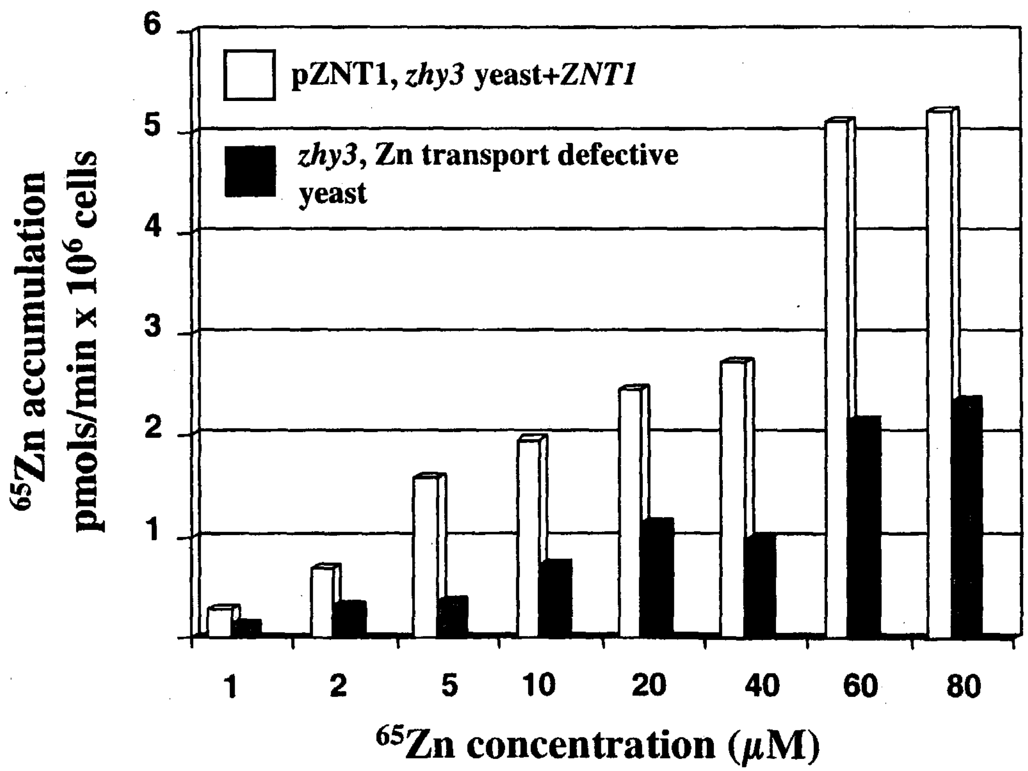


Figure 5. Zn uptake in yeast Zn transport defective mutant, *zhy3*, and in yeast mutant transformed with *ZNT1*. Cells were exposed to ^{65}Zn concentrations shown. After 20 min, cells were separated from the uptake solution by centrifugation through a layer of silicon oil and gamma activity measured.

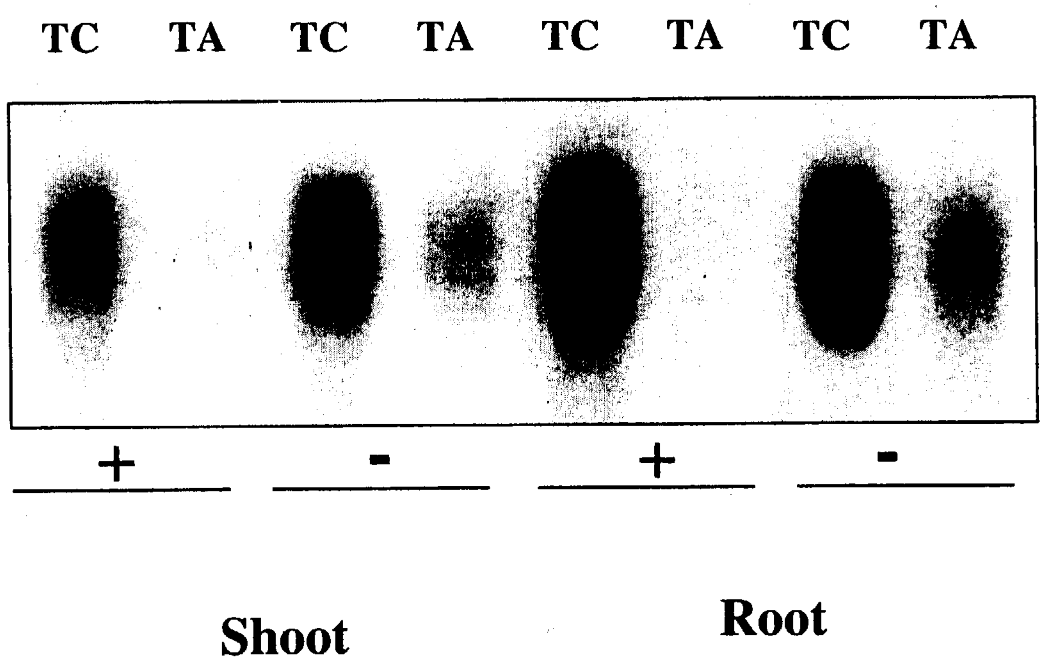


Figure 6. Northern analysis of *ZNT1* expression in shoots and roots of *T. caerulescens* (TC) and *T. arvense* (TA) grown on Zn-sufficient (+) or Zn deficient (-) medium.

PLUME CONTROL: SIMULATIONS AND FORECAS5

Chasing Subsurface Contaminants

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Dr. Burken received his Ph.D. in Civil & Environmental Engineering from the University of Iowa, December 1996. He subsequently took a position as an Assistant Professor of Civil Engineering at the University of Missouri- Rolla. The primary focus of his research has been in the area of phytoremediation of organic pollutants. Dr. Burken has authored 11 articles and book chapters, primarily in the area of phytoremediation. Dr. Burken's work has resulted in a 1999 National Science Foundation Career Award, a 1999 Faculty Excellence Award from the University of Missouri-Rolla, and the 1998 Rudolph Hering Medal for the Most Valuable Contribution to the Environmental Branch of Engineering, American Society of Civil Engineers.

Dr. Burken is the advisor to the UMR Student Chapter of Water Environment Federation, assistant advisor to Chi Epsilon Civil Engineering Honor Society, and advisor to Department of Conservation Stream Team #1293. He also serves as Chairman of the Student Organizations Committee -Assoc. of Environmental Engineering & Science Professors and as Vice President/President elect; Midwest Missouri Section, American Society of Civil Engineers.

Abstract

This talk investigates the mechanisms that can impact the translocation and fate of contaminants in the subsurface, in a theoretical look at contaminant transport in a phytoremediation system. Laboratory data pertaining to uptake, transport, degradation, and volatilization will be used to gain better understanding of these mechanisms in action. Finally the talk includes an overview of how these mechanisms might be impacted when moving to field-scale systems and of why field results and laboratory results are somewhat divergent.

Introduction

Phytoremediation of organic contaminants has rapidly grown from a novel idea to a full-scale treatment process in under a decade. When a literature search was performed in 1991, the literature search engine used produced only six papers in total. The majority of the papers that were located focused upon metals remediation, which was the first use of plants in remediation of contaminated sites. Since that time, there has been a "chase" in the field of organic contaminant phytoremediation. This chase has led to numerous studies into the impacts that plants have on contaminated sites. Figure 1 highlights the mass flows and biological processes of plants. Studies have focused upon the interaction of contaminants and plant systems, investigating how these processes can be exploited for use in remedial efforts. The summary presented here will overview studies performed at the University or Iowa and University of Missouri-Rolla, as well as related studies from other sources.

Rhizodegradation

Rhizodegradation is the enhanced degradation of organic contaminants in the rhizosphere. The rhizosphere is considered to be the area of soil impacted by the vascular root system of plants. Definitions of the rhizosphere range from the soil volume in intimate contact with the root system, extending only a few millimeters out from the roots, to much of the vadose zone, where the impacts might be physical disturbance of the overall soil structure, to altered water table elevation. In the close proximity of the roots, there are known to be greater microbial populations than in the bulk soil. Reports have shown that microbial populations are an average of 2- to 10-fold greater in the rhizosphere than in bulk soil. With the greater microbial numbers, increased microbial degradation was expected. In many studies there has been an increase in the microbial degradation and even mineralization (Anderson and Walton, 1995; Aprill and Sims, 1990; Schwab and Banks, 1994). However in some experiments, the mineralization of organic compounds was actually decreased (Nair *et al*., 1993). The decreased mineralization was contrary to the anticipated results. Further study into the fate of organics in plant/soil systems brought about new hypotheses and new considerations. One consideration is the population dynamics of the rhizosphere microbes. While total microbial numbers are generally higher in the rhizosphere, it has also been shown that certain strains can predominate in the rhizosphere. If these microbes are not capable of degrading the contaminants of concern, microbial degradation could be suppressed. Another hypothesis that could explain the decreased

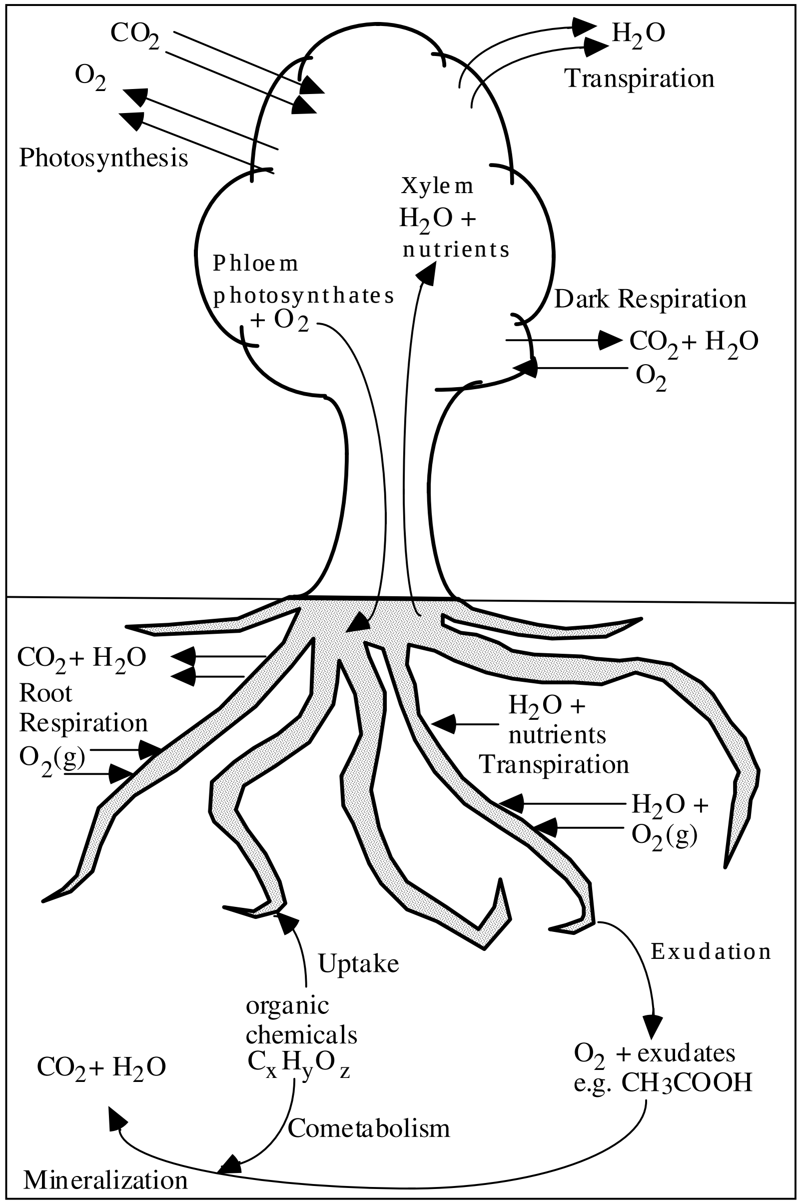

Figure 1. Mass flows in *Populus* spp. that may impact organic contaminants in phytoremediation. (Burken, 1996)

mineralization in the rhizosphere is altered availability of the contaminants to the microbes present. Plant uptake of the organic contaminants is a potential fate pathway that can make the contaminants unavailable for microbial degradation. In total, the effect of the rhizosphere is considered to be beneficial concerning the fate of organic contaminants, however this is far from being a universal constant.

Uptake in Laboratory Studies

Phytodegradation is the plant-mediated metabolism of contaminants. The term "plant-mediated" is used because in many cases the true mechanism of degradation is not fully known and could include microbial contributions. However, direct metabolic activity by the plants has been proven. The first step in the phytodegradation process is the interaction (or contact) of the plant and contaminant. This often occurs through transport of the organic compounds with the water used by the plants. Studies with atrazine that showed decreased mineralization in soil systems also showed that atrazine was taken up with the transpiration stream (Burken and Schnoor, 1997). In ^{14}C-labeled atrazine studies conducted in the laboratory, plant tissues were shown to contain large fractions of the ^{14}C at the termination of the experiments with the uptake being variable with soil and plant conditions. Such uptake has been shown for a variety of compounds and a variety of plants. Early work by Shone and Woods (1972) displayed the ability of organic compounds to be transported from soil water or hydroponic solutions into the plant tissues and move along with the transpiration stream. This "translocation" has been examined in many studies. The earliest studies on the uptake of organic compounds were looking at herbicidal compounds and crop species. Research by Briggs *et al*. (1982) proposed relationships for the uptake of herbicides (*o*-methylcarbamoyloximes and substituted phenylureas) by barley plants. The uptake of the compounds was related to the octanol-water partition coefficient, K_{ow}. Uptake was presented as the Transpiration Stream Coefficient Factor (TSCF). The TSCF is defined as the concentration in the transpiration stream of the plant divided by the concentration in the aqueous solution the plant is growing in at the time. Determining the transpiration stream concentration has been approached in many ways. In some studies the final concentration in the plant after the uptake has occurred is measured (Briggs, *et al.* 1982; Burken and Schnoor, 1998) and in other studies the concentration in the stream has been directly measured (Hsu *et al.*, 1990). The TSCF relationships that have been developed are not precise, but show a general trend related to the Log K_{ow} of the compound in question. Uptake from aqueous solutions appears to be highest for compounds with a Log K_{ow} between 1.5 and 3.5. The plant in question also plays a large role in the uptake, i.e. uptake is species-specific. Briggs *et al*. (1982) compiled data from many studies and plotted the data vs. the relationship which they proposed. For the same contaminants, uptake varied greatly between uptake studies on lettuce and turnip vs. carrot and parsnip or vs. barley and wheat.

The uptake of contaminants varies greatly with the availability of the contaminant. In the case atrazine, uptake was greatly impacted by the soil or media in which the poplar cutting was grown. In relatively organic carbon-free silica sand, uptake of over 90% of the applied label occurred in less than ten days. Whereas in an organic carbon-rich silt loam, uptake reached a relative maximum of 20% of the applied label after 80 days. A modeling approach by Ryan *et al*. (1988) approximated the impact of soil organic matter, predicting the uptake-inhibiting effect that was shown in the atrazine studies discussed here. In this model, the compounds with a Log K_{ow} between 1 and 2 are still mobile in the soil profile and are taken up in the transpiration stream. This approach shows the importance of environmental conditions. Many of the uptake studies have been conducted in hydroponic laboratory studies, without the impacts of sorption to soil. The conditions of experiments such as growth media, lighting, and reactor design should be considered when interpreting data that is gathered. Experimental conditions can greatly impact the outcomes.

Phytodegradation and Volatilization

Contaminants that enter plant tissues can still have a number of fates. Compounds can be retained in the tissues as the parent compound. Retention of the parent compound is an undesired fate, as it could increase the availability of the compound to insects and herbivores, and thus entry into the food chain. Retention and storage has been observed for some compounds such as RDX (Thompson *et al.,* 1999), but this does not appear to be the fate most commonly observed. Even RDX concentrations appear to dissipate in plant tissues over time (Burken *et al*., 2000). Compounds can also be metabolized when retained in plant tissue. A number of studies have shown plant metabolism to occur for a number of compounds (Hughes *et al*., 1997; Newman *et al*., 1997; Bhadra *et al*., 1999). One model of plant metabolism that has been put forth and supported suggests that compounds translocated by plants can subsequently be transformed, conjugated, and sequestered permanently in the tissues. The term "green-liver model" has been used to describe this metabolism (Sandermann, 1994; Trapp 1995). Plants generally rely on photosynthates as their carbon source and thus metabolism of xenobiotic compounds is considered to be a defense mechanism, and thus the term "green liver." The three steps are a sequential process. After a compound has entered the plant tissues, a transformation step takes place in the green liver process. Hydrolysis reactions are the predominant transformation, although reduction and oxidation reactions have also been observed (Komoßa *et al*., 1995). Hydroxylation reactions have been identified as a key first step and have been shown to be catalyzed by cytochrome P-450.

Conjugation reactions are the second step in the green liver model. Compounds synthesized by the plant are responsible for the conjugation. Glucose and malonate are examples of the plant generated conjugating compounds that are added to the transformation product by glucosyltransferases and malonyltransferases, respectively (Coleman *et al.*, 1997). Sequestration is the final step in the green liver model. Conjugation is followed by sequestration in the lignin fraction or in the cell vacuole. Once sequestered, these compounds are commonly called "bound residue." Bound residues exhibit very low bioavailability. Numerous studies have investigated the fate of compounds that have been sequestered and generally have found that parent compounds are not available, however some studies have questioned the bioavailability to ruminant animals. In most cases the complete impact of the bound residues is not fully understood.

Volatile organic compounds (VOCs) have yet another potential fate following uptake into plant tissues. Laboratory studies have shown that VOCs are transpired or volatilized from plant tissues (Newman *et al*., 1997; Burken and Schnoor, 1997). These studies have shown that compounds such at trichloroethylene (TCE) can be captured in the off-gas from the aerial portion of hybrid poplars. However in many field locations, studies searching for VOCs from leaves enclosed in teflon bags (Newman *et al*., 1997; Compton *et al*., 1998) or using FTIR analysis, have found little detectable volatilization. Recent studies detected chlorinated VOCs (TCE, tetrachloroethylene, and dichloroethylene) (Vroblesky *et al.*, 1998, Schumacher and Burken 2000), while BTEX compounds, MTBE and other hydrocarbons have also been detected in tree cores at a number of sites (Landesmeyer, 2000). These tree core studies have shown clear evidence that VOCs are in the transpiration stream within the tree trunks, however VOCs are not being detected in the leaf tissues at similar concentrations or emanating from the leaves.

Lab/Field

The differences mentioned above, regarding the volatilization of VOCs from the plant tissues, is a prime example of the disparity that can exist between laboratory and field studies. Laboratory studies are designed to isolate certain reactions or interactions and remove as much variability as possible. Only by eliminating inconsistencies except for the experimental variables being studied, can the impacts and rates of the variables in question be understood. In doing so, laboratory studies become inherently non-representative of the conditions that exist in nature. Many laboratory studies are done with plant cell cultures, plant cultures, sterile conditions, and artificial lights. While these studies do provide much knowledge right down to the molecular level of plant metabolism, they do not provide information that is directly transferable to field conditions. Laboratory studies should obviously be conducted and the data gathered be closely examined. However the findings gathered should not be used alone for field design.

Engineering Advancements

The current state of the art for phytoremediation generally relies on the inherent capabilities of plant systems, and applying the plant systems in ways to utilize the inherent capabilities to remediate contaminated sites. This approach generally leads to planting contaminated sites and little more. Some applications have gone beyond this to incorporate current engineering techniques. One such application is the use of impermeable sleeves to encase hybrid poplar cuttings. This method was pioneered and patented by Applied Natural Systems of Ohio. In this method, the poplars are planted to great depths and rooting is "forced" at the depth as the open end of the sleeve is the only source of water. Other design aspects must be addressed to allow the trees to survive this type of planting. At another site, the Portsmouth Gas Diffusion Plant in Ohio, contaminated ground water at a considerable depth was treated in a different manner. The contaminated groundwater was located beyond the reach of conventionally rooted hybrid poplars in a confined aquifer, which was at pressure. In order to use phytoremediation the contaminated water must be brought into contact with the poplar trees. To bring the contaminated water to the trees, bore holes were drilled in the impermeable clay layers that overlay the confined aquifer, and the bore holes were backfilled with sand. The natural potential of the water (pressure) forced the water to up-well through the bore holes and into trenches where the trees were planted. This method served as a natural "pump and treat," where the pressure in the confined aquifer delivers the water to the rooted poplars and the transpiration by the poplars continues to pump the water from the trenches. A schematic of this system is seen in Figure 2 (Rieske *et al.* 2000).

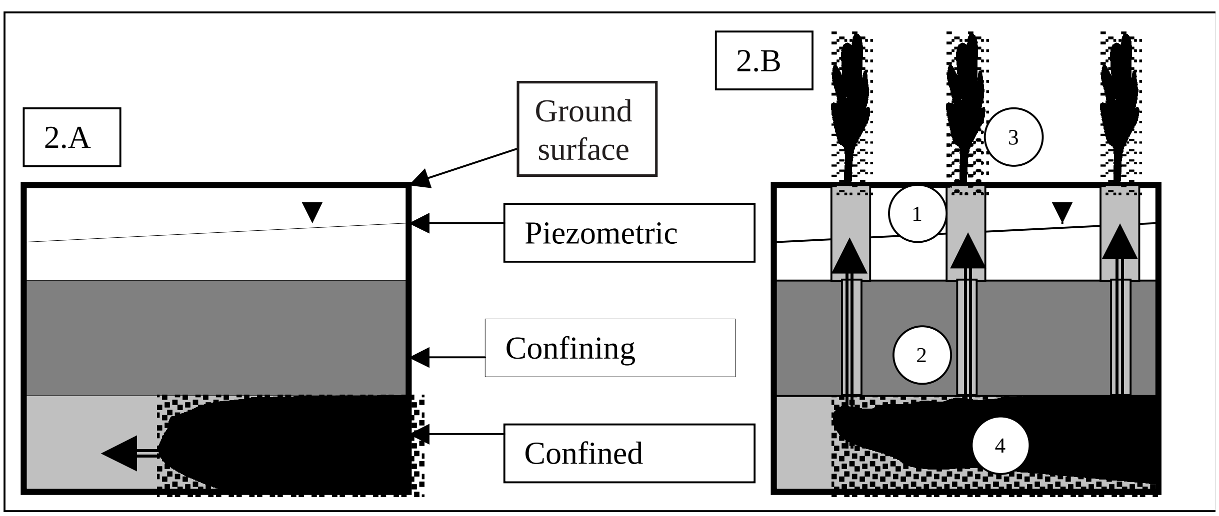

Figure 2 A. Shows the site prior to treatment. B. Shows the current phytoremediation application where: 1. Trenches were formed, 2. Bore-holes were placed through the confining aquitard to the underlying, contaminated aquifer, 3. Hybrid poplar and willows were planted, 4. Proposed movement of contaminated water up bore-holes to phytoremediation system planted above.

Engineering the way that phytoremediation tools are applied is one method that can have benefit. Engineering of the phytore1mediation tools at the molecular level is another way that engineering can improve phytoremediation. Currently, efforts are underway at a number of institutes to engineer the metabolic capabilities of the plants themselves. These efforts range from engineering metal resistance into plants, engineering metal transformation pathways, or engineering enzymes to metabolize organic contaminants. These methods of engineering the plants themselves lead to enhanced results in phytoremediation applications (Hooker and Skeen, 1999). Other methods to reach the same end result, degradation and even mineralization, include engineering the plant-microbe symbiotic relationship. Researchers have taken the approach to inoculate the seeds or cuttings used in phytoremediation with organisms known to degrade the targeted pollutants (Siciliano and Germida, 1998). Other research has taken the approach to inoculate the seeds or cuttings with genetically engineered microorganisms (Yee *et al* 1998, Crowley *et al*. 1996). Some results of such efforts can be seen in the speakers notes associated with this talk, and in Figure 3. In the experiment that generated these data, microbes were cultured from hybrid poplar cuttings. These cultures were selected from plating the natural hetertrophs growing on the poplar roots and selecting colonies that appeared to be most prevalent. A genetic sequence for a toluene-*o*-monoxygenase (TOM) was then incorporated in the host genome and recombinant strains were generated. These recombinants and others generated from two rhizobium strains acquired from the American Test Culture Center (ATCC) were tested for growth rates and TCE degrading capacity. Figure 3 shows the results where two recombinants (one from the poplar rhizosphere and one rhizobium) were able to degrade the TCE in the sealed reactors. This and other related work prove that the concept of combining genetically engineered microbes has tremendous potential and requires further study.

Concluding Comments

Phytoremediation of organic contaminants has undergone a number of rapid advancements. Following these rapid advancements in the field and in laboratory research, gaps have appeared between the understanding of the science involved and the application in the field. As these gaps have appeared, the best efforts

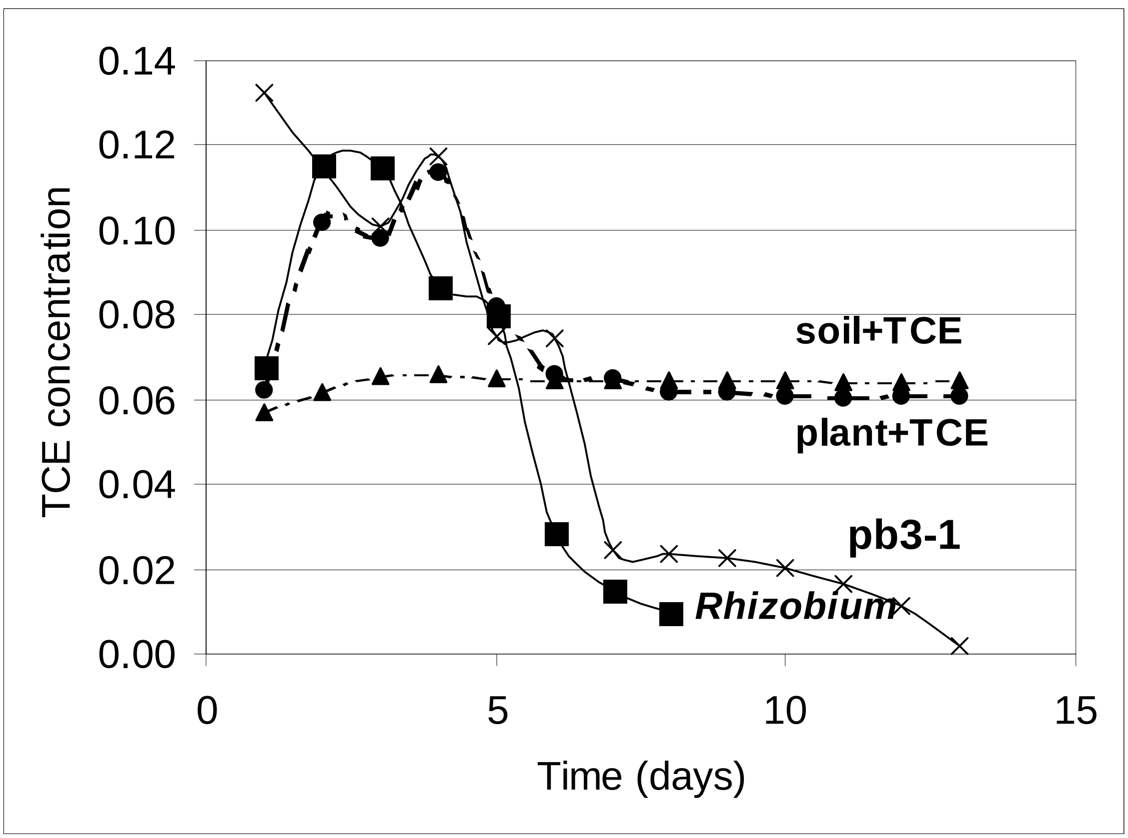

Figure 3 TCE concentrations in sealed 2 liter reactors. Sampling was done in the headspace. The two reactors inoculated with recombinant strains pb 3-1 and rhizobium

have been made to ever increase our understanding of what is happening and how the systems can be improved, thus the "chase of contaminants" has continued. This chase has come to include molecular sciences and genetic engineering, and the current indication is that this chase will continue and that the successful application and redefining of phytoremediation systems will also continue.

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Chasing Subsurface Contaminants

Joel G. Burken, Assistant Professor

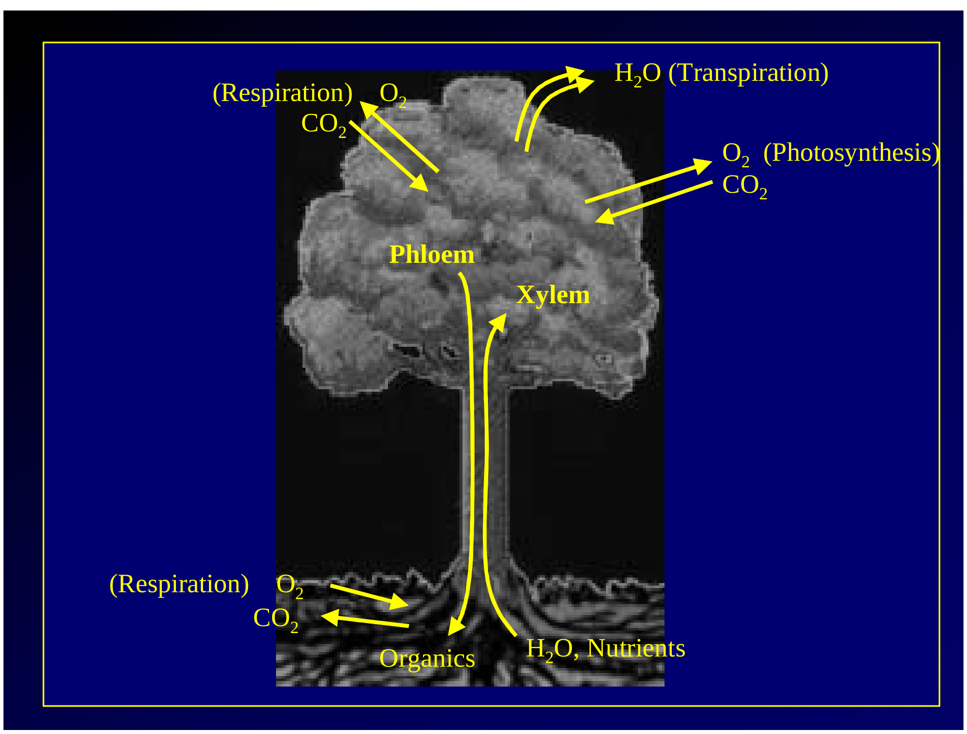
Department of Civil Engineering
University of Missouri-Rolla

Outline

- What's in a title?
- Mechanisms at work
- Lab Stories
- Looking Back
- Looking Ahead

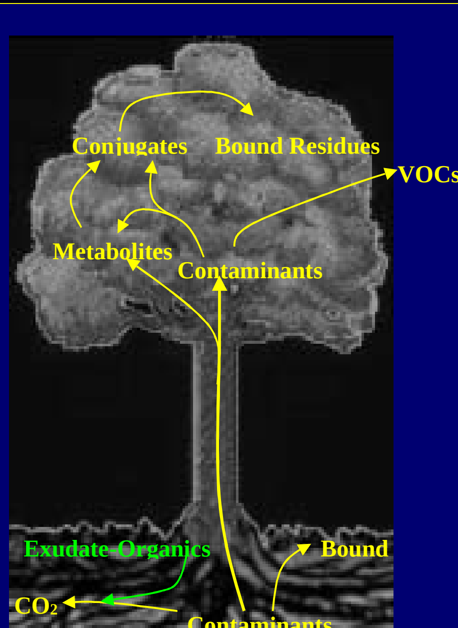
Rationale: Why chase contaminants?

- Solar driven pumps, with metabolic abilities and many potential advantages.
- Plant/organic chemicals research was primarily agri-crop related <1990.
- Laboratory studies provide laboratory data.
  Remediation is not completed under lab conditions… The Chase Continues



Field of Phytoremediation

- Metals
  - Phytoextraction - uptake & harvest, goal of 1%
  - Rhizofiltration - binding to roots, generally aquatic
  - Physical stabilization - less transport & leaching
- Organics
  - Uptake - transport to above ground, ?fate?
    - Phytodegradation - Direct metabolism
    - Volatilization - Direct from leaf/plant tissues
  - Rhizodegradation - increased degradation & binding
  - Physical stabilization - less transport & leaching



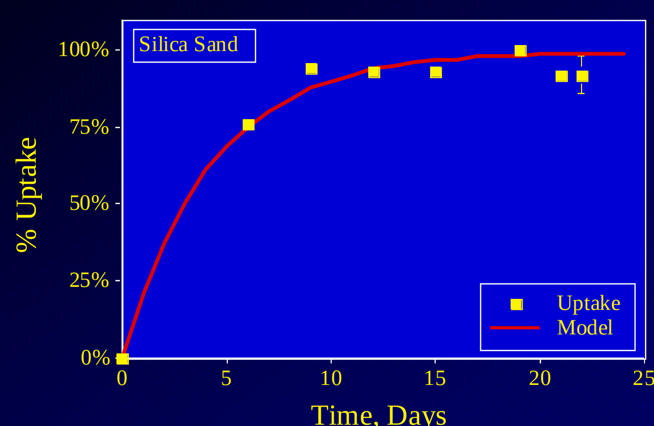
Story of Atrazine

- Most widely used herbicide, found in groundwater, surface water, even rainwater.
- Persistent, will degrade aerobically, but slowly'
- No efficient treatment methods.

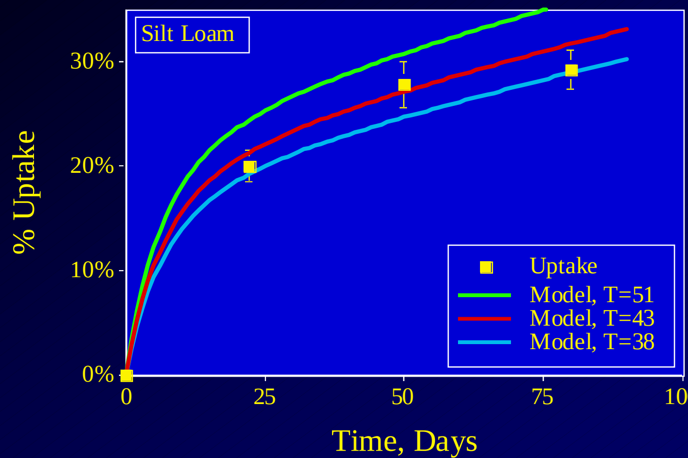
- Will plants increase degradation?

NO. Plants decreased mineralization in all tests. Root biomass stimulated some degradation.
.

Poplar Uptake of ^{14}C Labeled Atrazine from Silica Sand (<0.1% o.m.), Transpiration = 60 mL/day

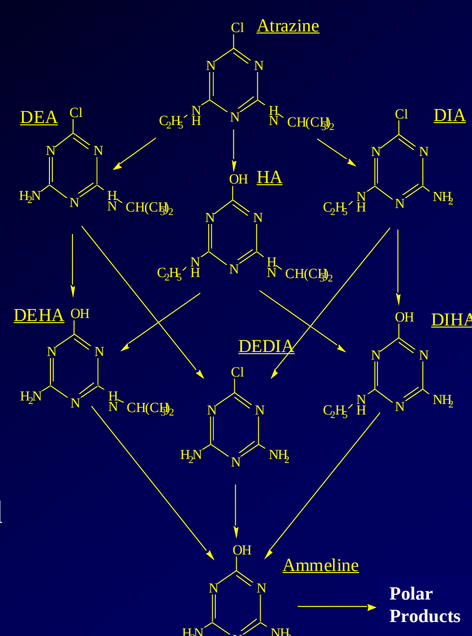


Poplar Uptake of ^{14}C Labeled Atrazine from Silt-Loam Soil (2.4% o.m.) (trans. in mL/d)

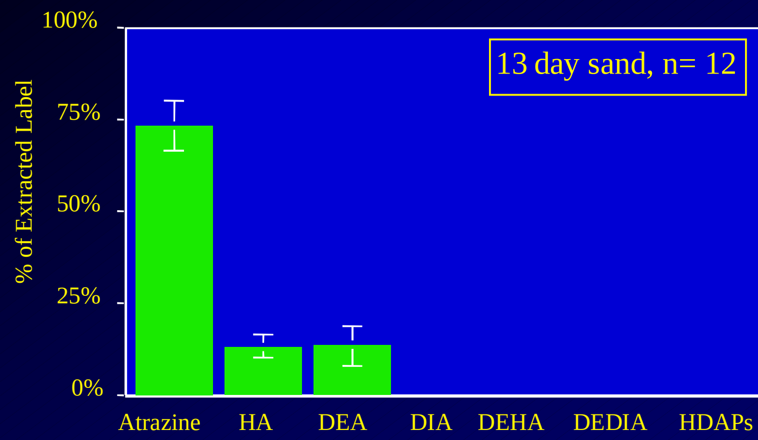


Atrazine degradation:
8 products were found,
suggested compounds
displayed.

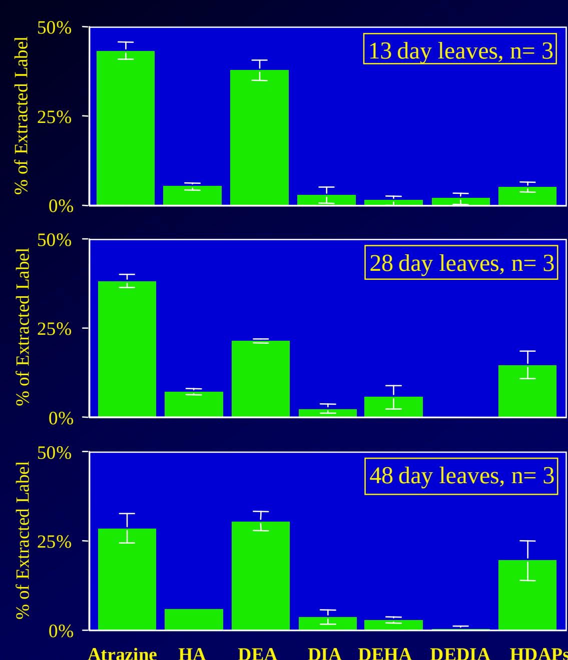
Proposed Mechanism:
Products not confirmed

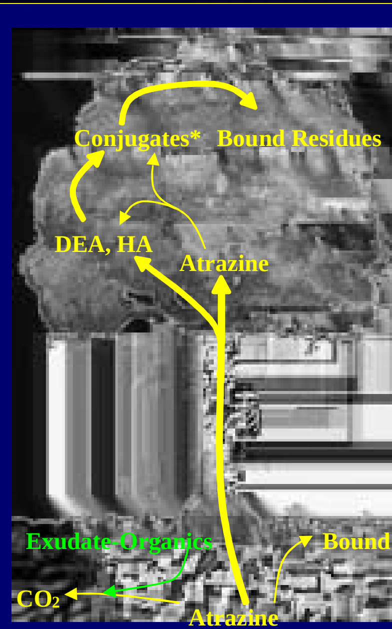


Composition of sand porewater when removed on day 13



Metabolism in sand grown poplars as a function of time. Atrazine and metabolites removed from media at day 13.

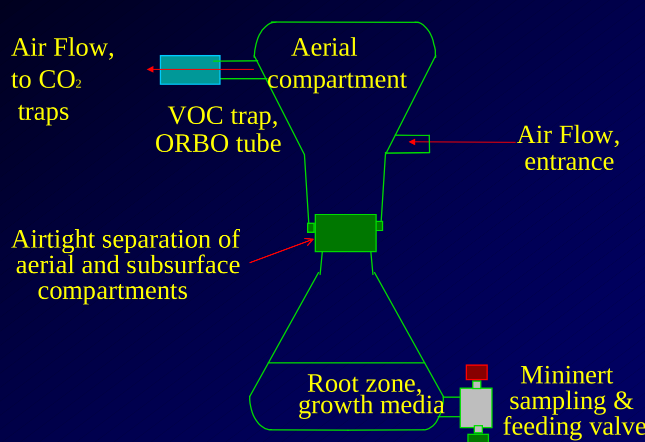




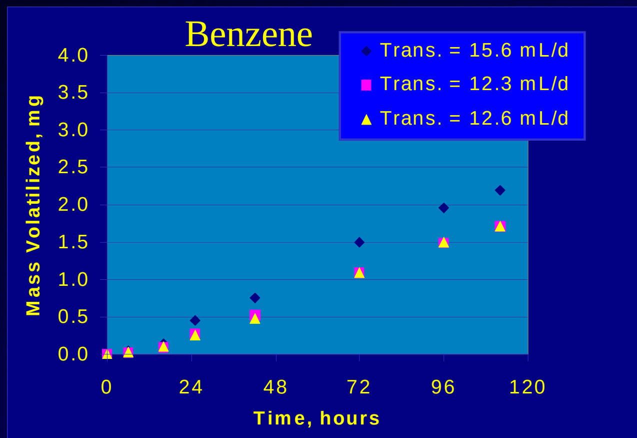
Martelle Cooperative, Iowa

Martelle Cooperative, Iowa

Hydroponic Reactor, VOC studies



Mass Volatilized from leaves



Volatile Organic Compounds:

- What is the impact of plants in VOC contaminated sites?

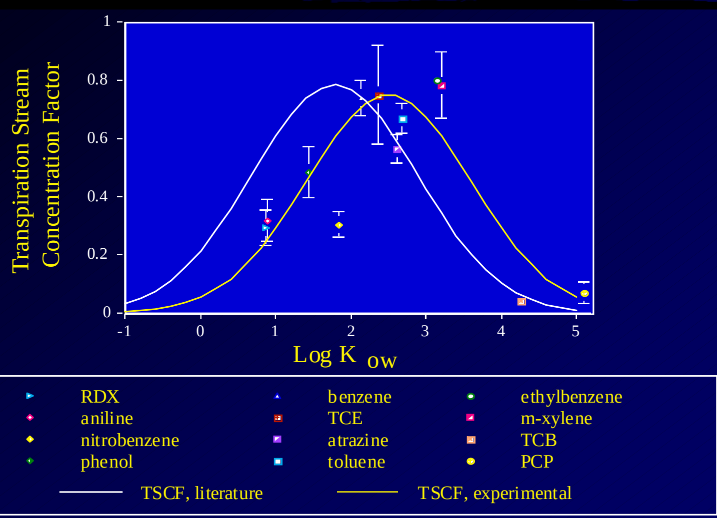
- Alfalfa did not enhance degradation of benzene in laboratory studies.
- Stomatal pathways dominated uptake & transformation.
- Benzene and toluene conversion in leaves occurs with the aromatic ring cleavage & incorporation.
- Benzene oxidation by intact chloroplasts and enzyme preparation from spinach leaves resulted in phenol being detected as an intermediate product .

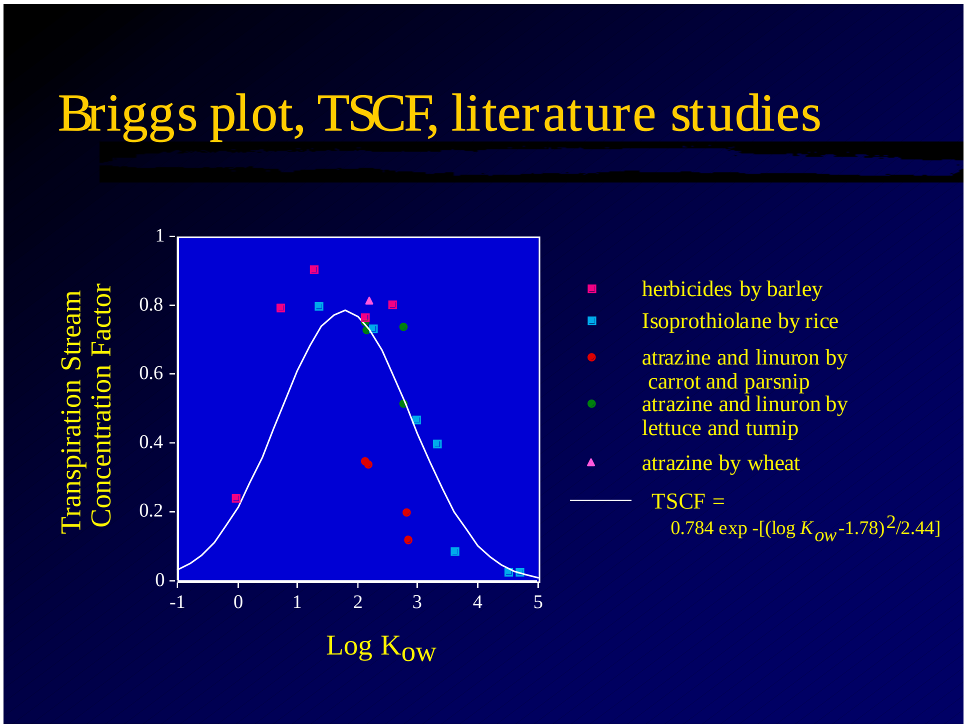
Organic Compound Fate

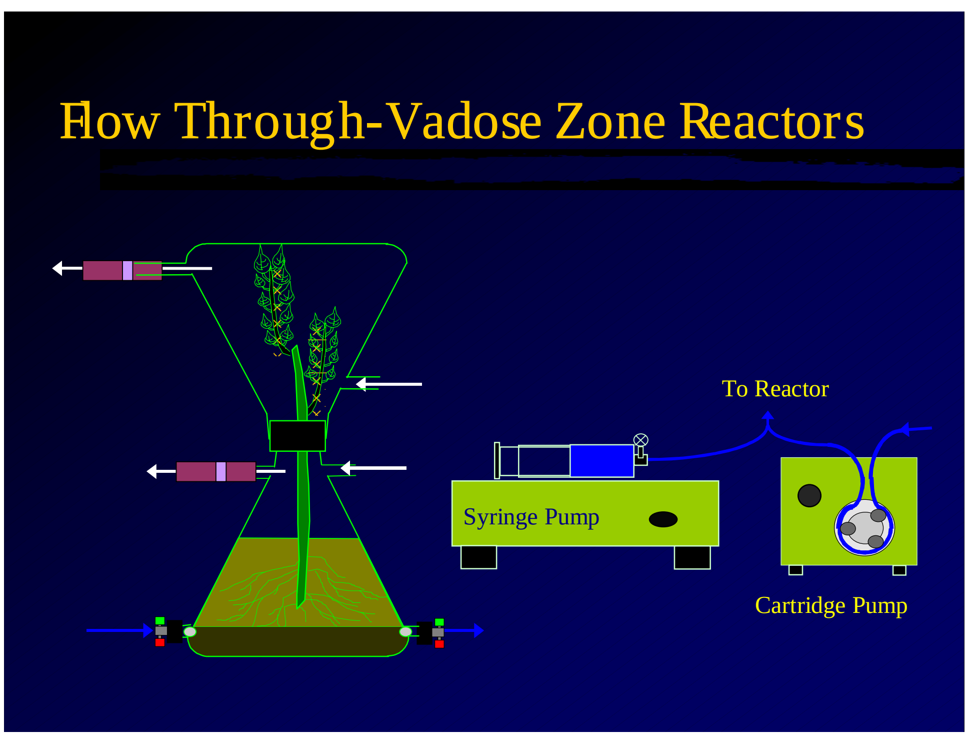
- For all compounds the movement in the plant tissues was followed.
- Transpiration Stream Concentration Factors (TSCFs) were determined.

$$\text{TSCF} = \frac{\text{Concentration in the Trans. Stream}}{\text{Concentration in the bulk Solution}}$$

TSCF Relationship



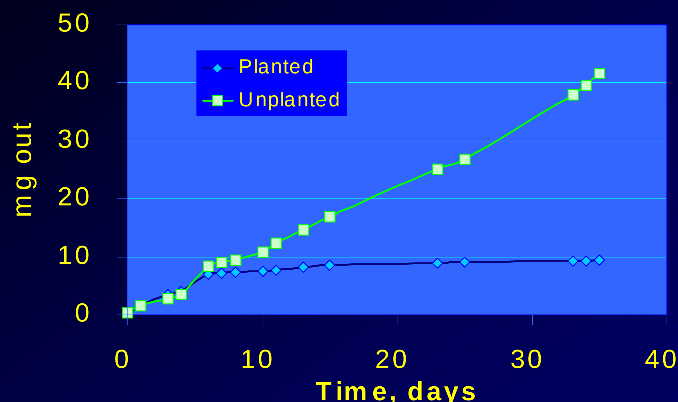

Briggs plot, TSCF, literature studies
Transpiration Stream Concentration Factor
Log K_{OW}
herbicides by barley
Isoprothiolane by rice
atrazine and linuron by carrot and parsnip
atrazine and linuron by lettuce and tumip
atrazine by wheat
TSCF = 0.784 exp -[(log K_{ow}-1.78)^2/2.44]


Flow Through-Vadose Zone Reactors
To Reactor
Syringe Pump
Cartridge Pump

Laboratory Set-up

- Light 210 µmol/m²-sec, mercury halide
- 16 hour photo period
- 20-30° C
- Air $_t$ = 2 L/minute
- Air $_b$ = 0.1- 0.5 L/minute
- H_2O ≈ 100 mL/day
- Benzene = 25 mg/L

Cumulative Mass in Effluent

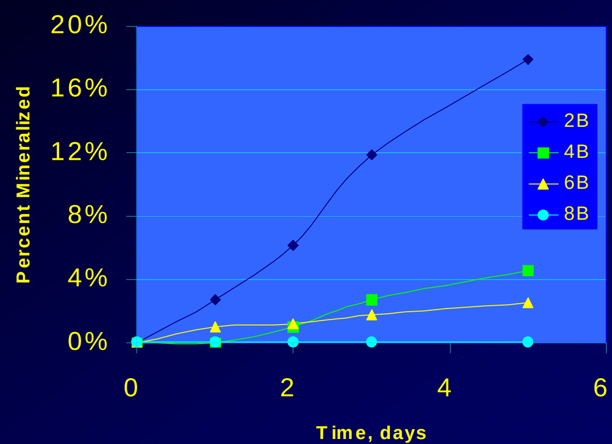


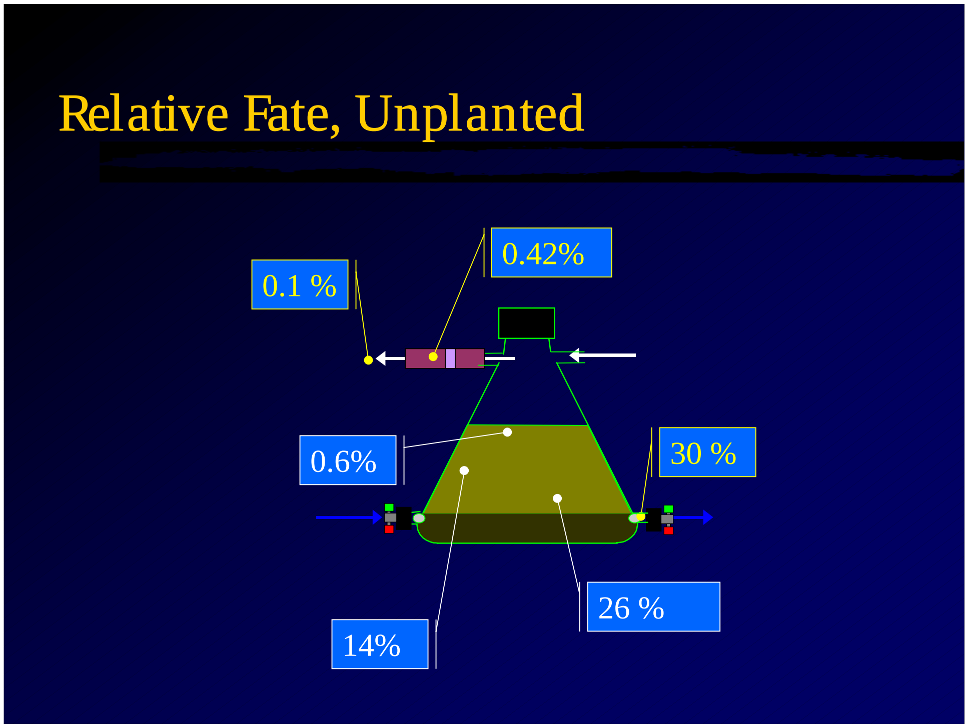
Total input for time period shown above = 69 mg ± 1.27

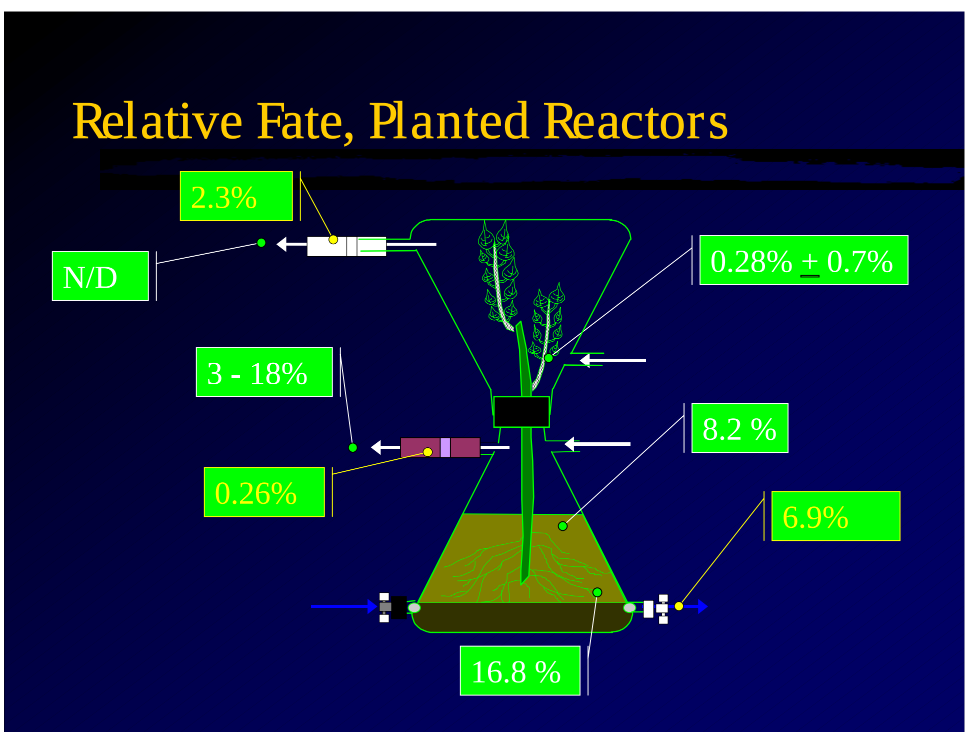
^{14}C Input and Data

- Input of 15μCi, over a three day period
- Injected directly into the flow path, one time per day.
- Effluent $^{14}CO_2$ to quantify mineralization, trapping effluent CO_2 in 1N NaOH.
- Biological Oxidation of plant tissues and soil samples, followed by LSC.

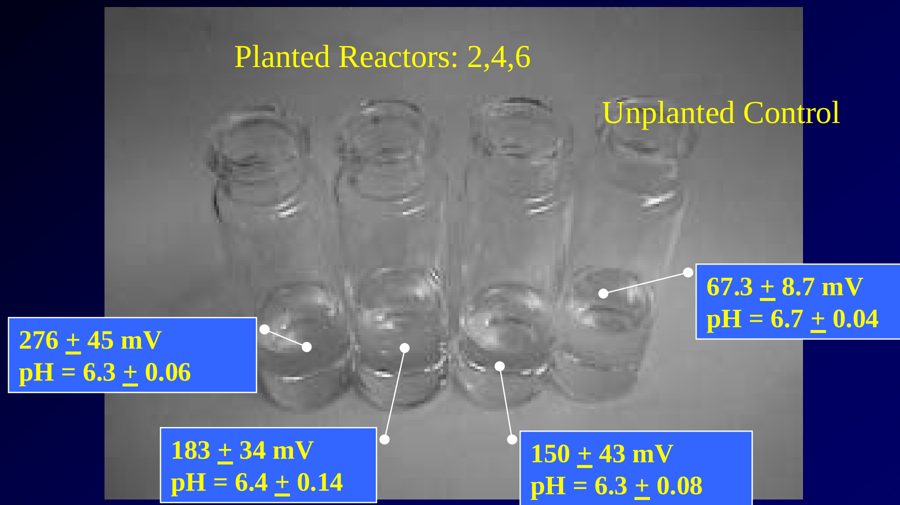
Effluent $^{14}CO_2$ as % of input ^{14}C



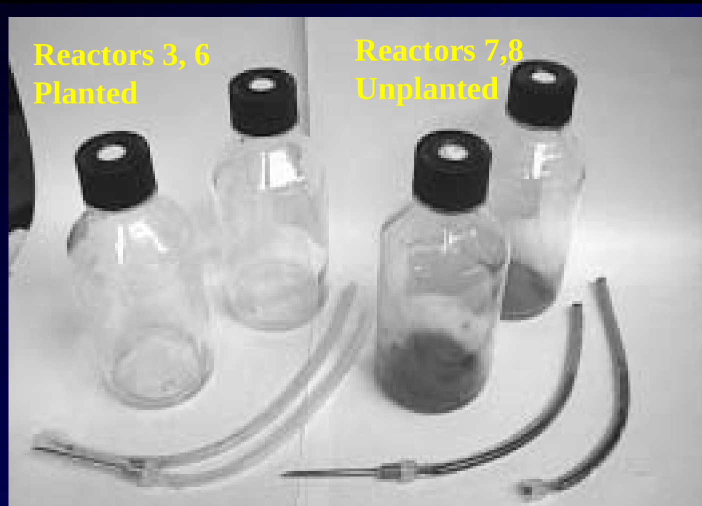

Relative Fate, Unplanted
0.1 %
0.42%
0.6%
30 %
26 %
14%


Relative Fate, Planted Reactors
2.3%
N/D
0.28% + 0.7%
3 - 18%
8.2 %
0.26%
6.9%
16.8 %

Effluent Redox Potential & pH



Visual Observations



Summary VOC Hydroponic / Soil

- Effluent concentrations and mass were much greater for unplanted controls.
- Elevated soil levels of $^{14}CO_2$ were in the presence of the poplar cuttings.
- Storage of benzene or metabolites was negligible (0.27%) in plant tissues.
- Volatilization was much lower than hydroponic studies.

Summary, Looking back

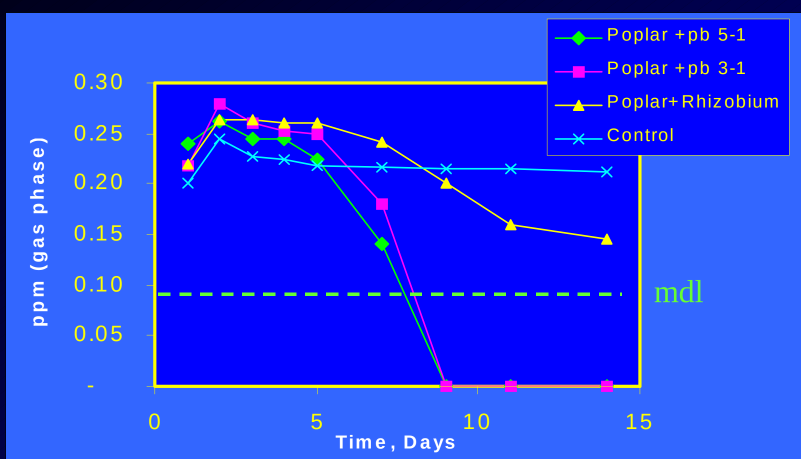
- Root zone of planted reactors was aerobic, whereas the unplanted controls were O_2 deprived, requiring the utilization of alternate terminal electron acceptors (not O_2 required for aerobic respiration).
- Earlier hydroponic experiments appear to be adequate in some aspects, however uptake from the vadose zone is not represented.

TCE degradation

Recombinant	Specific growth rate (hr^{-1}) Recombinant	Host	Initial TCE degradation rate (nmol/min•mg protein)
Pb3-1 [A]	**0.949**	**1.179**	**1.15**
Pb5-1 [A]	**1.056**	**1.006**	**0.83**
10320D [B]	**0.727**	**0.792**	**1.90**
35645A [B]	**0.805**	**0.593**	**1.21**
2-79TOM [C]	**0.754**	**0.770**	**0.50**

[A] (poplar isolate) [B] *Rhizobium* sp. [C] P. fluorescens

TCE Degradation, Reactor studies



Genetically Engineered Materials/Phytoremediat

- Recombinant strains retain competitiveness.
- Recombinants are stable w.r.t. TOM activity and expression.
- No inducer needed (phenol, toluene).
- Plants appear to control viability of the GEMs, and there is specificity to plant species.

Why Phyto?

- Natural approach: Simplistic elegance,
- Long term solution-short term cost,
- Potentially favorable fates/outcomes,
- Restoration & remediation,
- Public Acceptance.

What is the outcome?

- Where will the Chase end?

Acknowledgments

- Juel Gibbons, Carla Ross, Lisa Harrison, Lars Zetterstrom, Adrian Marsh (UMR), Tom Wood, Hojae Shim (U. Connecticut), Craig Just, Jerry Schnoor (U. Iowa), Lou Licht (EcoloTree)
- EPA Regions 7 & 8 - Hazardous Substances Research Center, Kansas State University
- Center for Environmental Science and Technology, University of Missouri-Rolla
- Department of Agriculture, #99-35106-8244

Effect of Woody Plants on Groundwater Hydrology and Contaminant Concentrations

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James E. Landmeyer, Ph.D., received a B.S. in Geology/Chemistry from Allegheny College in 1989, and a M.S. and Ph.D. in Geology/Microbiology from the University of South Carolina in 1991 and 1995, respectively. He has been employed by the U.S. Geological Survey, Water Resources Division, since 1990, and currently lives in Columbia, SC. His research interests include how microorganisms and plants effect both pristine and contaminated groundwater systems. He has authored or co-authored more than 20 papers.

Abstract

The effect of woody plants on groundwater hydrology and contaminant fate at two sites in South Carolina has been investigated since the late 1990s. At the first site, in 1998 up to 600 poplar trees (*Populus deltoides x Populus nigra* - clone DN-34) were planted at an historically contaminated site near Charleston, SC, currently undergoing significant commercial redevelopment. The trees are now about 14-ft tall, and evidence from excavation activities has confirmed that the roots have grown down to about 1-ft above the water table, located about 4-ft below land surface. In this shallow aquifer, groundwater levels have been monitored using pressure transducers placed in wells near representative trees. In some cases, the lowest daily groundwater level is around noontime, coinciding with the period of peak solar radiation measured by an on-site PAR sensor. This preliminary data provides at least indirect evidence that even the 1-yr old trees were using ground water to meet transpiration demands (less than 0.1 gallons/day/tree). The groundwater level fluctuation evidence is indirect, however, because an adjacent tidally influenced river also can potentially affect groundwater levels. Nonetheless, the Penmann-Montieth equation was used to determine the potential evapotranspiration rate (PET) for these trees, using meteorological data collected at our weather station located on site. As such, a PET rate of 0.55 in/day was estimated. When applied over the total planted area (18,000 ft^2), this PET rate translates to about 2,000 gallons of ground water/soil moisture used per day. Finally, because it has yet to be unequivocally demonstrated that the young poplar trees are indeed removing substantial amounts of ground water from the shallow water table beneath the planted area, observed changes in concentrations of dissolved-phase groundwater contaminants (PAH's and BTEX) in the aquifer cannot yet be attributed to uptake by the trees.

At the second site, we examined the potential for previously established, mature (>40 years old) oak trees *(Quercus virginiana)* growing above a gasoline plume near Beaufort, SC, to take up and remove MTBE and other gasoline compounds from a shallow aquifer contaminated by a leaky underground storage tank. Using material cored from the oaks, MTBE and the conventional gasoline compounds benzene, toluene, ethylbenzene, and the isomers of xylene and trimethylbenzene were detected and identified using purge-and-trap gas chromatography/mass spectrometry methods in the live oaks located above the plume. Conversely, these gasoline compounds were not detected in core material of oaks located outside of the gasoline plume. This detection of gasoline compounds in trees at a contaminated field site is important, particularly for the more soluble and less biodegradable MTBE, because it provides unequivocal field evidence that trees can act as sinks to remove such contaminants from groundwater systems. Moreover, if the uptaken MTBE is volatilized from leaf surfaces, the half-life of MTBE in the atmosphere is orders of magnitude less than the range of half-lives of MTBE under aerobic or anaerobic conditions in contaminated aquifer systems.

Effect of Woody Plants on Ground-Water Hydrology and Contaminant Fate

By

James E. Landmeyer

U.S. Geological Survey

EPA Phyto Meeting, Boston, MA May 2000

Two Field Sites in South Carolina

- Charleston (1998-)
- Beaufort (1997-)

Main Objectives:

- Can we get the poplar trees to grow?
- Do poplar roots reach the water table (2-4 ft below ground)?
- Do the poplars use ground water?
- Do the poplars effect ground-water geochemistry (DO, etc)?
- Do the poplars take up dissolved-phase contaminants (PAHs, BTEX, etc.)?

December 1998 (whip planting)

April 1999 (Beginning of drought)

September 1999

Main Objectives:

- Can poplar trees grow in Charleston?
- Do poplar roots reach the water table (2-4 ft below ground)?
- Do the poplars use ground water?
- Do the poplars effect ground-water geochemistry (DO, etc)?
- Do the poplars take up dissolved-phase contaminants (PAHs, BTEX, etc.)?

Root penetration into or near capillary zone of water table

3’

Average Water Table

Theoretical Approach - Penmann Equation

- **Wind Speed**
- **Air Temperature**
- **Precipitation**
- **Solar Radiation (400-700 nm)**
- **Relative Humidity**

Meterological Station

- -PAR
- -Barometric P
- -Wind speed/direction
- -Air Temp/ Humidity
- -Rainfall
- -Leaf temp/wetness

Located In Poplar Tree Stand

Results for Theoretical Ground-Water Use :

- PET = 0.5 mm/hr (0.5 in/day) For 1-yr old poplars
- 18,000 ft^2 area of poplars planted
- Est. GW use = 2,000 gpd (for 12 hour period)
- Est. GW flux through area = 1,500 gpd
- Need to monitor GW levels!

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science for a changing world

Ground-water level monitoring station

USGS
science for a changing world

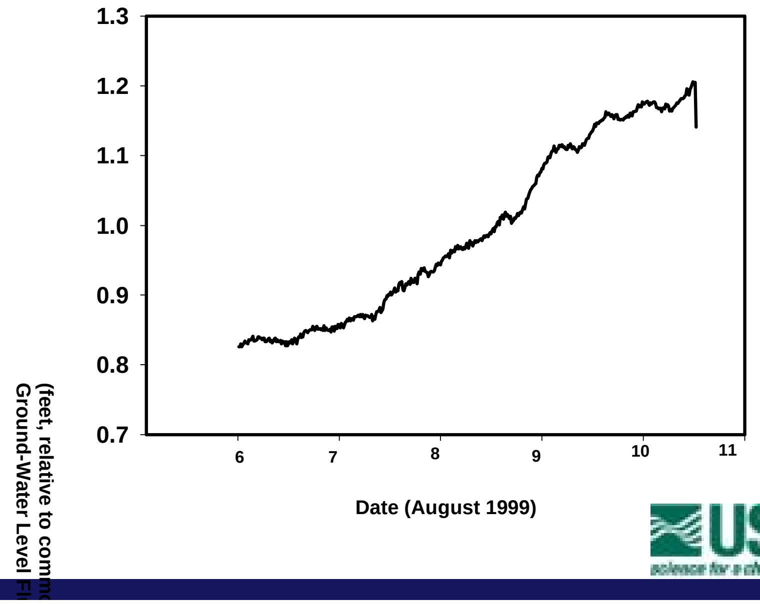
Pumping ground water
from drive-point sampler
Near 1-yr old poplar

Ground-Water Fluctuations

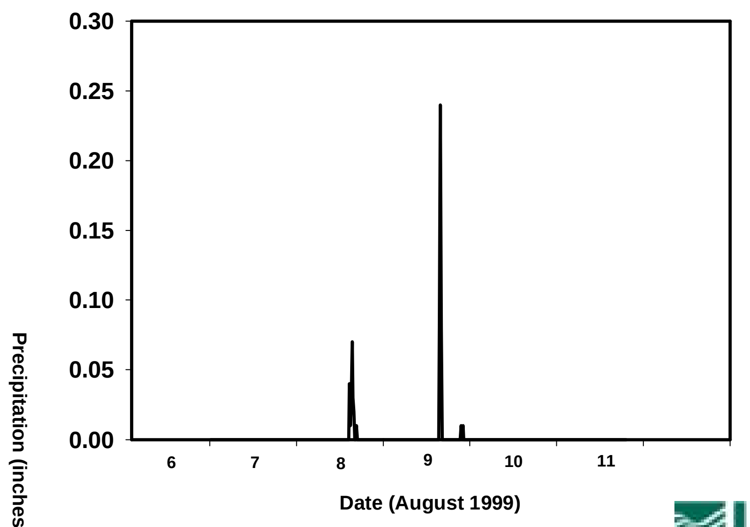
- Early August 1999
- Late August-September 1999

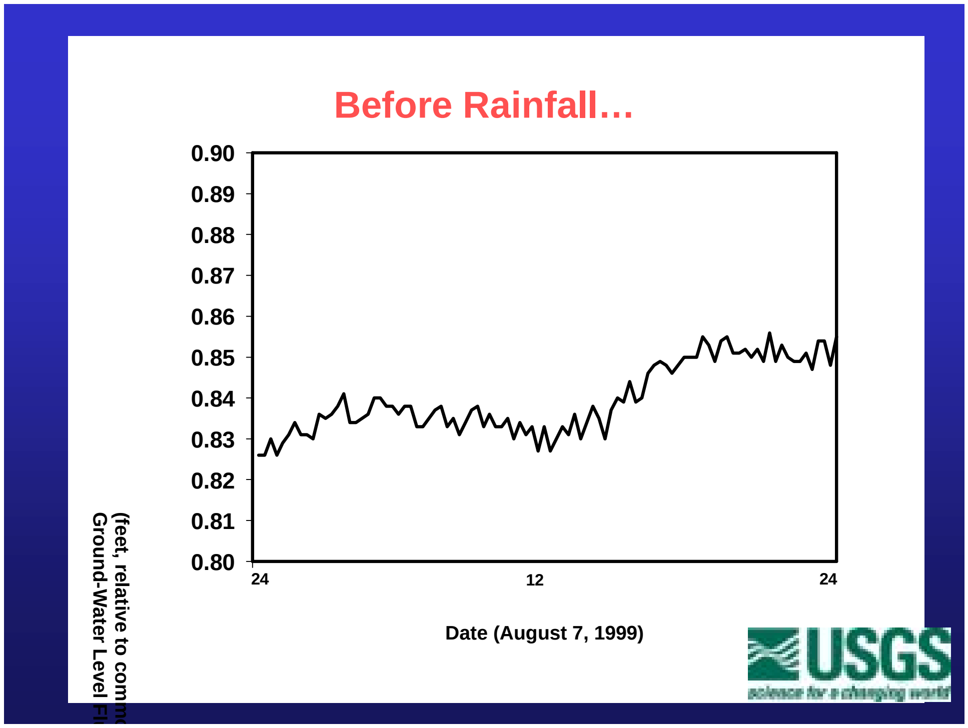
- Early April 2000

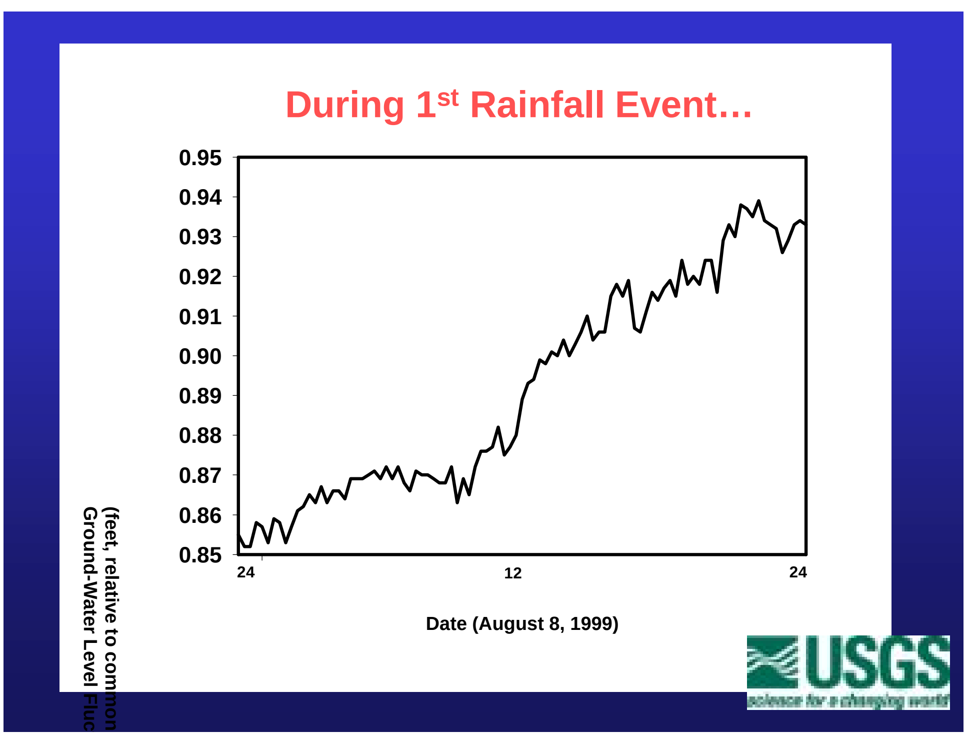
First Time Series of Ground-Water Levels



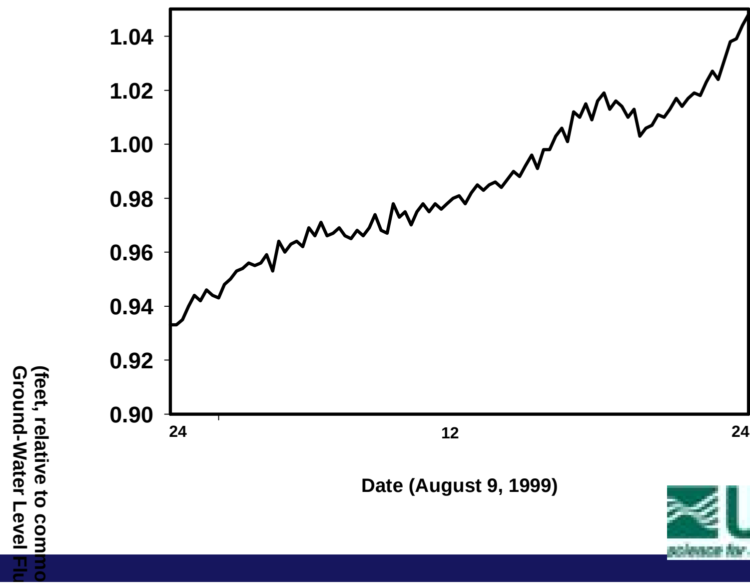
Precipitation




Before Rainfall…
0.90
0.89
0.88
0.87
0.86
0.85
0.84
0.83
0.82
0.81
0.80
24
12
24
Date (August 7, 1999)
Ground-Water Level
(feet, relative to
USGS
science for a changing world


During 1st Rainfall Event…
0.95
0.94
0.93
0.92
0.91
0.90
0.89
0.88
0.87
0.86
0.85
24
12
24
Date (August 8, 1999)
Ground-Water Level
(feet, relative to common
USGS
science for a changing world

During 2nd Rainfall Event…



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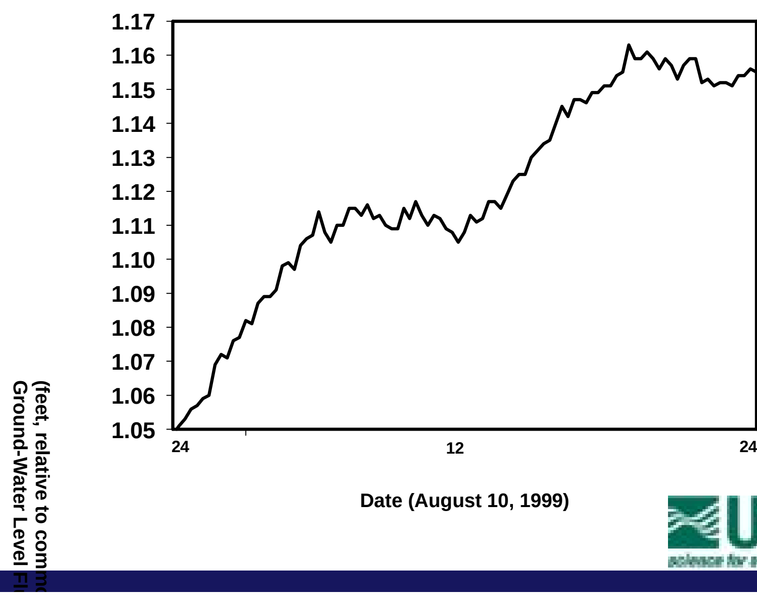
After Rainfall…



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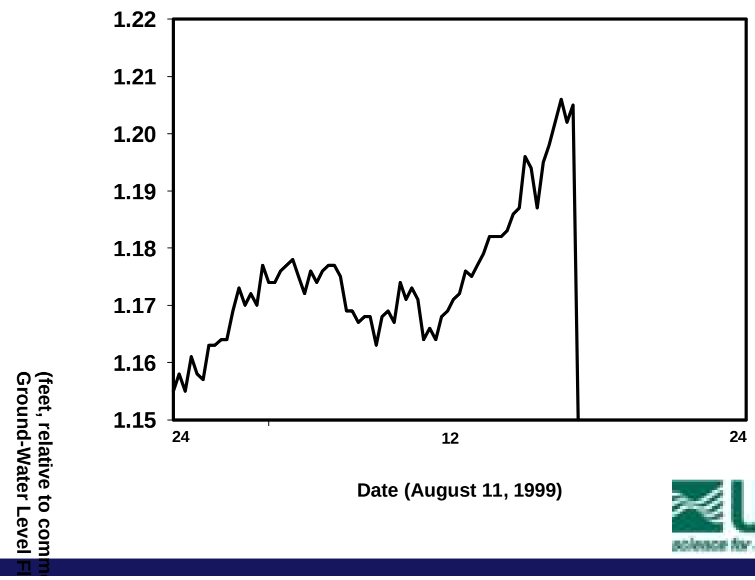
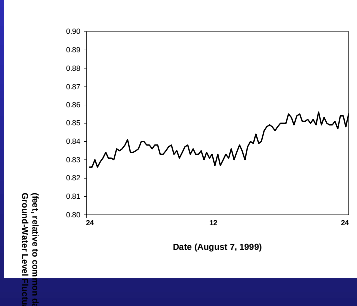
…Removed Transducer

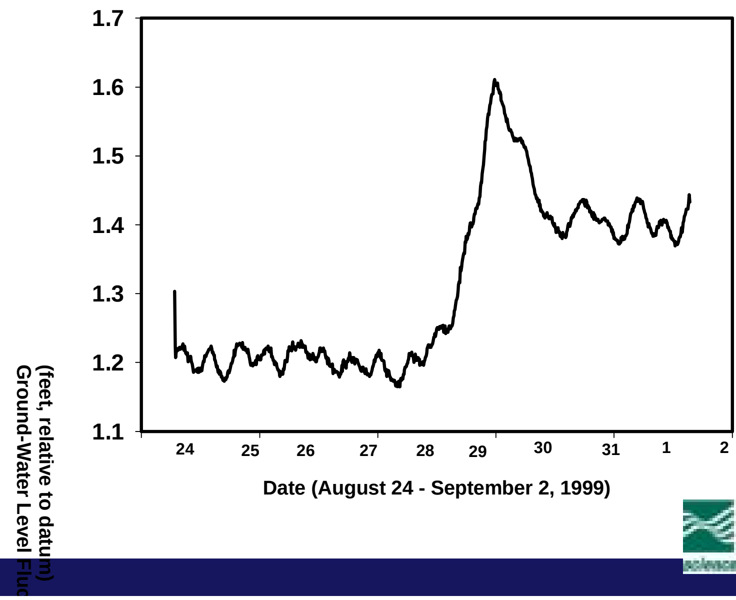


Estimated Ground-Water Use:

- Average Head Change (about 0.12 inches)
- 0.12 inches over 4 ft^2 0.30 porosity
- 0.08 gallons per day per tree
- Q = 0.0002 gpm
- Average specific yield of 8 MW's at site = Less than 0.5 gpm



Second Time Series of Ground-Water Levels



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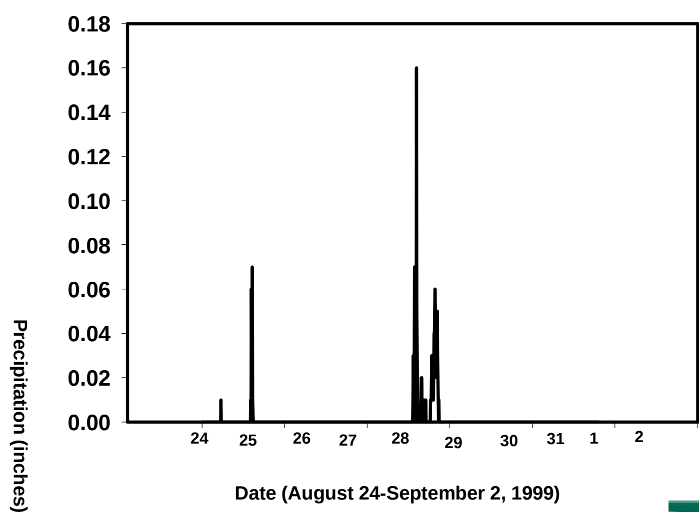
Precipitation



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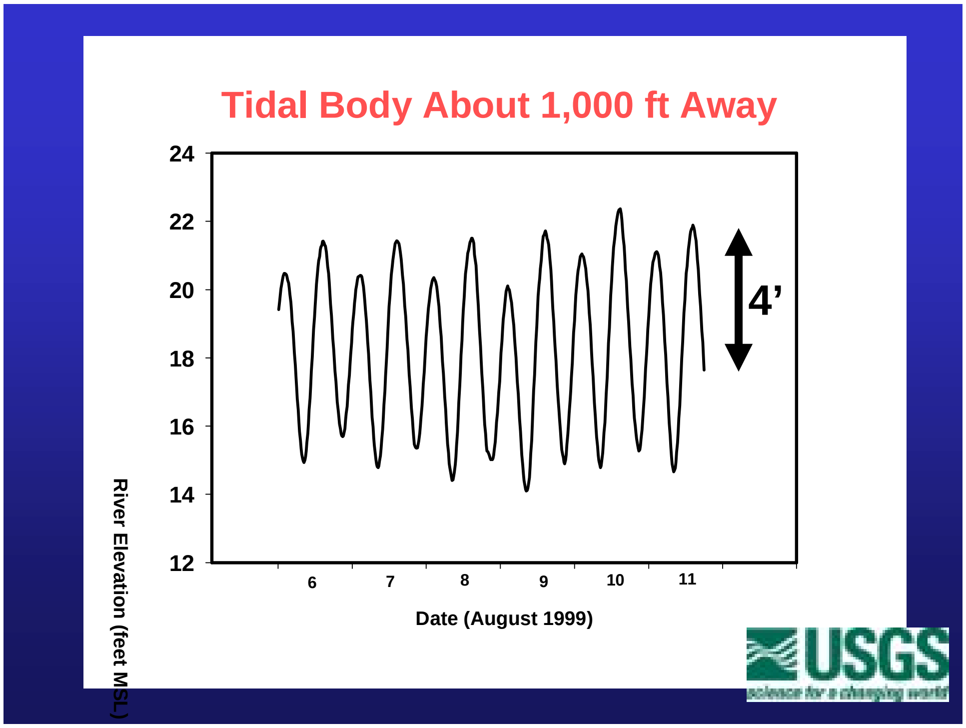
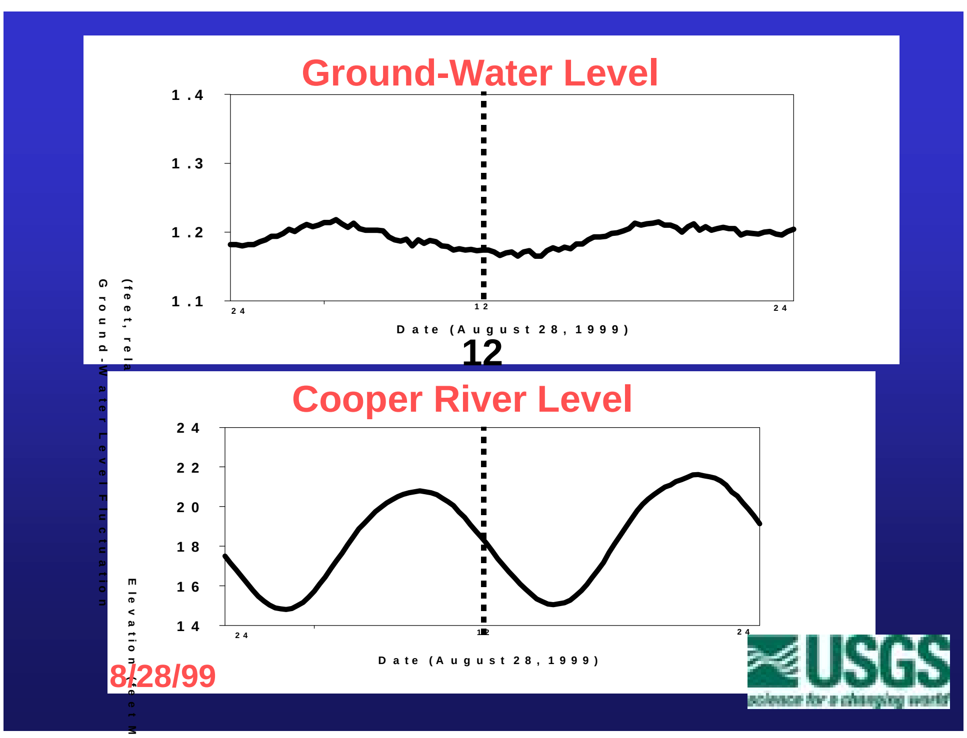
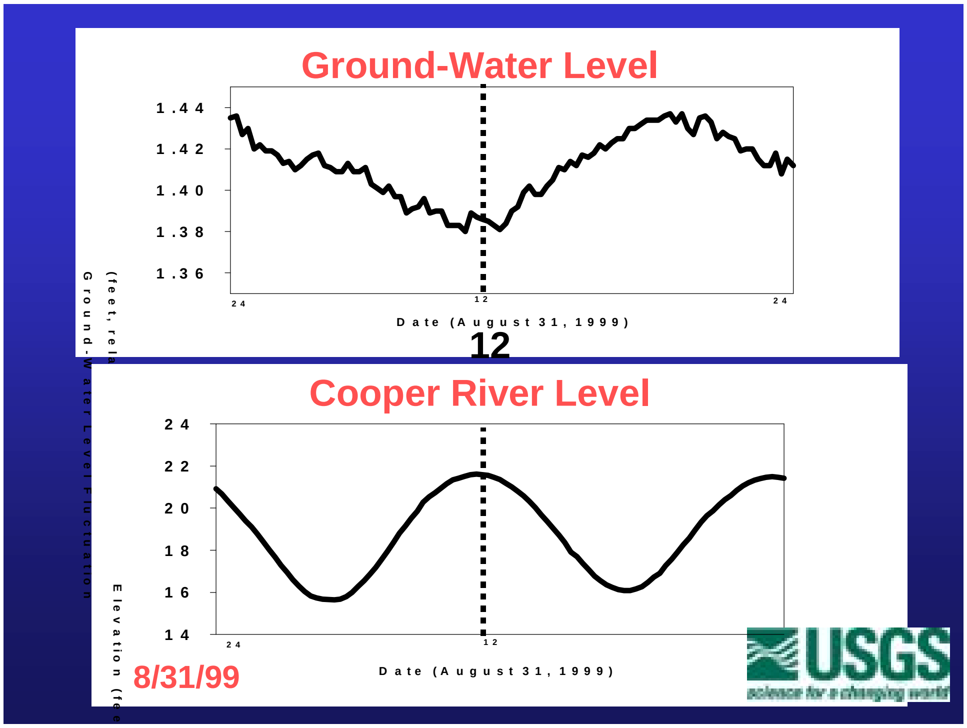
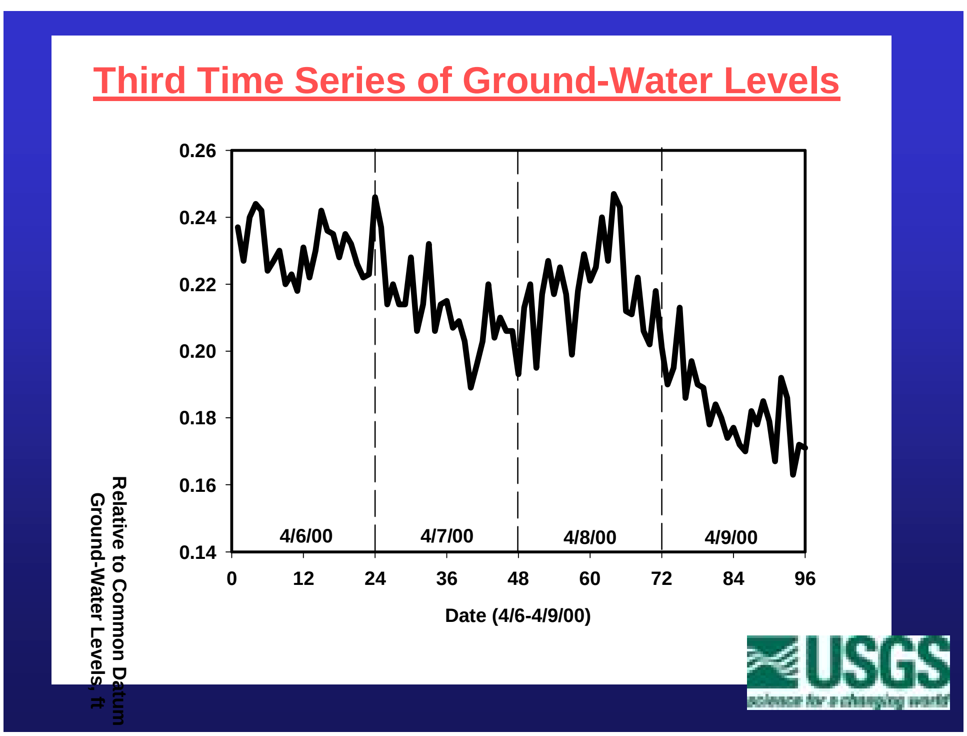

Tidal Body About 1,000 ft Away
24
22
20
18
16
14
12
River Elevation (feet MSL)
6
7
8
9
10
11
Date (August 1999)
4'
USGS
science for a changing world


Ground-Water Level
1.4
1.3
1.2
1.1
24
12
24
Date (August 28, 1999)
12
Cooper River Level
24
22
20
18
16
14
24
12
24
Date (August 28, 1999)
8/28/99
USGS
science for a changing world


Ground-Water Level
1.44
1.42
1.40
1.38
1.36
24
12
24
Date (August 31, 1999)
12
Cooper River Level
24
22
20
18
16
14
24
12
Date (August 31, 1999)
8/31/99
USGS
science for a changing world


Third Time Series of Ground-Water Levels
0.26
0.24
0.22
0.20
0.18
0.16
0.14
4/6/00
4/7/00
4/8/00
4/9/00
0
12
24
36
48
60
72
84
96
Date (4/6-4/9/00)
Ground-Water Levels, ft
Relative to Common Datum
USGS
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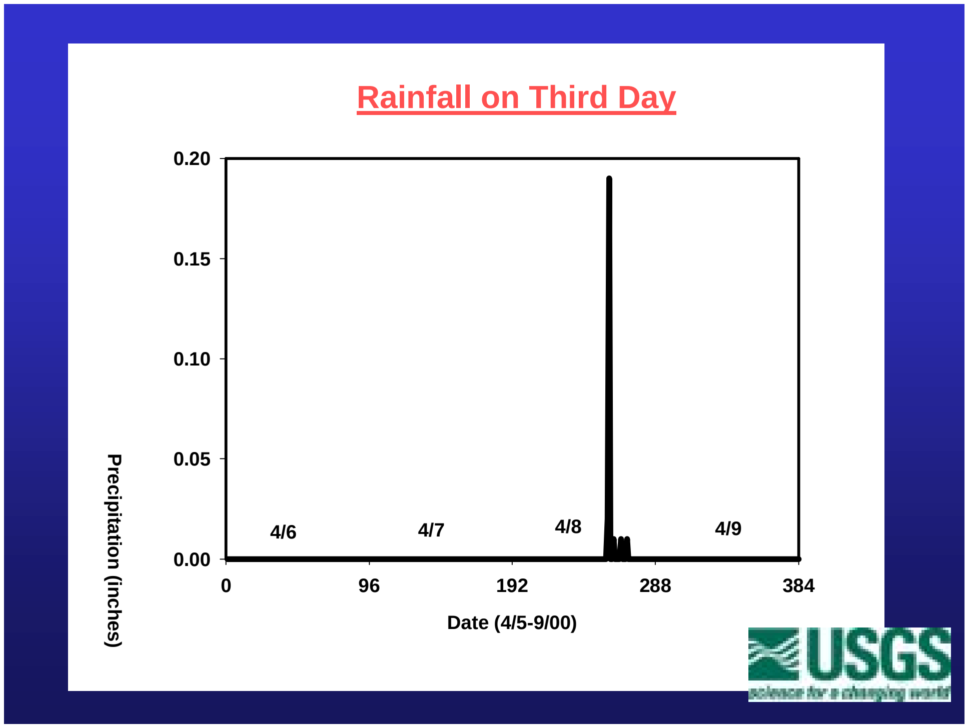
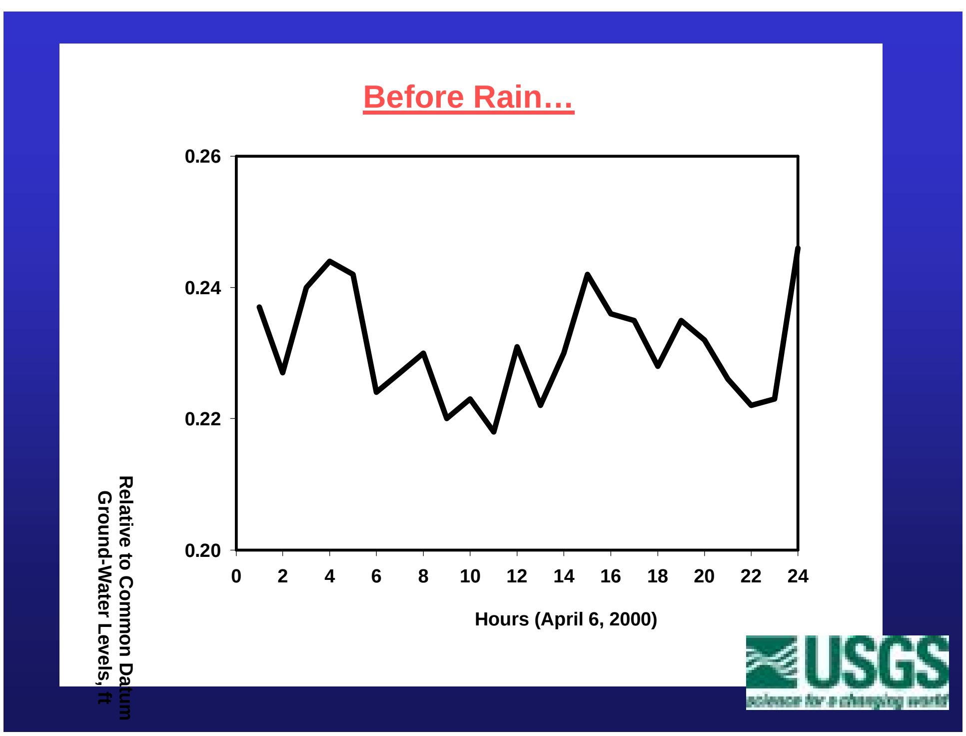
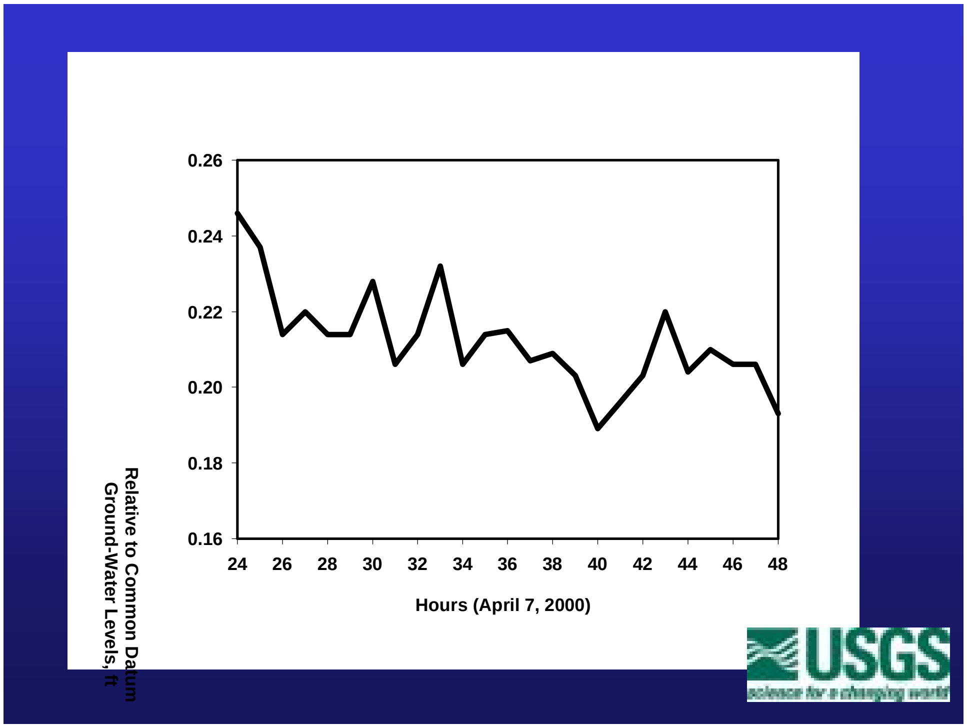
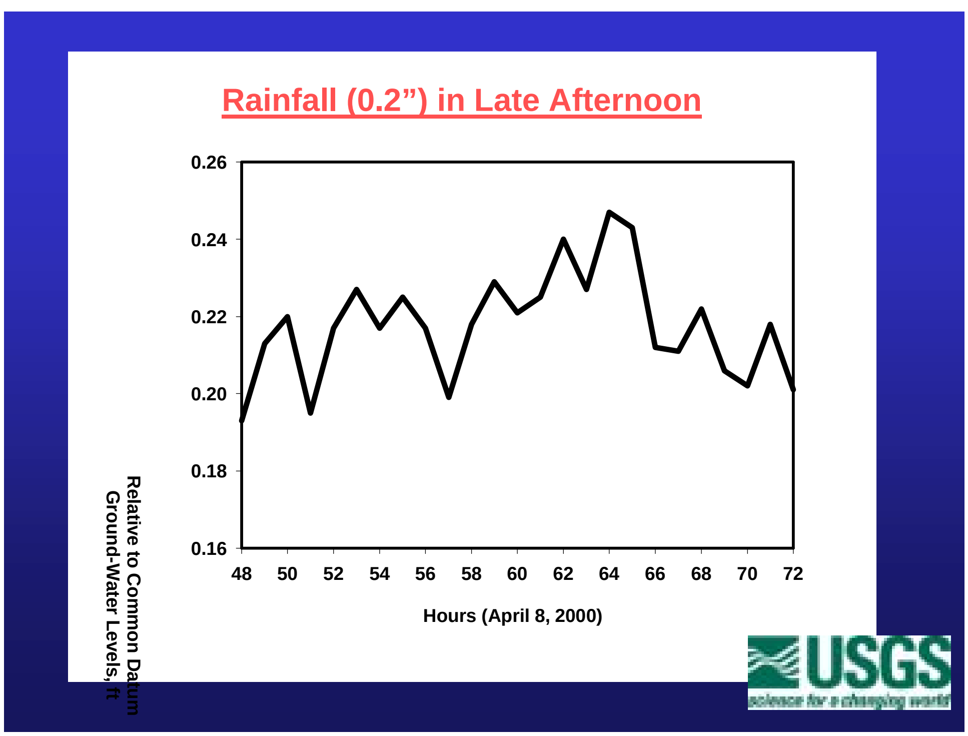
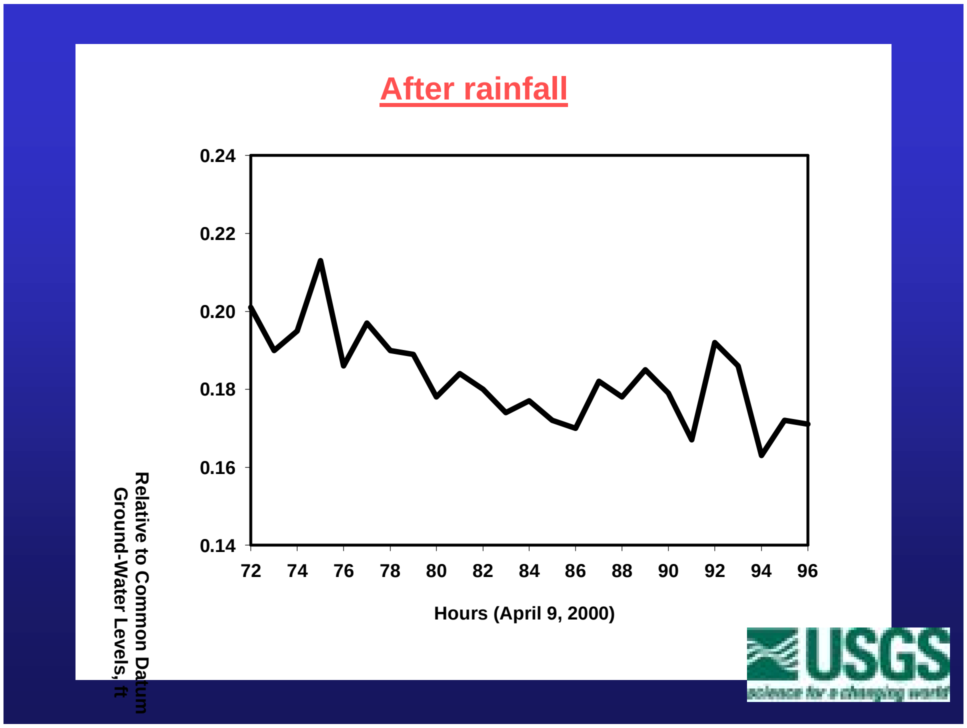
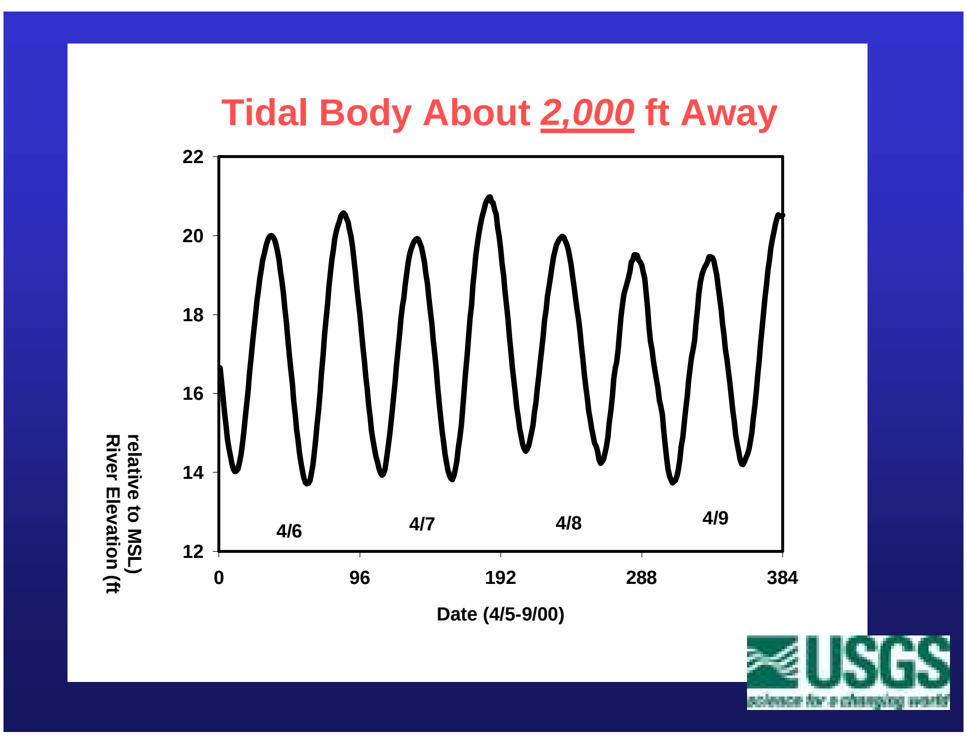

Rainfall on Third Day
0.20
0.15
0.10
0.05
0.00
Precipitation (inches)
4/6
4/7
4/8
4/9
0
96
192
288
384
Date (4/5-9/00)
USGS
science for a changing world

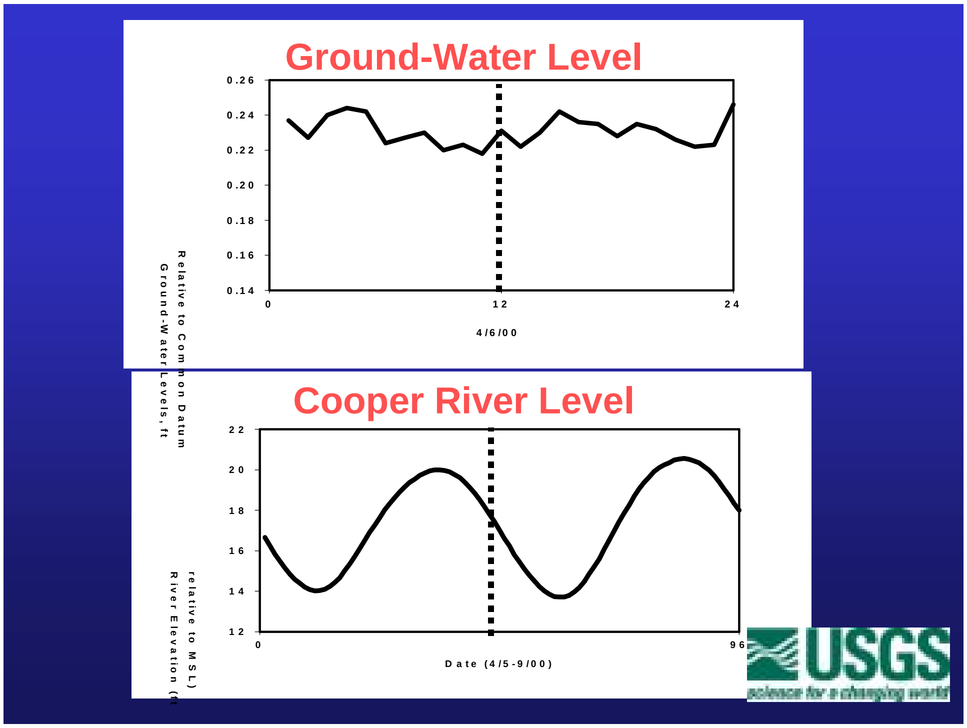

Before Rain…
0.26
0.24
0.22
0.20
Ground-Water Levels, ft
Relative to Common Datum
0
2
4
6
8
10
12
14
16
18
20
22
24
Hours (April 6, 2000)
USGS
science for a changing world

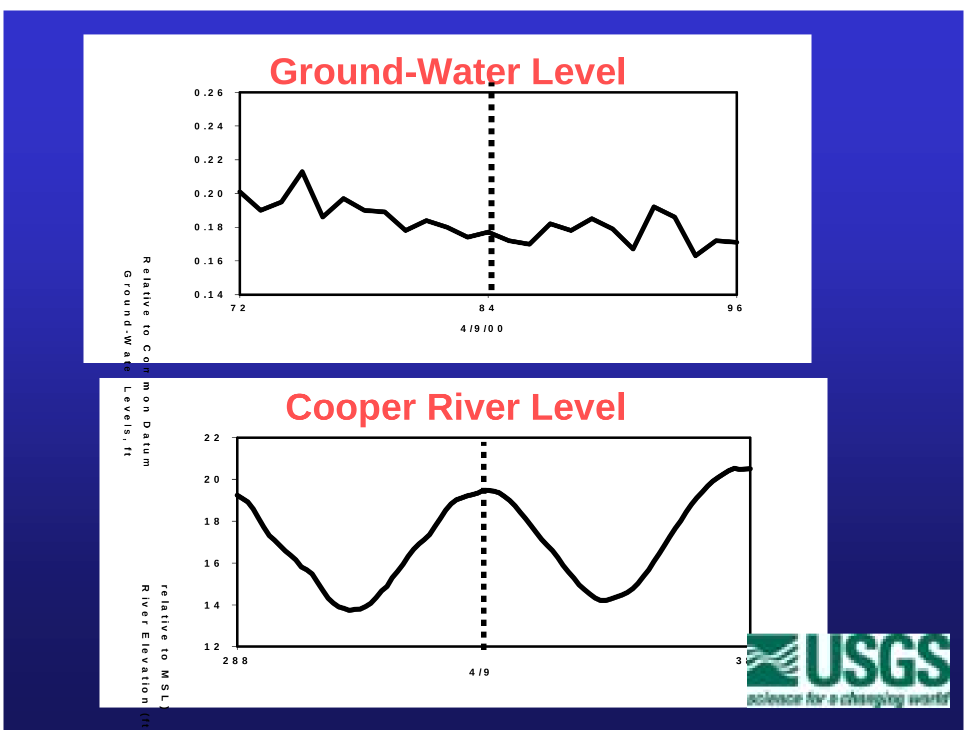

0.26
0.24
0.22
0.20
0.18
0.16
24 26 28 30 32 34 36 38 40 42 44 46 48
Hours (April 7, 2000)
Ground-Water Levels, ft
Relative to Common Datum
USGS
science for a changing world


Rainfall (0.2") in Late Afternoon
0.26
0.24
0.22
0.20
0.18
0.16
48 50 52 54 56 58 60 62 64 66 68 70 72
Hours (April 8, 2000)
Ground-Water Levels, ft
Relative to Common Datum
USGS
science for a changing world


After rainfall
0.24
0.22
0.20
0.18
0.16
0.14
72 74 76 78 80 82 84 86 88 90 92 94 96
Hours (April 9, 2000)
Ground-Water Levels, ft
Relative to Common Datum
USGS
science for a changing world


Tidal Body About 2,000 ft Away
22
20
18
16
14
12
4/6
4/7
4/8
4/9
0 96 192 288 384
Date (4/5-9/00)
River Elevation (ft
relative to MSL)
USGS
science for a changing world


Ground-Water Level
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0
12
24
4/6/00
Ground-Water Levels, ft
Relative to Common Datum
Cooper River Level
22
20
18
16
14
12
0
96
Date (4/5-9/00)
River Elevation
relative to MSL)
science for a changing world


Ground-Water Level
0.26
0.24
0.22
0.20
0.18
0.16
0.14
72
84
96
4/9/00
Relative to Common Datum
Cooper River Level
22
20
18
16
14
12
288
4/9
relative to MSL)
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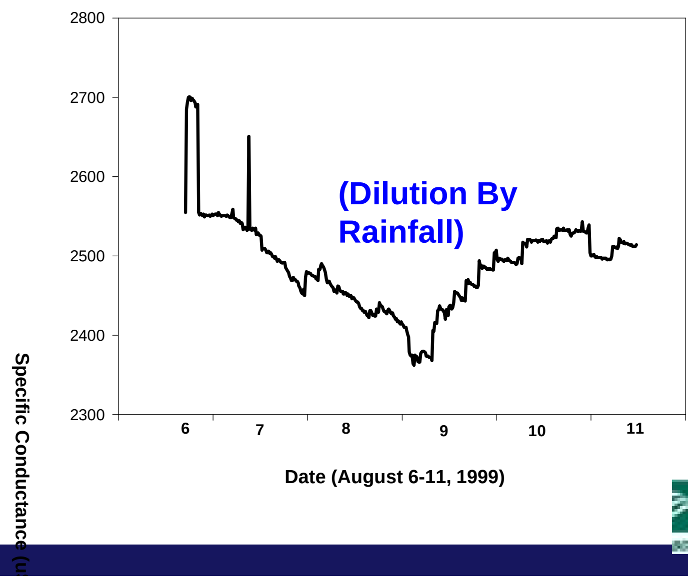
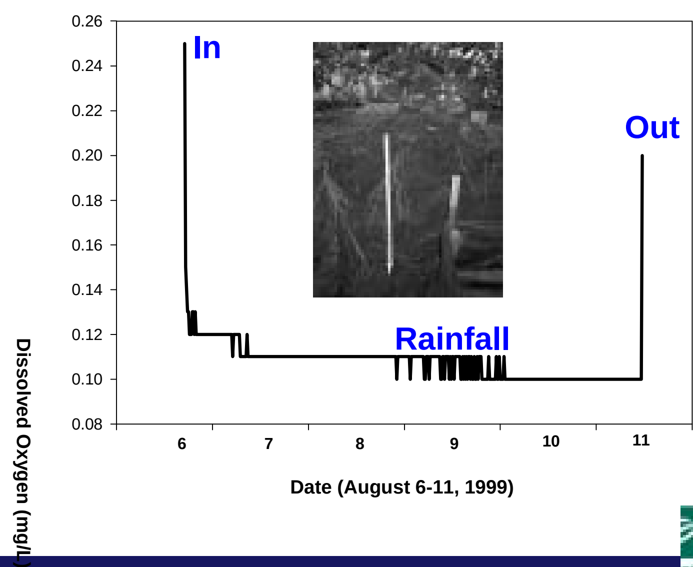
About 600 mg/L Chloride



Dissolved Oxygen (mg/L) in Ground Water



Conclusions at Charleston Site:

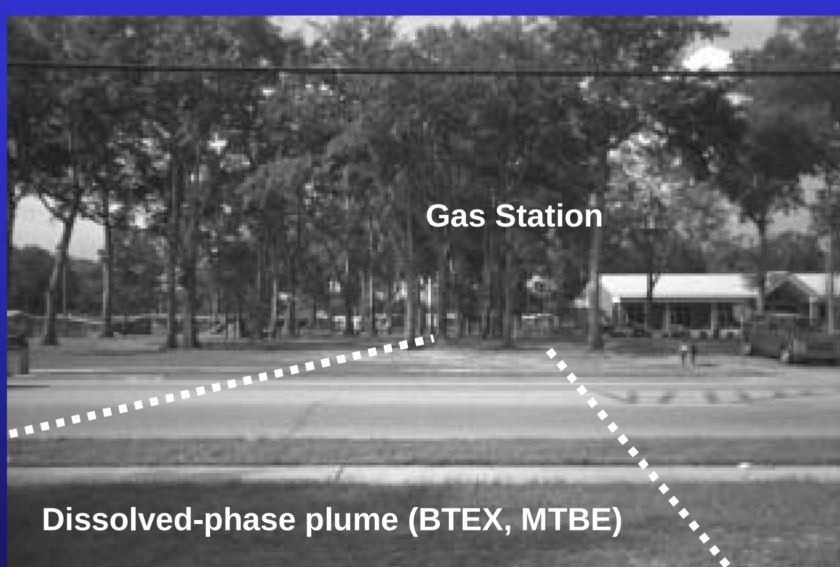
- **Ground-Water Hydrology-**
  - Trees survived drought (*anecdotal*)
  - Some evidence of plant uptake of ground water using transducers
  - Trees were 1 year old; Q=0.0002 gpm
  - No evidence of hydraulic "capture"
  - Tidal influences
  - Sap Flow in 2000

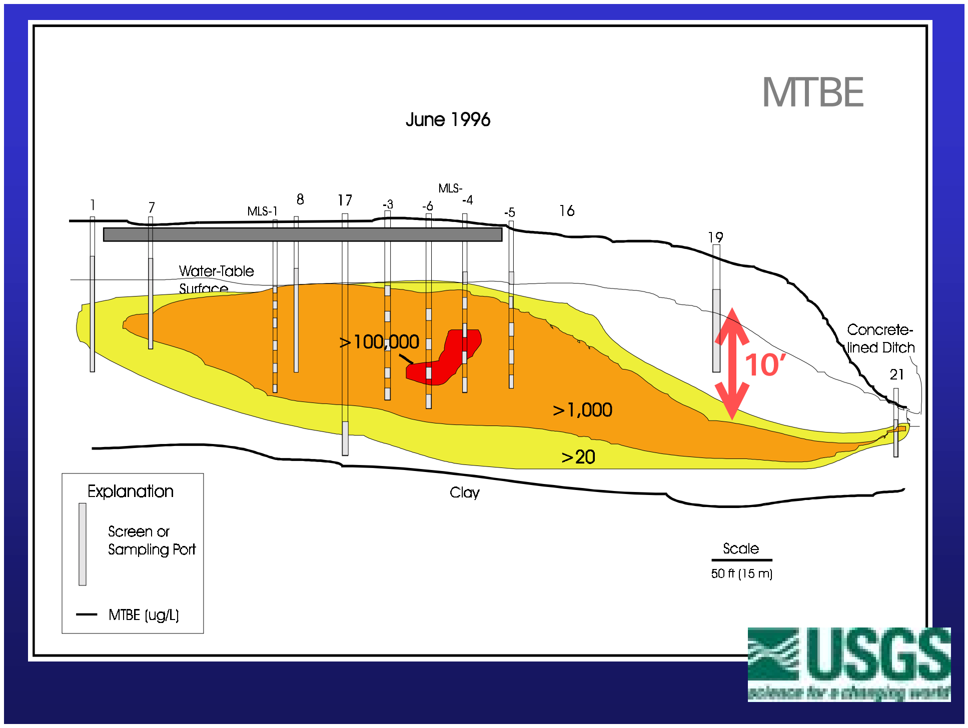
Conclusions at Charleston Site:

- **Contaminant Fate:**
  - PAHs and BTEX in ground water
  - Evidence of some PAHs and BTEX in Tree Leaves using GC/MS
  - BUT, inconclusive at this time if mechanism was by ground-water uptake, b/c of equivocal evidence of ground-water use by 1-yr old trees

Two Field Sites in South Carolina

- Charleston (1998-)
- Beaufort (1997-)





MTBE
June 1996
1
7
MLS-1
8
17
-3
MLS-
-6
-4
-5
16
19
Water-Table Surface
>100,000
10′
Concrete-lined Ditch
21
>1,000
>20
Clay
Explanation
Screen or Sampling Port
MTBE (ug/L)
Scale
50 ft (15 m)
USGS
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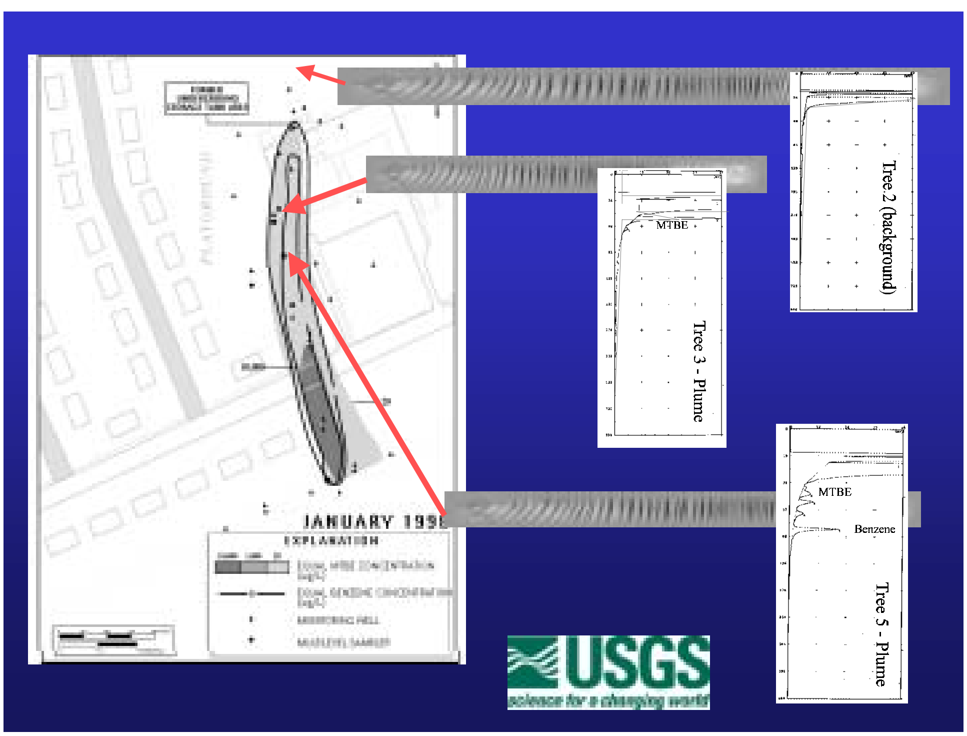

EXPLANATION
MTBE
Tree 2 (background)
Tree 3 - Plume
MTBE
Benzene
Tree 5 - Plume
USGS
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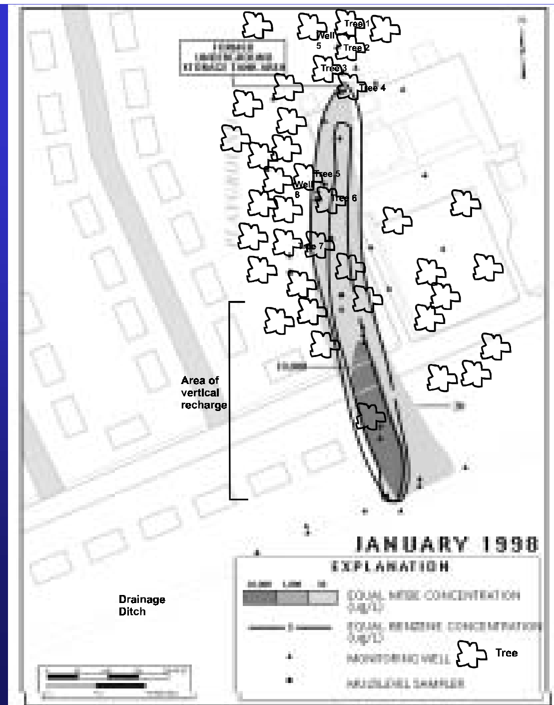
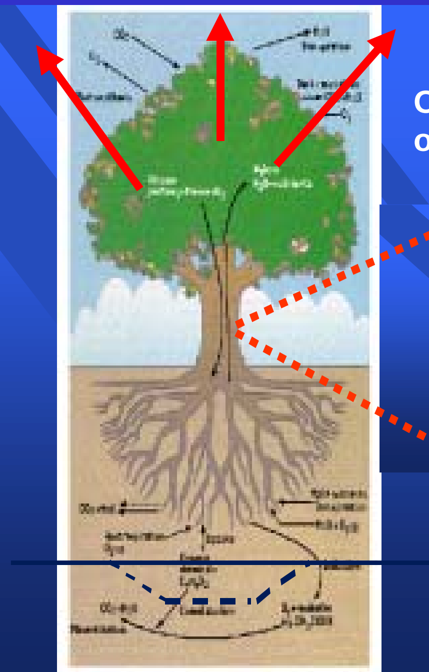
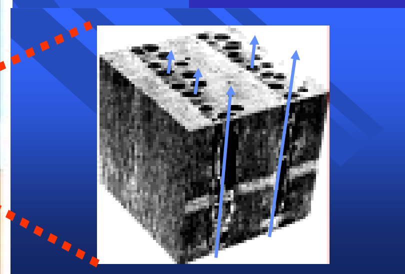


	Upgradient of Former Source Area		Former Source Area I		Dissolved-Phase Plume			Vertical Flow Area
Compound	Tree 1	Tree 2	Tree 3	Tree 4	Tree 5	Tree 6	Well 8 8/1998	Tree 7
MTBE	nd	nd	nd	nd	9.4	54	5,800	nd
Benzene	nd	nd	nd	nd	7.2	4.8	508	nd
Toluene	nd	nd	5.4	nd	26.2	10.1	674	nd
Ethylbenzene	nd	nd	nd	nd	nd	8.5	149	nd
m,p-Xylene	nd	nd	nd	5.0	10.1	10.8	580	nd
o-Xylene	nd	nd	nd	6.3	5.6	7.4		nd
1,3,5-TMB	nd	nd	nd	nd	7.8	6.1	na	nd
1,2,4-TMB	nd	nd	6.0	19.6	5.[illegible]	5.[illegible]	na	nd

(Landmeyer et al., submitted)



Oaks remove 10’s-100’s of gallons of water/day



What about cross-media contaminant transfer?

- MTBE half-life in anaerobic aquifer on order of years

- MTBE half-life in atmosphere on order of hours to days

Conclusions at Beaufort Site:

- Trees take up BTEX and MTBE dissolved in ground water used for ET
- No hydraulic "capture", b/c flow rate is too fast (100+ ft/yr) and ground water too deep (16 ft)

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PLUME CONTROL: SIMULATIONS AND FORECAST

Modeling Plume Capture at Argonne National Laboratory - East

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Argonne National Laboratory
Argonne, IL 60439

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Abstract

Phytoremediation is becoming a viable technology for remediating volatile organic compounds (VOCs) and other contaminants in groundwater and soil. Phreatophytes such as poplars transpire VOCs through their leaves during the growing season, metabolize VOCs in the rhizosphere through the biotic activity of fungi and bacteria growing symbiotically along the roots, and depress water levels in an aquifer by removal of groundwater through transpiration. One technique is the use of engineered systems of hybrid poplars with roots directed to relatively deep aquifers.

In 1999, approximately 450 such poplars were planted in a groundwater remediation project at Argonne National Laboratory-East (ANL-E), near Chicago. Trees were planted in large-diameter boreholes drilled through approximately 30 ft of glacial tills and perched saturated zones to a contaminated sand and gravel unit. The boreholes were lined with plastic and filled with mixtures of topsoil, manure, and sand to constrain the developing roots downward.

Groundwater modeling was performed to evaluate the anticipated effects of the trees on the groundwater flow system. Initially the modeling determined best estimates of input parameters and boundary conditions to provide a suitable match to pre-remedial transient conditions. Then the future effects of mature, deep-rooted hybrid poplars on the flow system were modeled, including transient seasonal effects. Estimates of the transpirative stresses of the poplars were developed to model the month-by-month water use of the developing trees. The modeling suggests that the mature trees will provide containment of groundwater from the upgradient source areas despite the trees' dormant winter periods, and groundwater will have a residence time of 5 to 17 months in the microbially active rhizosphere of the poplars. During the summer, dewatering of portions of the aquifer is likely due to the high water demand of the trees combined with the decreased flux of water into the aquifer.

Introduction

Phytoremediation offers the potential for remediating groundwater and soil with the following benefits: reasonably low installation cost, remediation within a suitable time frame, low operation and maintenance costs, aesthetic value, low ecological impact, and public approval.

In the last decade, hybrid poplars have been studied to determine their ability to remove or destroy contaminants such as volatile organic compounds (VOCs). Other advantages of using poplars in certain phytoremediation systems include their fast growth rates and their ability to use vast amounts of water. Poplars can achieve growth rates as high as 10 to 16 ft/yr (3 to 5 m/yr) (Chappell, 1998). While they can transpire tremendous amounts of water (Nyer and Gatliff, 1996), the rate varies, depending on climatic factors and tree density (Chappell 1998). Their ability to lower the water table indicates that they have the potential to provide groundwater containment (Nyer and Gatliff, 1996; Compton et al., 1998; Newman et al., 1999).

Poplars are phreatophytes; they extend their roots into the capillary fringe and can survive periods of being within the saturated zone of an aquifer as water levels fluctuate. Because phreatophytes send roots into both the vadose and phreatic zones, they have the potential to remediate soil, groundwater, and saturated soil media. In terms of total root length, a stand of poplars may have as much as 75,000 miles per acre (300,000 krn per hectare) (Gordon et al., 1997). The subsurface may consist of units of widely varying lateral or vertical extent, with gradational or sharp transitions in permeability. The fibrous nature of the roots allows the trees to penetrate and remediate both the relatively fast-flowing pore spaces and the less permeable zones. Fundamentally, this distinguishes phytoremediation from extraction wells, which remove water mainly from the most permeable aquifer media (Gatliff, 1994).

Groundwater modeling was performed in support of a large-scale phytoremediation project. The modeling focused on evaluating the seasonal containment capability of a deep-rooted hybrid poplar phytoremediation system installed at Argonne National Laboratory (ANL) in June 1999. The study included a detailed analysis of subsurface hydrogeological conditions, seasonal hydrologic changes, and the seasonality of the phytoremediation system. Animated visualizations were generated to facilitate understanding the results. The large-scale program and the complexity of the subsurface make the site challenging in terms of understanding its history, hydrogeology, seasonality, and implementation of the remedial technology.

Study Area

Past waste disposal practices at the 317 and 319 Areas at ANL near Chicago, Illinois have resulted in the presence of VOCs and tritium in groundwater. Historical groundwater VOC concentrations near the 317 French Drain have been in the thousands and ten of thousands of parts per billion. Contaminants are transported off the ANL property at fairly low concentrations and appear at several seeps in ravines of adjacent forest preserve property. In 1999, a groundwater and soil treatment program was initiated that relies on phytoremediation to (1) provide hydraulic containment in the aquifer of concern, (2) extract and transpire contaminants, (3) incorporate and/or degrade the contaminants in the biomass, and (4) cometabolize VOCs in the root zone. More than 800 trees were planted in the summer of 1999 to achieve these goals. Willows were generally planted at the surface in areas of contaminated soil. Four hundred twenty poplars were specially installed using TreeWellTm technology. These trees were planted in 2-ft (0.6 m) diameter caisson boreholes lined with plastic sleeves in order to direct the roots to the main contaminated aquifer, exclude shallow groundwater, and optimize deep groundwater removal efficiency. This technology was necessary for implementing the phytoremediation system because of the site's hydrogeological setting. The boreholes were filled with a mixture of topsoil, sand, peat, and manure to promote root growth and tree development.

The study focused on modeling the predicted effect of the engineered deployment of the 420 specially installed poplars with roots directed to a confined aquifer 25 to 30 ft (8 to 9 m) deep. An additional 389 surficially planted willows and poplars were not included in the analysis because their purpose is to remediate contaminated soil or shallow groundwater that is essentially separated from the aquifer of interest.

Hydrogeological Setting And Conceptual Flow Model

The subsurface is a complex arrangement of approximately 60 ft (18 m) of glacial geologic deposits over Silurian dolomite bedrock. The glacial sequence is composed of Lemont Drift overlain by the Wadsworth Formation. Both units are dominated by fine-grained, low-permeability till. Permeable zones of varying character and thickness are present in each. These materials range from silty sands, to sandy, clayey gravels, to gravelly sands. In some locations, pure silt is encountered. If deep enough, this silt is saturated and assumed to play an important role in the flow of groundwater in the study area. The permeable zones vary widely in shape, including thin, lenticular, alluvial deposits; thick plugs of possible slump or channel-fill material; interfingerings; and a thick, basal, proglacial sand and gravel. In general, the permeable units are poorly sorted, and many of them may represent slope-induced mass movement, which results in transport and mixing of sediments (e.g., Lawson, 1982). Their thicknesses range from less than 1 ft (0.3 m) to roughly 15 ft (4.5 m), and they have limited lateral extent.

The modeling was focused on phytoremediation efforts directed at the site's main contaminated aquifer. Over 75 continuously sampled boreholes give an indication of the structure of this unit. The depth to the top of this unit ranges from 22 to 28 ft (6.7 to 8.5 m) in the 317 French Drain area, to 22 to 34 ft (6.7 to 10.4 m) at the southern edge of the ANL site. Because its top and bottom surfaces vary spatially, its thickness is variable. The unit has been delineated on the basis of stratigraphy, a southeast trend in head data, and, where available, contaminant tracer data. This "aquifer" is best described as consisting of numerous permeable bodies of varying character and geometry that share some similarity in depth and that have some degree of hydraulic connection. The aquifer is not present everywhere, and in some locations, the stratigraphic data may not support the presence of an aquifer within a reasonable depth interval.

On the basis of the southeast trend in water levels, while considering stratigraphic and well construction information, 23 monitoring wells with up to 10 years of seasonal head data were assumed to represent the main aquifer of interest and, therefore, were useful in calibrating the transient flow model.

The conceptual model of groundwater flow is as follows. Groundwater in the aquifer is, in general, confined and flows to the southeast. This finding is supported by historical head measurements and is in keeping with the notion of regional flow mimicking the topography and flowing toward the Des Plaines River valley to the southeast. The aquifer of interest is assumed to receive input from upgradient sandy units to the northwest and from infiltration from above. The recharge from infiltration may be localized and originates as seepage from shallower perched aquifers or directly from precipitation and conveyed by fractures within the overlying till. Recharge to the dolomite aquifer beneath ANL has been estimated by Walton (1965), who suggested a value of 3.3 in./yr (8.3 cm/yr). At the site scale, however, surficial recharge to the aquifer of interest is likely to be less than this value because of the predominance of low-permeability till units at the surface.

Hydraulic conductivity estimates are available in the form of a pump test and 12 slug tests. The pump test data indicated a range of 4.4 to 10.5 ft/d (1.6 x 10-3to 3.7 x 10"' cm/s), or an average of 8.8 ft/d (3 x 10-3 cm/s). Slug tests in the 12 appropriate monitoring wells indicate values of 0.011 to 170 ft/d (4 x 10-6to 6 x 10"' cm/s), with an average of 10.8 ft/d (3.8 x 10-3cm/s). The slug tests indicate variable permeability across the site, without any trend. The permeability likely varies greatly over extremely short distances.

Most groundwater in the aquifer of interest travels southeast to the forest preserve where it discharges as seepage, either in the deep portions of the ravines or along the base of the main bluff of the Des Plaines valley. The seepage along the bluff is expected to be transient, and it may consist of a combination of localized, flowing seeps and broad, diffuse seepage that is subject to transpiration and evaporation. A minimal amount of this groundwater may recharge the dolomite aquifer.

Natural Transient Conditions

Modeling Approach

The U.S. Geological Survey finite-difference code MODFLOW (McDonald and Harbaugh, 1988) was selected because of its capability to address steady-state and transient flow, varying upper and lower aquifer surfaces, and aquifer 'input and output. MODFLOW has efficient solvers, and the code includes the capability of rewetting model cells that have been dewatered (McDonald et al., 1991). To analyze and display the rate of groundwater movement, MODPATH (Pollock, 1994) was used in combination with MODFLOW flow output.

A discussion of the modeling domain and boundary conditions may be found in Quinn et al. (2000). Cells in the computational grid were a uniform 10 ft x 10 ft (3 m x 3 m); the thickness varied according to the spatially irregular upper and lower surfaces of the permeable zone. This grid spacing was small relative to the distances between monitoring wells to provide high resolution of results in the modeling domain. The design allowed the placement of each tree into a model cell at any reasonable tree spacing.

Results

Calibration was achieved by striving to match not only the target heads from the monitoring well network, but also discharge measurements at the contaminated seeps. A discussion of the steady state and transient calibration methods and resulting parameter values may be found in Quinn et al. (2000). Animations of the calibrated natural transient flowfield may be viewed at *http://web.ead.anl.gov/Phyto*

Prediction Of Effect Of Mature Phytoremediation System

Modeling Approach

The calibrated transient flow model was then used to model the effect of the phytoremediation on the groundwater flow system. The modeling covered a period of six years. The initial three years simulated the effect over the plantation's development; the following three years modeled the first three years of the mature plantations, when the canopies have closed together and water consumption is maximized. The trees, which are planted on 16-ft (4.9-m) centers, were each placed in an individual model cell. Because of the difference in the model cell spacing compared with the tree spacing, the tree locations did not appear as orderly as their actual locations; however, for the purposes of the model, they were accurately placed. To model the trees' pumping effect, the variable recharge and upgradient boundary condition were used, as described above. The leaf-on period was assumed to be six months, from April through September, with water use rates assigned as tabulated. The rates are conservative estimates derived on the basis of studies of phreatophytes, such as poplar, willow, and tamarisk (Fletcher and Elmendorf, 1955; Robinson, 1964), and on literature values for water use by another phreatrophyte, alfalfa (Jensen, Burman, and Allen, 1990). These estimates are also supported by experience with the luxury water consumption conditions that are expected to occur at the site. The tabulated water usage is similar to the range found in studies of poplars in various growing conditions (Wullschleger, Meinzer, and Vertessy, 1998; Hinckley et al., 1994).

The tabulated maximum transpiration was attainable when the head in a model cell was at or above the top of the aquifer. Transpiration decreased linearly with decreasing head to a cutoff depth, which was assigned as the midpoint of each model cell containing a tree.

Results

Calculations indicated a significant, seasonal effect on groundwater flow caused by the trees. The influence of the trees was apparent as early as the summer of the second year (2001). Attached figures illustrate representative results for a low-head period resulting from transpiration of mature trees and decreases in seasonal flux (e.g., September of the fourth year, 2003) and for a high-head period resulting from recharge of the aquifer (e.g., April of the fifth year, 2004), respectively. Animations of the results are available at *http://web.ead.anl.gov/Phyto*. The animations allow visualization of the changes occurring in each month of the three years of tree development and in the first three years of maturity. The heads and the sizes of the dewatered areas in years 4 through 6 are essentially the same, which indicates that the pumping effects of the plantations are not cumulative, but rather that the mature phytoremedation system maintains the same cycle of change each year.

Because the penetration depth of roots is limited in the model, dewatering of a given model cell is not caused by a tree that may be in the cell, but by cumulative transpirative stresses that lower the water table to the elevation of the bottom of the aquifer. These dewatered areas are depicted in the figures as areas bounded by polygons. The onset of dewatering coincides with the highest elevations in the bottom surface of the aquifer. Rewetting of many of the dewatered model cells occurred during recharge periods (e.g., November through April).

A particle tracking analysis was performed to evaluate the hydraulic capture potential of the plantations and to determine the residence time of contaminated groundwater in the microbially active rhizosphere created by the poplars' roots and associated microbes. Particle starting locations were set to the center depth of the aquifer of interest along the upgradient edges of the plantations. Starting times for particles were in January 2000, which coincides with the beginning of the six-year simulation period. The results indicate that the trees provide a large degree of hydraulic containment. In the 317 Area, most of the particles are captured; however, one particle trace skirts the edge of the 317 Area trees before essentially stagnating east of the plantation. In the 319 Area, most groundwater is captured. A small portion escapes because of the gap in the plantation along a deep, steeply banked surface drainage. The trend of this drainage happens to be aligned with the overall groundwater flow direction. Monitoring of heads over the next few years will indicate whether containment is being achieved, and whether the system should be modified with additional deep-rooted poplars.

Inflections along the particle traces indicated the response of the flow system to changes in the transpirative stresses and to changes in the seasonal inputs to the system. The monthly particle locations showed variable spacing, which represents relatively slower movement of groundwater during natural gradient periods (i. e., leaf-off) and relatively faster flow during pumping periods (i. e., leaf-on).

The monthly particle locations may be used to estimate the residence time of groundwater in the microbially active rhizosphere. Particles started north of the main 317 planting area are in the rhizosphere approximately 6 to 24 months before being withdrawn by the plants. In the 319 Area, particles started north of the planting area are either removed after 3 to 10 months, or may pass through the remediation system. Those particles that escape have residence times of approximately 10 months in the rhizosphere of the 319 plantation. The range in these estimates is due to numerous factors: the spatially variable saturated thickness of the aquifer, the seasonal changes in groundwater flux into the system, the seasonal leaf-on and leaf-off periods, and the composite pumping effect of nearby trees.

Summary And Conclusions

This study demonstrates the usefulness of numerical groundwater modeling in addressing several issues pertaining to the design or evaluation of a phytoremediation system that relies on phreatophytes. While uptake or destruction of contaminants is not explicitly addressed, the engineered system of deep-rooted poplars was predicted to provide a large degree of hydraulic control, despite seasonal variation in water use rates by the plantation. The results indicated areas that are typically dewatered because of high seasonal water use and irregular aquifer geometry; this information may be useful in the future for explaining possible different rates of tree development across the planting areas. Modeling clearly has application at phytoremediation sites for evaluating or designing a containment system with respect to factors such as tree planting density, plume width versus groundwater flow rate, seasonal effects, residence time of groundwater within the microbially active rhizosphere, prediction of regions where seasonal dewatering may occur, and future modifications to the system design to improve the likelihood of hydraulic capture.

Future analysis at the ANL site will include a comparison of model results with measured water use by trees and measured water levels. An improved understanding of root development (i.e., lateral and downward growth) will provide a better conceptualization and implementation of roots in numerical models.

Acknowledgment

Work supported by the U-S. Department of Energy, Office of Environmental Management, under contract W-31-109-ENG-38.

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Modeling Plume Capture at ANL-E

An Analysis of the Effect of the Argonne Phytoremediation System on Groundwater Flow

John J. Quinn
Argonne National Laboratory
Argonne, IL

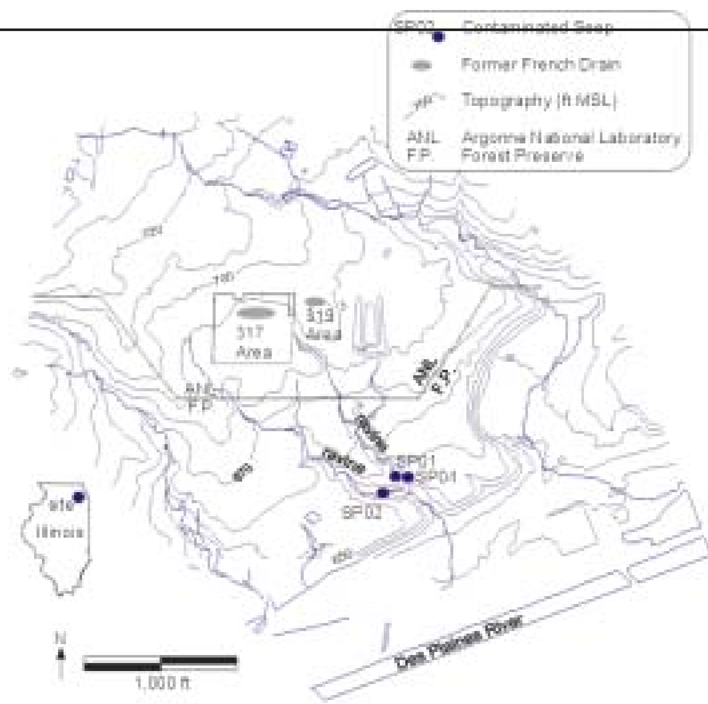
Work supported by the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, under contract W-31-109-ENG-38.

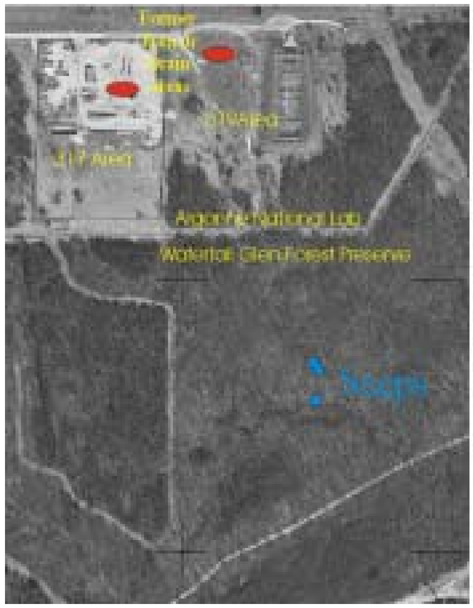
Phreatophytes (poplar and willow) useful in some settings

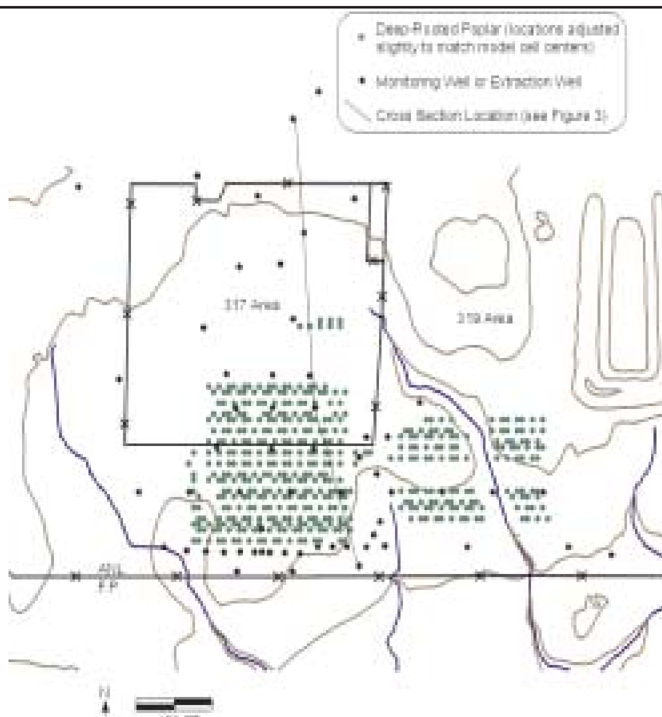
- Transpire contaminants (VOCs, tritium)
- metabolize VOCs in rhizosphere
- degradation within the plant
- depress water table --> containment

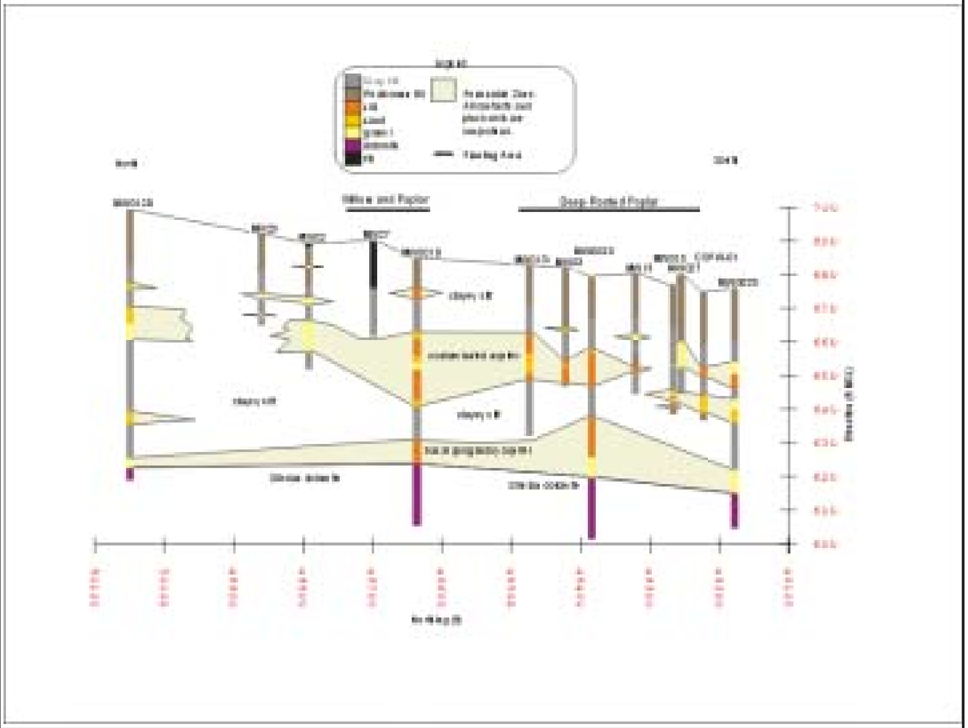
Study Area:
Argonne National Laboratory
317/319 Area

- Prior waste disposal area (french drains, rad waste vaults, landfill)
- contaminants of concern are solvents and tritium




317 Area
Argonne National Lab
Waterfall Glen Forest Preserve

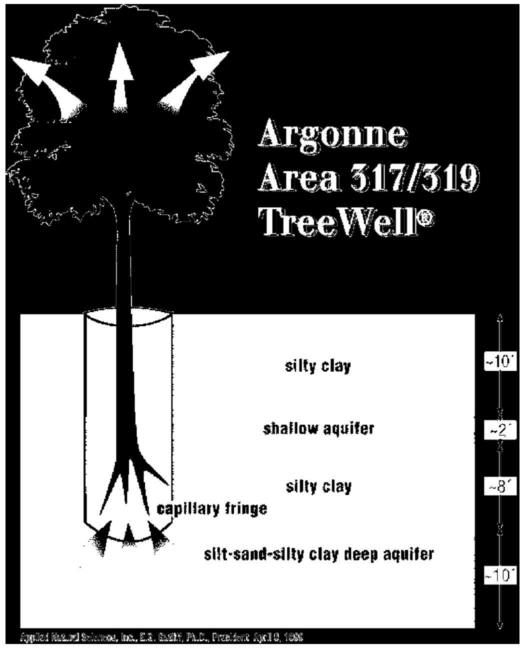

Deep-Rooted Poplar (locations adjusted slightly to match model cell centers)
Monitoring Well or Extraction Well
Cross Section Location (see Figure 3)
317 Area
319 Area
N
150 FT



Problem: contaminants 30 feet deep

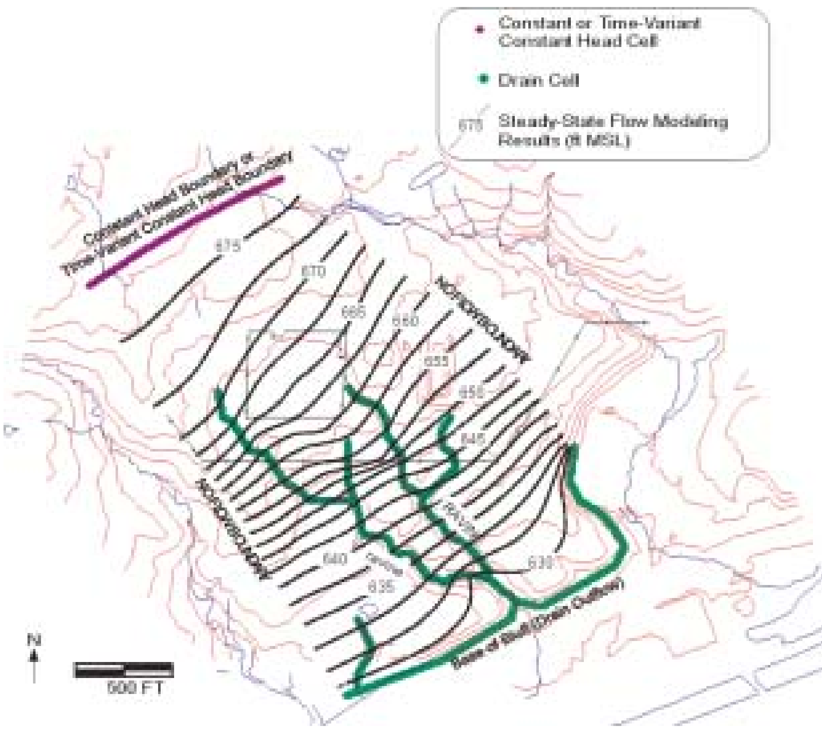
Solution: engineered phytoremediation system

- 389 willows and poplars planted at or near the surface
- 420 specially installed poplars (roots directed to target aquifer)



Evaluation of Effect of Phytoremediation System on Groundwater Flow

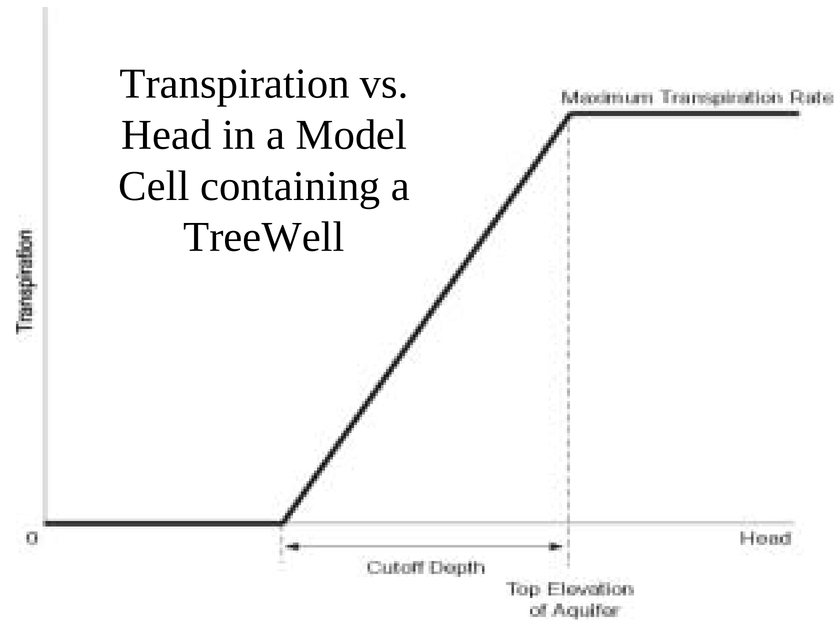
- focus on aquifer of interest
- ignore shallower perched system
- calibrate initial transient model to the pre-phytoremediation flow field



Estimated Water Use for Developing Plantation

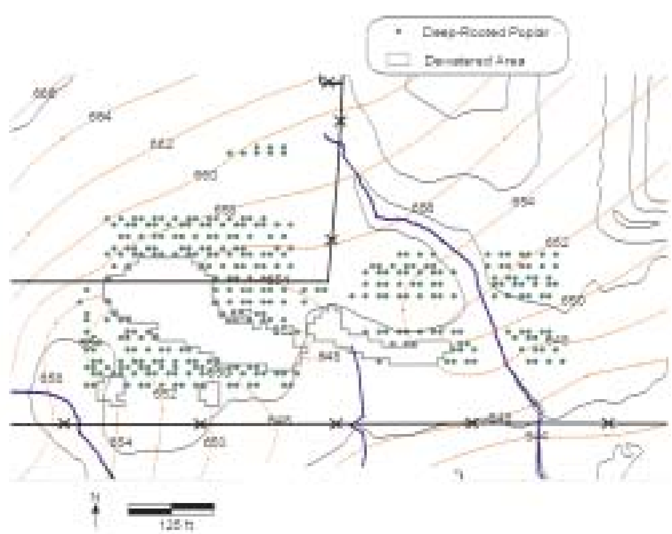
	ANL tree water use rates (at 174 trees/acre)											
	jan	feb	mar	apr	may	june	july	aug	sept	oct	nov	dec
year 0 (1999)	0	0	0	0	0	0	2	3	2	1	0	0
year 1 (2000)	0	0	0	0	2	8.75	12.5	12.5	8.75	2	0	0
year 2 (2001)	0	0	0	0	5	17.5	25	25	17.5	5	0	0
year 3 (2002)	0	0	0	0	7	24.5	37.5	37.5	24.5	7	0	0
year 4 (2003) and beyond	0	0	0	0	10	35	50	50	35	10	0	0

Transpiration vs. Head in a Model Cell containing a TreeWell



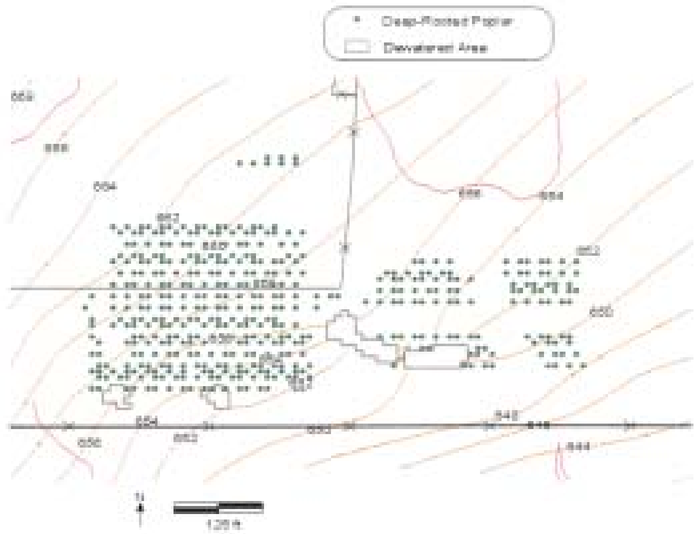
Low Heads of Mature Phyto System

(Sept. of fourth year)



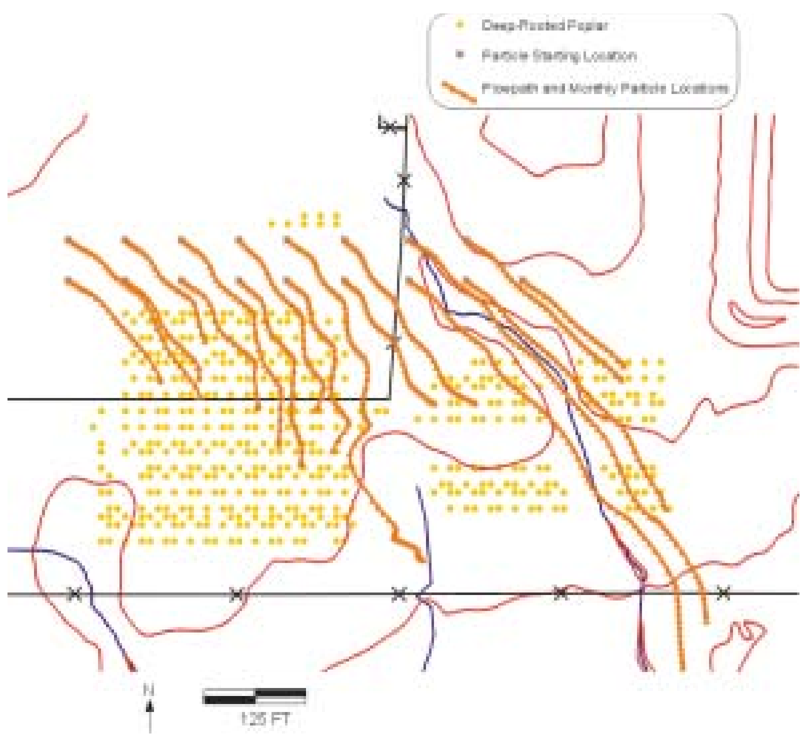
High Heads of Mature Phyto System

(April of fifth year)



Particle Tracking Results

(particles start in January 2000)



Effect of Phytoremediation on the Groundwater Flow Field…

- Best-estimate predictive modeling suggests
  - containment of groundwater by mature plantation, even during dormant winter months
  - interim extraction well system phase out
  - residence time of groundwater in microbially active rhizosphere of 5-17 months

... and vice versa… The Effect of the Groundwater Flow Field on the Phytoremediation System

- Dewatering of aquifer of interest could stress the poplars
  - ➤ future thinning of tree density

What Next?

- Groundwater sampling
- Water level measurements
- Weather data
- Tissue sampling
- Transpirate sampling
- Rhizosphere soil sampling
- Viewing tubes

For your viewing pleasure…

- web.ead.anl.gov/phyto
  - animated visualization of transient flow field under pre- and post-phytoremediation conditions

Phytoremediation Potential of a Chlorinated Solvents Plume in Central Florida

Stacy Lewis Hutchinson
and
James Weaver

Stacy Lewis Hutchinson has a B.S. in civil engineering from Montana State University and a M.S. and Ph.D. in civil engineering from Kansas State University. She is currently a research environmental engineer at the Ecosystem Research Division of the Office of Research and Development of the U.S. Environmental Protection Agency. Dr. Hutchinson works as part of a multidisciplinary team on phytoprocesses in support of multimedia modeling efforts for assessing risks from chemicals to human health and the environment. Her research focuses on the phytoremediation of water, sediments, and soils contaminated with toxic and hazardous chemicals and quantifying this remediation through changes in soil biological, chemical, and physical health.

Phytoremediation Potential of a Chlorinated Solvents Plume in Central Florida

Stacy Lewis Hutchinson
and
James W. Weaver

Ecosystems Research Division
National Exposure Research Laboratory
United States Environmental Protection Agency
Athens, Georgia

The potential for phytoremediation of a shallow chlorinated solvent plume was assessed by application of ground water flow and evapotranspiration (ET) models for a site in Orlando, Florida. The focus of the work was on the hydrologic and hydraulic factors that influence phytoremediation effectiveness. The primary phenomena of concern were observed plume diving, spatially varying recharge and evapotranspiration from existing and candidate trees. The observed contaminant distribution at the site showed sharp plume diving immediately down gradient from the suspect source with partial discharge to a lake approximately 250 feet down gradient. A ground water flow model was developed for the site that included the potential for vertical flow by including detailed bathymetry of the lake. Model results showed that the plume diving is directly attributable to focussing of recharge from paved areas near the source. Since plume diving represents the dominant feature of vertical flow at the site, the design for a phytoremediation system included diverting recharge water from the paved area and planting of trees to further minimize plume diving. Estimates of evapotranspiration rates were obtained from regional estimates, a simple model of ET and from a previous ET study conducted on site. These estimates provided design parameters for the remediation system and an assessment of the amount of plume control possible at the site.

Phytoremediation Potential of a Chlorinated Solvents Plume in Central Florida

Stacy Lewis Hutchinson and Jim Weaver

Ecosystems Research Division
National Exposure Research Laboratory
United States Environmental Protection Agency
Athens, Georgia

Phytoremediation Effectiveness

- The water balance at a site determines
  - pattern of flow in the aquifer
  - amount of water withdrawn by vegetation
  - first order effectiveness of phytoremediation

Water Balance Equation

$$\nabla \bullet (Kb\nabla h) + q + P + I - Q_s - ET = S\frac{\partial h}{\partial t}$$

•Scientific principle governing ground water flow

•Equation solved in ground water flow models

- K = hydraulic Conductivity
- b = aquifer thickness
- h = hydraulic head
- q = source/sink
- P = precipitation
- I = irrigation
- Q_s = surface runoff
- ET = evapotranspiration
- S = storage coefficient/ specific yield

Ground Water Flow Equation

Parameters

$$\nabla \bullet (Kb\nabla h) + q + P + I - Q_s - ET = S\frac{\partial h}{\partial t}$$

• K = hydraulic Conductivity	• aquifer test	
• b = aquifer thickness	• core	
• q = source/sink	• site information	
• S = storage coefficient/ specific yield	• pump test	Calibration
• P = precipitation	• climatic data	
• I = irrigation	• site information	
• Q_s = surface runoff	• estimate	
• ET = evapotranspiration	• estimate	

Ground Water Flow Modeling

- Majority of ground water flow modeling is based upon steady state assumption
  - in solute transport--contaminant transport is slow compared to ground water response time
  - climate becomes averaged

Design Approach

- Estimation of evapotranspiration rates
- Local pattern of aquifer recharge
- Effects on plume location and potential for phytoremediation

Evapotranspiration ET

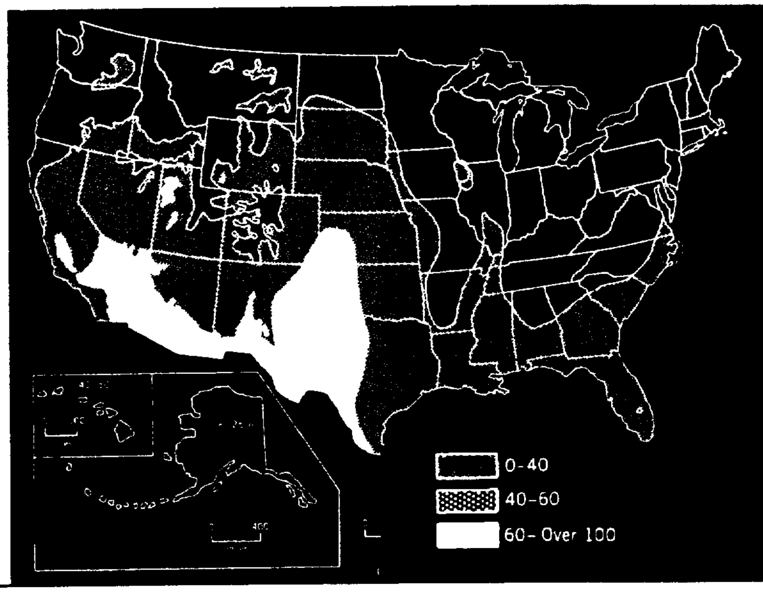
- Reduces average net recharge of the aquifer
- May prevent plume diving
- May create upward flux of water

Penman-Monteith Equation

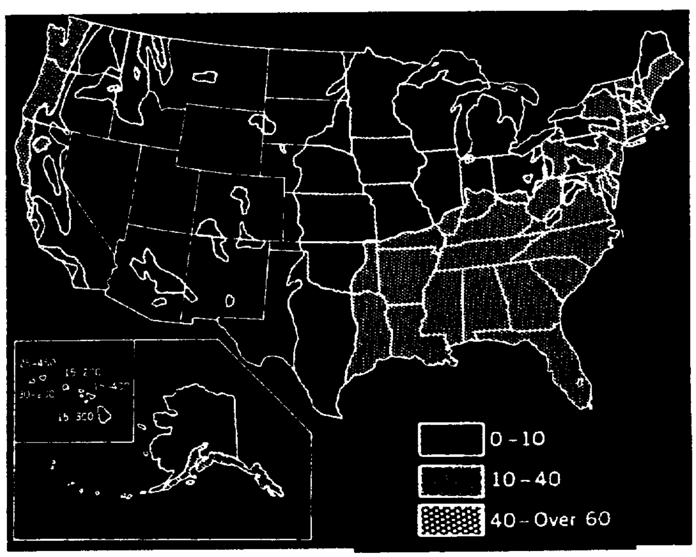
$$E_{rc} = F^1_{rc} A + F^2_{rc} D$$

= reference crop evapotranspiration (mm/day)
= available energy for ET (mm/day)
= average vapor pressure deficit (kPa)
and F^2_{rc} = function of temperature wind speed, and site elevation

Pan Evaporation in Inches



Annual Precipitation in Inches



Evapotranspiration Estimates

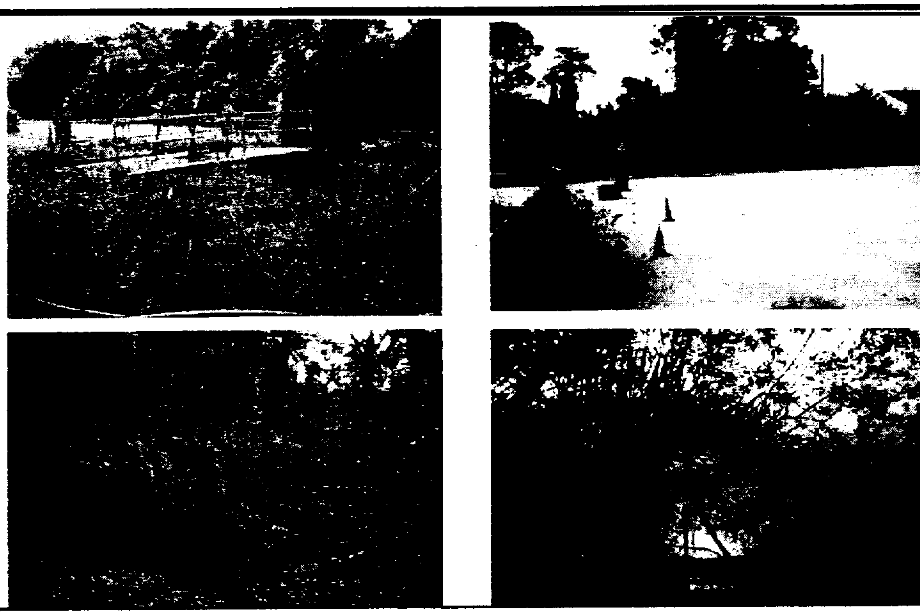
- Central Florida---130 cm/year (Florida Agricultural Extension Service)
- Orange Groves---50 cm/year (USGS Report 96-4244)
- Site Specific---80 cm/year (Vose et al.)
  - contribution of understory not determined

- Precipitation Estimate---140 cm/yr

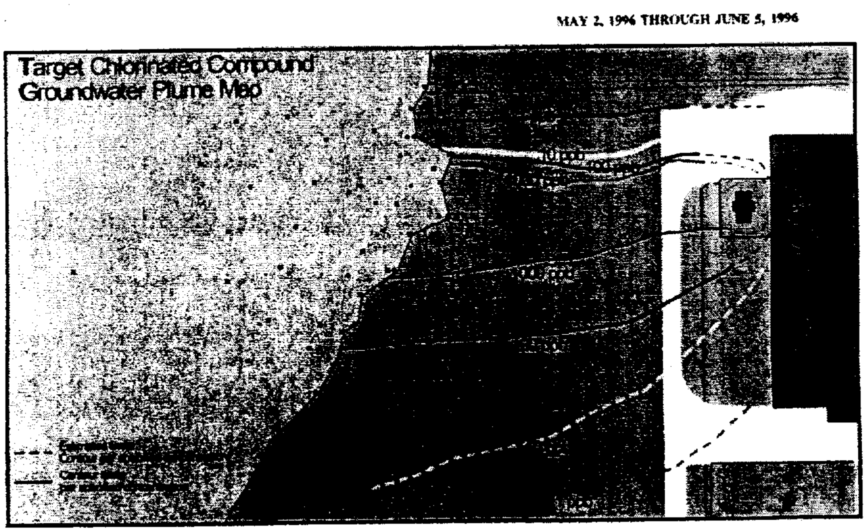
Orlando

- BRAC site
- PCE/TCE source in a sump
- Flow toward and discharge into Lake Druid
- Flow Path Land Use
  - Building>Paved>Ditch>Grass>Jungle>Shore

Orlando

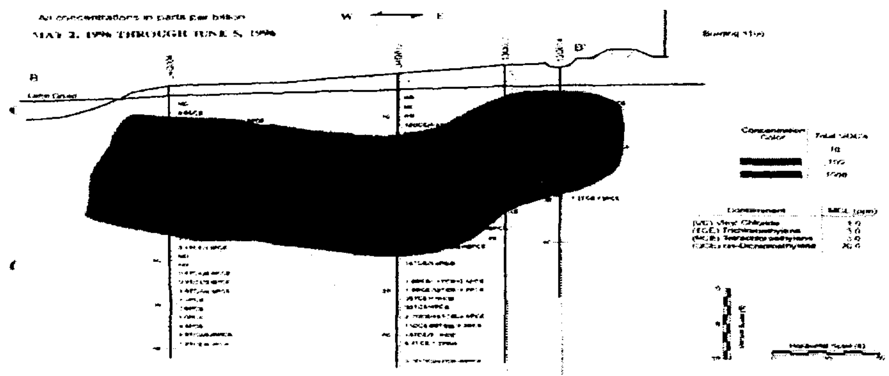


Orlando Site

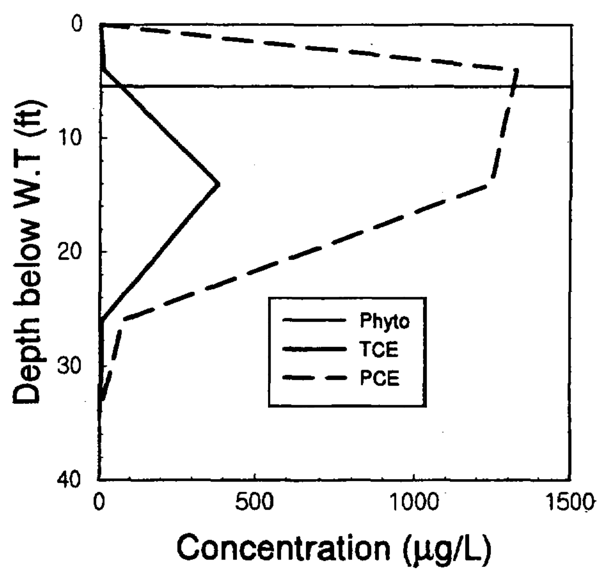


Orlando NAS Site

- Observed plume diving
  - from vertical contaminant distribution
  - dramatic/short distance/local



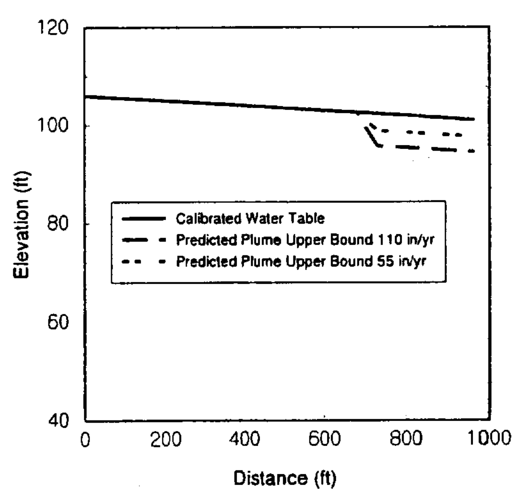
Contaminant Distribution at Source



Analytical Recharge Model

- One-dimensional analytical element model
- Flow in a water table aquifer
- Predicts the upperbound of contaminant distribution based on aquifer parameters and recharge rate
- Match observed plume diving to input recharge rate

Analytical Model Results



Numerical Model

- MODFLOW 3D, Steady State Ground Water Flow
- Based on USGS regional flow model
  - source of calibrated parameters, boundary conditions
- Fine scale layering to simulate plume diving and ET losses

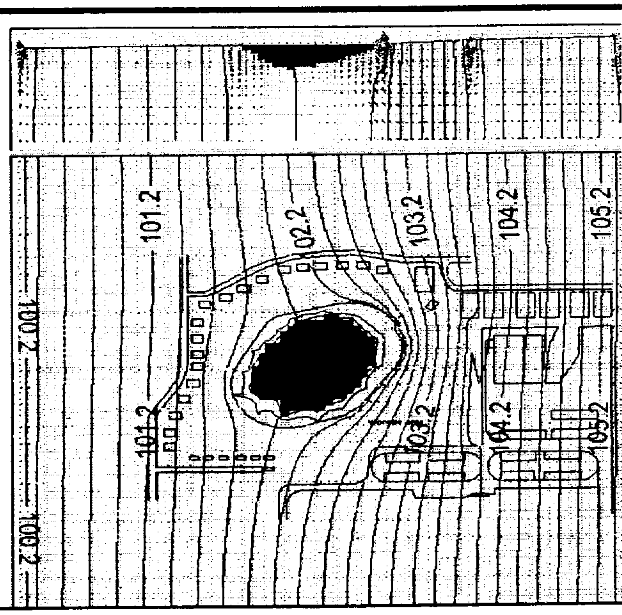
MODFLOW Model

- Two layers of differing conductivity
  - upper 10 ft/d Ks, 3.8 ft/d vertical
  - lower 40 ft/d Ks, 17 ft/d vertical
- Fine layering to define Lake Bathymetry
  - 11--2 foot thick layers
  - lower layers 5 or 10 feet thick
  - 18 layers total

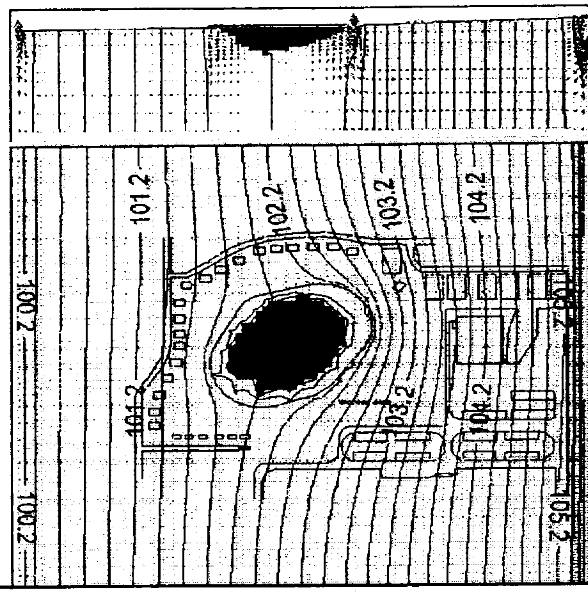
MODFLOW Model

- Simulate
  - existing conditions with enhanced recharge from ditch
  - Plume diving with diversion of water from ditch
  - ET with trees planted through parking lot (no recharge), but ET at 50, 80 and 130 cm/yr

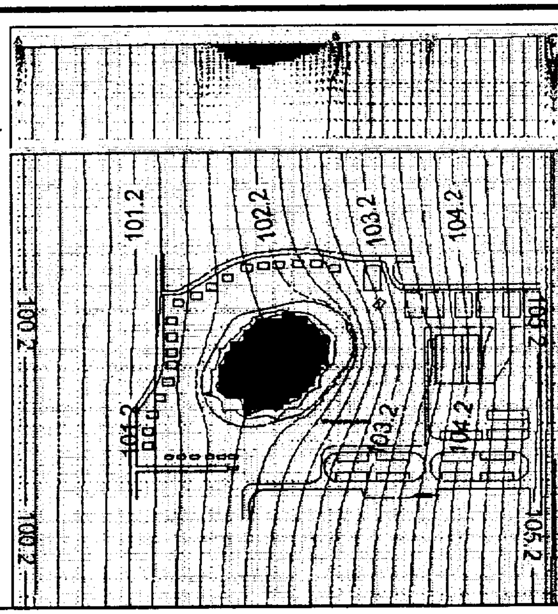
Orlando Current Conditions



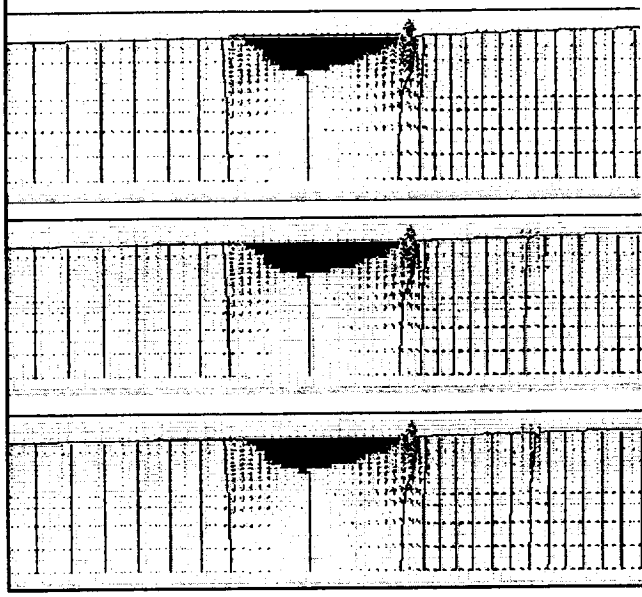
Re-route Runoff



Tree Plantation near Source



Comparison of Water Usage



Re-route Recharge

Tree Plantation using 80 cm/yr

Tree Plantation using 130 cm/yr

Results

- Penetration depth:
  - 80 cm/yr ET; upward gradient to 23 ft
  - 130 cm/yr ET; upward gradient to 30 ft
- Contamination depth is 34 ft

Conclusions

- Vertical characterization is required for delineating plumes (esp. Those considered for phytoremediation)
- Localized recharge distribution controls plume diving (accepting stratigraphy)
- ET estimates have uncertainty
  - generally bounded by pan evaporation rates

Conclusions--Orlando

- Numerical model with fine scale vertical discretization needed for 3D flow features.
- Potential to control plume by diversion of runoff.
- Existing vegetation is ineffective in removing water/contaminants
- Tree plantation at source potentially affects a maximum of 77% to 88% of the contaminant depth.
  - ET = 80 to 130 cm/yr
  - Recharge = 0

PLUME CONTROL: ON THE GROUND EXPERIENCE

Phytoremediation at Aberdeen Proving Ground, Maryland: Operation and Maintenance, Monitoring and Modeling

Steven R. Hirsh U.S. EPA
Region III
Office of Superfund
Federal Facilities Section

Steven Hirsh graduated from Temple University with a degree in Environmental Engineering 1980. Steven is currently taking Engineering Geology courses at Drexel University. Steven has worked at the U.S. EPA for 20 years. Work at EPA includes Wastewater Permitting, Emergency Response, Federal Facility Compliance and Superfund Project Management. Steven previously served as EPA's Project Manager for the Spring Valley Chemical Munition Site.

Steven is also the Work Leader for all Federal Facility Superfund Sites in the State of Maryland. Steven serves as the Remedial Project Manager for the Aberdeen Proving Ground Superfund Sites, and as On Scene Coordinator for Munitions Removal activities at the Former Nansemond Ordnance Depot Site in Tidewater Virginia. Steven is the technical lead of a US team providing remediation support and training for the Government of the Czech Republic.

EPA honors include bronze and gold medals for work related to implementation of Superfund at Federal Facilities.

Abstract

This talk summarizes the development of a remedial clean-up option designed to remove contaminants (primarily 1,1,2,2-tetrachloroethane and trichloroethene) and provide hydraulic containment in a shallow water table aquifer at the U.S. Army Aberdeen Proving Ground. Phytoremediation at the Aberdeen Site consists of over 200 hybrid poplars planted in the flowpath of a high concentration (hundreds of PPM) plume. Monitoring natural attenuation parameters has shown that aerobic and anaerobic indigenous microorganisms are significantly reducing contaminants. The phytoremediation plantation increases the degradation of the VOCs. Current field efforts are being conducted to quantify this increased contaminant destruction.

After three seasons of developing and refining phytoremediation monitoring techniques, the EPA and the Army are finalizing a Feasibility Study for the site which requires phytoremediation be analyzed as a potential remedial option, and compared to other remedial technologies. A component of this analysis is an evaluation of the costs associated with installation and operation and maintenance of a phytoremediation plantation. This analysis is being assisted by the use of several groundwater-modeling techniques. The monitoring program provides the data necessary for measuring the effectiveness of phytoremediation in achieving remediation goals, and provides input parameters for the modeling effort. Monitoring has also provided data for evaluation of existing and potential environmental contamination pathways. Groundwater withdrawal rates have been estimated by measuring sap flow using the Dynamax DynagageTM Flow 32 system. Sap flow and on-site weather conditions were examined seasonally over a three-year period. Hydraulic containment was evidenced through continuous groundwater level monitoring which showed a depression in the groundwater table during summer and early fall.

Operation and maintenance of the plantation has included installation of replacement trees, additional tree plantings in areas of contamination previously unknown, fertilization to maintain and improve tree health, and tree maintenance following severe storms.

Phytoremediation Systems Designed to Control Contaminant Migration

A. Ferro[1], R. Kjelgren[2], D. Turner[3], B. Chard[1], T. Montague[2], and ,J. Chard[1]

[1]Phytokinetics, Inc. Logan, Utah; [2]Utah State University, Logan, Utah; [3]NDR Consulting, Cove, Utah.

Ari Ferro is President of Phytokinetics, Inc., and an Adjunct Associate Professor at Utah State University. He and Jean Kennedy founded Phytokinetics in 1994 in Logan, Utah with the objective of commercializing phytoremediation. The company's focus has been phytoremediation of organic chemical contaminants in soils and groundwater. Dr. Ferro earned a Ph.D. in biochemistry from the University of Utah in 1973, and completed postdoctoral training at the University of Hamburg and University of California at San Francisco. Before founding Phytokinetics, he held a position as a Research Faculty member at the University of Utah, Department of Biology.

Abstract

Two phytoremediation projects are discussed which illustrate the use of trees to help control the migration of contaminants. The first example is a phytoremediation project at Chevron's former Light Petroleum Products Terminal in Ogden, Utah. Groundwater at the site contains petroleum hydrocarbons, and in 1996, a dense triple row of hybrid poplar trees was installed perpendicular to the direction of groundwater flow. The trees were planted directly into the saturated zone in order to establish deep-rooted plants that use groundwater as their primary source of moisture. Sap velocity measurements have been conducted in order to estimate total transpirational water use. In addition, the structure of the root system of a single deep-rooted tree was investigated. Performance of the system has been evaluated by obtaining ground-water elevation and contaminant concentration data from piezometers located up-gradient, down-gradient, and within the planted zone. Preliminary data suggest that the concentrations of BTEX compounds and TPH decreased as the groundwater passed through the rows of trees. Portions of this

study were conducted as part of the US EPA's SITE Demonstration Program. The second example is a project planned for the Bofors-Nobel Superfund site in Muskegon, Michigan. Within a four-acre portion of the site are several drained sludge lagoons devoid of vegetation. The sludge layer contains a complex mixture of contaminants that have the potential to leach into the groundwater. The planned phytoremediation system involves the installation of deep-rooted trees within the lagoons. We expect that transpirational water use by the trees will reduce contaminant leaching. Other beneficial effects of the vegetation may include immobilization of contaminants by binding to root tissue and enhanced rhizosphere degradation. A small-scale outdoor study is underway to evaluate the tolerance of several tree species to the sludge, as well as the efficacy of various planting methods to encourage the formation of deep roots. After almost one year of growth, the trees in all treatments appear to be healthy. A greenhouse study is planned to evaluate sludge phytotoxicity and to assess the rate of removal of the contaminants from planted soil.

Ogden, Utah

A phytoremediation system was installed at Chevron's former Light Petroleum Products Terminal in Ogden, Utah to control the migration of groundwater contaminants. Groundwater at the site contains petroleum hydrocarbons ranging in concentration from 5 to 10,000 parts per billion (ppb) and the water table at the site is 4 to 9 feet below ground surface (bgs).

Installation

In April 1996, a dense triple row of hybrid poplar trees ('Imperial Carolina', *Populus deltoides* x *P. nigra,* DN34) was installed perpendicular to the direction of groundwater flow. Each of the three tree rows is 100 ft. long with 7.5 ft. between trees and 6 ft. between rows. Individual boreholes were drilled and the trees (40 total) were planted directly into the saturated zone in order to establish deep-rooted plants that use groundwater as their primary source of moisture. The trees were planted as long hardwood cuttings and have grown rapidly, at a rate of approximately 10 ft. per year without any supplemental irrigation. Five piezometers were installed to monitor groundwater quality and to measure changes in water table elevation.

The water table elevation (WTE) at the Ogden site was measured manually and groundwater samples were taken at each of the five piezometers at six sampling times from 8/98 to 8/99. Groundwater samples were analyzed for BTEX and TPH using EPA Methods 8020 and 8015 modified, respectively. In addition, as part of the USEPA SITE Demonstration Program, WTE data were measured continuously from 5/98 to 8/98 using in-well pressure transducers.

Transpirational Water Use by the Tree Stand

The total volumetric water use by a stand of trees (Vt) during a given time period can be estimated using the following equation:

$$Vt = PET * Kc * LAI * A \qquad \text{[Eq. 1]}$$

where

PET = potential evapotranspiration during the time period,

Kc = "crop coefficient" = rate of water use per leaf as a percentage of PET, LAI = leaf area index = the leaf area per unit area of ground surface, and A = area of the stand of trees.

Values for PET are site-specific. For a dense stand of poplar trees, values for leaf area index (LAI) increase gradually from years 2 through 5 and reach a plateau at.the time of crown closure. Values for crop coefficient (Kc) increase as the roots become better established, and then decrease slightly in year 5 due to self-shading in the dense crown.

In 1998, a temporary weather station was erected at the Ogden site to record the parameters necessary for calculation of PET (Allen et al., 1994). In addition, four trees within the stand were equipped with thermal dissipation probes to measure sap velocity, and transpirational water use was calculated for the individual trees. Each tree was then completely defoliated and leaf area was estimated by running a subsample of the harvested leaves though a leaf area meter. LAI was then calculated for the ground area, A, covered by the tree canopy. The study was carried out in mid to late September 1998, when the stand was at the end of its third growing season. The following values were obtained:

- Vt = 5.6 gallons per day per tree
- PET = 4.0 inches per month
- LAI = 2.9 ft2leaf area per ft2ground area

Rearranging Eq. l, a value for Kc was calculated using the measured values for Vt, PET, and LAI.

- Kc = 0.5 (dimensionless)

These measured and calculated third year (1998) values validated our Vt, Kc and LAI estimates made previously for the third growing season.

Using our estimated values for Vt, Kc, and LAI for the fourth growing season (1999), we calculated that the stand of 40 trees transpired approximately 480 gallons of groundwater per day. To determine whether transpirational water use by the trees at the Ogden site was significant relative to the total flow of groundwater, we approximated the volume of water flowing beneath a vertical cross-section of the stand. The rate of groundwater flux through a 1-ft.-thick vertical cross-section spanning the width of the stand's canopy (110 ft.) was calculated using Darcy's Law to be approximately 44 gallons per day. Although our water use estimates indicate that the trees transpired a volume of water equivalent to an 11-ft. thickness of the saturated zone, our WTE data for 1999 did not indicate a depression in the water table. We are currently investigating plausible explanations for the observation that an obvious zone of depression in groundwater elevation was not observed in the root zone of the trees (c.f. Ferro et al., 1997).

Root Distribution Analysis

In the fall of 1998, the root system of a single poplar tree at the southwest corner of the stand was systematically characterized using classical methods for root analysis (Bbhm, 1979). A backhoe was used to dig two trenches near the base of a single tree. Roots along the trench walls were exposed and systematically counted using a grid system. A needle board was then placed in along the vertical trench face closest to the tree and stiff wire 'needles' driven through the board and into the root zone of the tree. The portion of the root system penetrated by the needles was isolated by digging a monolith (2 1/3 ft. wide, 1 1/2 ft. thick, 3 ft. high) and the soil washed away while the needles held the roots in position. The analyses indicated that the tree roots grew out of the borehole and extended laterally > 5 ft. throughout the vadose zone. Within the vadose zone, the largest.roots proliferated in and around the borehole. Near and within the saturated zone, the roots were heavily concentrated in the borehole. The most deeply penetrating roots extended from highly branched roots near the surface (< 2 ft. bgs) rather than from the original, deeply planted cutting.

Contaminant Removal/Evidencefor Plume Control

Groundwater samples were collected at each of the five piezometers at six different times from 8/98 to 8/99. The multiresponse permutation procedure (Mielke,1995) was used to assess statistical differences in contaminant concentration data at the various sampling times. The preliminary data indicate that the dense triple row of poplar trees was effective at removing BTEX and TPH from the groundwater. At each sampling time, BTEX and TPH contaminant concentrations decreased significantly ($p < 0.01$) from the up-gradient piezometers to the down-gradient piezometers. A decrease in concentration of both BTEX and TPH at the up-gradient piezometer was observed.

Muskegon, Michigan

A phytoremediation project is planned for the Bofors-Nobel Superfund Site in Muskegon, Michigan. Although the project is still in the pre-design stage, the conceptual design calls for the installation of approximately 13,000 trees of various species in four different zones on the 20-acre site. Industrial chemicals such as detergents, saccharin, dye intermediates, herbicides and pesticides were produced at the site from 1960 to 1980, during which time sludge and wastewater were disposed of in various lagoons. Bofors-Nobel filed for bankruptcy in 1985 and the site was placed on the National Priorities List in 1989. The contaminants of concern, localized primarily in several drained sludge lagoons, include halogenated semivolatile organics (trichlorobenzene, dichlorobenzidene, chloroaniline), non-halogenated semi-volatile organics (benzidine, azobenzene, aniline) and metals (chromium, lead, arsenic). The sludge material is calcium sulfate (CaS04), and in some lagoons, Zinc oxide (ZnO) is also present. Zone A is comprised of several of the most highly contaminated sludge lagoons. In this area, contaminant concentrations in the vadose zone are high. In Zones B and C, the contaminants occur primarily in the groundwater at 30 ft. bgs (Zone B) and 10 ft. bgs (Zone C). Zone D is an area with comparatively little contamination. A different phytoremediation strategy will be applied in each of the four zones, with the ultimate goal to prevent contaminant migration from the vadose zone to the groundwater and to prevent the offsite migration of already contaminated groundwater.

Pre-Design Study

A pre-design study was started in September 1999 and we expect that the study will continue through the 2002 growing season. The objective of the study is to assess the tolerance of seven tree species to the sludge and to evaluate various planting methods. The three treatments include 1) drilling boreholes in sludge lagoon 3 (in Zone A), backfilling with sand and compost, and planting the trees into the backfill; 2) planting trees directly into sludge lagoon 3; and 3) planting trees in an uncontaminated area adjacent to lagoon 3. There are five replicate plots per treatment and seven trees (one of each species) per replicate. The objective of Treatment 1 is to develop deep roots that penetrate through the sludge layer. Trees in Treatment 1 (planted in backfilled boreholes) are sub-irrigated using drip lines. Trees in Treatments 2 and 3 are surface irrigated using spray emitters. We plan to evaluate the root structures of trees in each treatment using methods similar to those described above for the Ogden site. As of June 2000, the trees subjected to the various treatments have not shown obvious signs of toxicity.

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Böhm, W. 1979. *Methods of studying root systems.* Volume 33 in the series, *Ecological studies: Analysis and synthesis,* 188 pp. (Billings, W. D. and Lange, O.L., Eds.). Berlin, Springer-Verlag.

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Mielke, P. W. Jr. 1995. Multiresponse permutation procedures. In: *Encyclopedia of Statistical Science,* Volume 5, pp. 724-727. New York, NY, John Wiley & Sons.

Deep Planting

Edward Gatliff

Edward G. Gatliff earned a Ph.D. in Agronomy from the University of Nebraska-Lincoln. He is founder and president of Applied Natural Sciences, Inc. of Hamilton, Ohio, an environmental consulting firm specializing in providing TreeMediation® and other PhytoEngineered™ phytoremediation programs such as the TreeWellTM methodology to treat specific horizons of soil or groundwater.

Since 1987, Dr. Gatliff has been active in the environmental industry, primarily applying his understanding of vegetation and agronomic principles to remediate contaminated soil and ground water. In the fall of 1990 he conceived an engineered approach to utilizing trees to remediate deep soil and ground water, now known as a TreeMediation program. With the implementation of a TreeMediation program in the fall of 1991, he pioneered an engineered approach to phytoremediation that has been used to remediate soil and groundwater more than 30 feet deep. Through Applied Natural Sciences, Dr. Gatliff has obtained 2 patents and continues to develop innovative approaches to phytoremediation, for projects nationwide.

Applied Natural Sciences, Inc.

"Deep" Tree Planting

Edward G. Gatliff, Ph.D.

presented at the
EPA Phytoremediation: State of the Science Conference
Boston, May 1-2, 2000

*contact: (513) 895-6061; ans@fuse.net

Deep Tree Planting

- How it all began -

- 1990, Cranbury, NJ
  - Nitrogen contamination in GW 16-20 feet bgs
  - Selected trees over alfalfa due to ability to manage & engineer deeper rooting
  - Evaluated several approaches

Deep Tree Planting?

- What is it
- Why & when do we use it
- How do we do it
- How effective is it
- How deep can we go
- How costly is it

What is Deep Tree Planting?

- Planting a tree to achieve root development to an aquifer or a horizon of soil that is greater than 3 feet deep.
- Typically accomplished by creating boreholes and/or trenching

Why Do We Need Deep Planting?

- To remediate or hydraulically control deep groundwater
  - Depending on climate and soil conditions, vegetation very often does not develop rooting activity deeper than the top 3 feet of soil.

Why deep plant when vegetation can develop deep rooting naturally

- To Readily Establish & Insure Hydraulic Control and/or Remedial Effect
  - In conditions where vegetation can develop rooting activity to the target horizon the predictability of timing and efficiency often precludes any meaningful assessment of the system's potential effect.

2 year old root system from borehole

How is Deep Planting Best Accomplished?

- Creating Boreholes or Trenches
- Casing the borehole or Trench
  - Types of casing and no casing
- Borehole Diameter
- Planting the tree as deep as possible in the borehole or trench

Creating Boreholes

- Diameter of hole and depth of boring often dictates the type of drill rig that should be used
- In general the following will apply
  - <5 feet a 3-point auger on a tractor
  - ≤10 feet a skid-steer with an auger extension
  - 10- 20 feet a medium sized drill rig with an 8 foot stroke
  - >20 feet a caisson rig

Boreholes < 10 feet

Boreholes >10 feet

Types of Casings

- **Casing**
  - ADS & metal culvert - cost, corrosion, handling & installation, erosion
  - sonotube - cost, degradation, handling & installation, erosion
  - plastic, handling & installation
- **No Casing**
  - clayey soil types

ADS & Metal Casings

- cost,
- corrosion and reactivity,
- handling & installation,
- erosion or channeling of surface water (depends on soil & site conditions)

Sonotube

- cost,
- degradability
- handling & installation,
- erosion or channeling of surface water (depends on soil & site conditions)

Plastic

- cost,
- degradability
- handling & installation,
- erosion or channeling of surface water (virtually eliminates)

No Casing

(or, Is Casing Important?)

- Depends on site conditions
  - Boreholes drilled into clayey soils will limit root development outside the borehole.
  - Without a casing, consideration must be given to the possibility that a preferential pathway for surface water to short-circuit to the GW has also been created.

No Casing

Field evaluation on non-clayey soils

- Root Excavation of Cased & Non-Cased Trees
  - non-cased tree growing in silt loam soil show primary root development near surface compared to cased tree

Borehole Diameter

- Boreholes from 3 inches to 3 feet
- With casing larger diameter boreholes are preferable
- With no casing 3 inch boreholes have been used with cuttings

Shallow Planting

- Shallow planting the rootball of the tree
  - with cased trees, irrigation may be required
  - longer time for roots to develop to depth

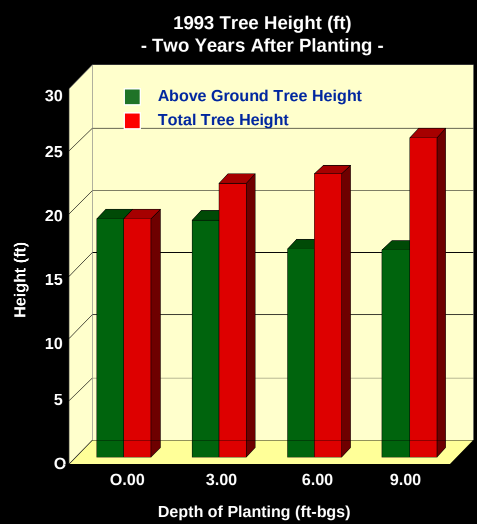
Deep Planting

- Deep planting the rootball of the tree
  - Roots reach depth quickly
  - Irrigation not normally needed

Effects of Deep Planting

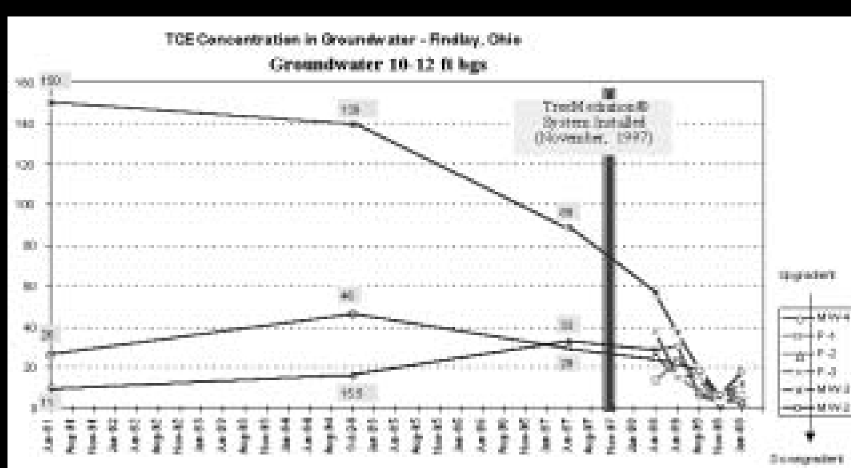
- Tree Growth Increased by Deep Planting
- Remediation Effect realized by year 2
- Hydraulic effect realized in year 1

Tree Growth Response to Deep Planting

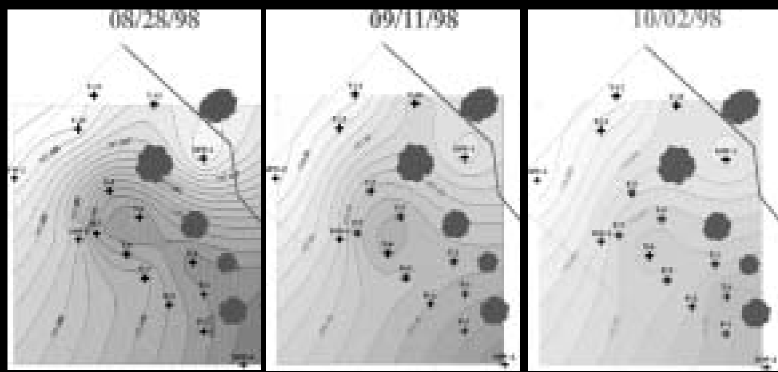


Tree Planted 6 feet bgs

TCE (mg/L) Removal in Response to Deep Planting



Hydraulic Effect on Aquifer in Response to 1997 Deep Planting



How Deep Can We Go?

- Acacia trees have been known to root as deep as 100 feet below ground surface
- Trees in semi-arid/arid areas known to root to GW as deep as 60 feet bgs
- At Staten Island, New York and Argonne, Illinois we are treating aquifers as deep as 35 feet below ground surface
- Root systems have been found developed to over 200 feet long

How Deep Can We Go?

- Deep placement
  - A fifteen foot tall tree can be planted at least 10 feet bgs
- Elongated Roots
  - pregrown tree roots can be developed 10 or more feet in length

Elongated Root Systems

- Tree root systems can be pregrown at designated lengths

Applied Natural Sciences, Inc.
Patented System

Example of Use

- Argonne National Laboratory Area 317/319 Phytoremediation Project
- Root-engineered trees (trees with predeveloped elongated root systems) were planted into 30 foot deep boreholes.
- Rootballs were placed 5-10 feet bgs with elongated roots suspended another 2 to 8 feet thereby achieving rooting activity up to 18 feet bgs at planting.

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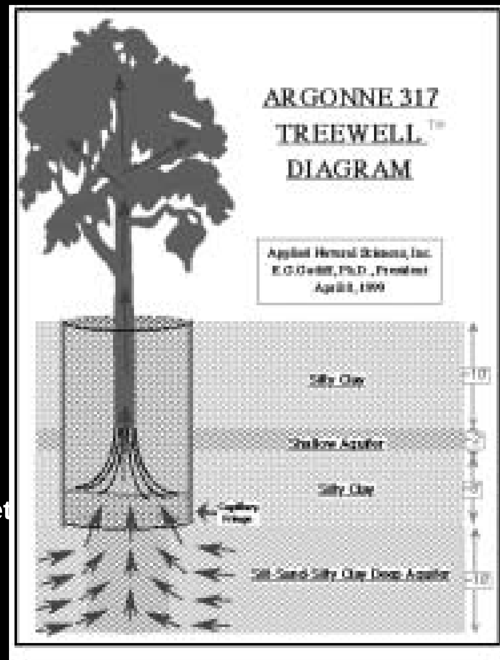
Patented System



Deep Planting Costs

- Implementation costs will vary significantly between sites due to site conditions, methodology employed and whether client is commercial or government
- For systems with a target depth of 10 feet or less
  - Per tree costs will range between $100 and $300 per tree (or $20,000 to $60,000 per acre)
- For systems with a target depth of 10-20 feet
  - Per tree costs will range between $250 and $500 per tree (or $50,000 to $100,000 per acre)
- For systems with a target depth of > 20 feet*
  - Per tree costs will range between $500 and $1,500 per tree (or $100,000 to $300,000 per acre)
    - * assumes fewer trees per acre with deeper depths

Summary

- Deep Plantings reaching depths of 35 feet have been demonstrated while depths of 50 feet or more are feasible
- Casing helps limit preferential shallow root development and surface water short-circuiting
- No casing has a place when used with clayey soils provided surface water short circuiting is accounted for
- Borehole diameter can vary with objectives but cased holes should be larger (>16")
- Effects can be readily realized and more predictable
- Costs can be controlled by utilizing the right methodologies and equipment for the given situation

Transpiration: Measurements and Forecasts

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Abstract

For soil and groundwater pollutants, a key factor in phytoremediation is choosing plants species that transpire a substantial quantity of water and subsequently metabolize or accumulate the contaminant. The successful application of phytoremediation technology requires a thorough and accurate assessment of water use patterns (i.e., transpiration rates, location of soil or groundwater uptake, interactions with climate and soil water availability) in plant species that are known metabolizers of the specific pollutant. Accurate determination of tree or stand-level transpiration in the field has, until recently, been difficult. Typically, three methods have been used: (1) precipitation minus runoff (P-RO) relationships on gaged watersheds, (2) energy balance (e.g., Penman-Montieth), and (3) hydrologic models. The first two methods are integrated estimates of the entire system and do not partition water losses based on transpiration and evaporation. Hydrologic models vary considerably in complexity, but usually only detailed physiologically based models that link vegetation, soils, and atmosphere provide accurate estimates of transpiration. Recent developments in sapflow techniques have made direct estimates of transpiration at the tree level under field conditions much more feasible. Modeling or other scaling techniques can be coupled with these sapflow measurements to scale tree-level to stand-level and extrapolate temporally. Overall approaches to measuring and modeling transpiration will be discussed, with emphasis on a case study comparing sapflow estimates of transpiration with those from a physiologically based transpiration model.

VEGETATIVE COVERS

Monitoring Alternative Covers

Craig Benson

Monitoring Alternative Covers: ACAP's Perspective

William H. Albright, Craig H. Benson, Michael M. Bolen, Glendon W. Gee, Steven Rock, A. Roesler

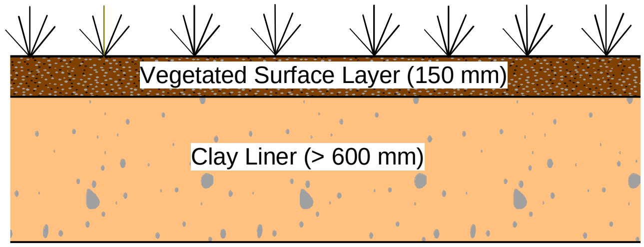
Purpose of Cover or Cap

- Limit percolation into underlying waste

- Control gases (methane, LFG, oxygen)

- Separate waste from surrounding environment

Conventional Covers: Compacted Clay

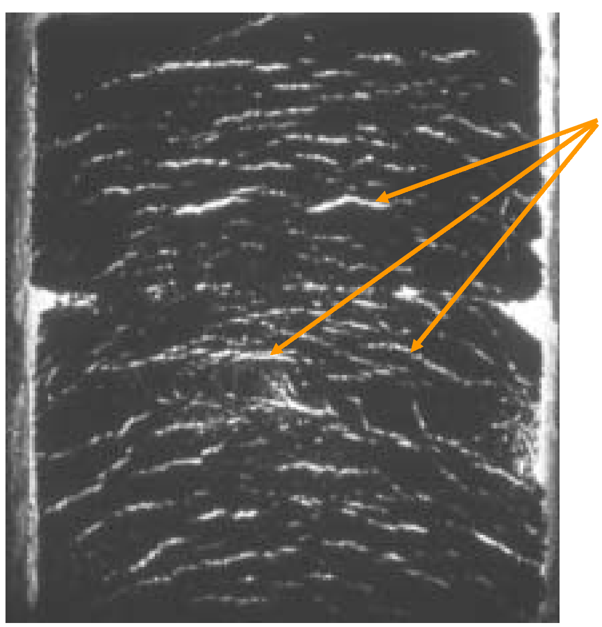


- Prone to problems: desiccation cracking, frost damage, differential settlement, root intrusion
- Fairly costly ($125,000 per acre)

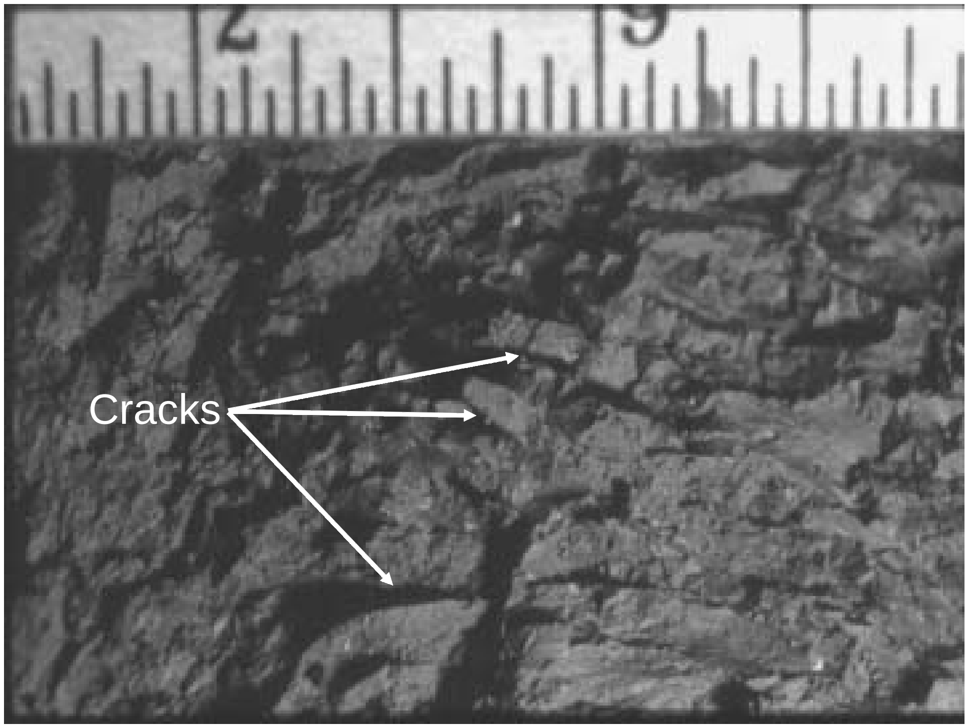
Frost Lenses in Compacted Clay

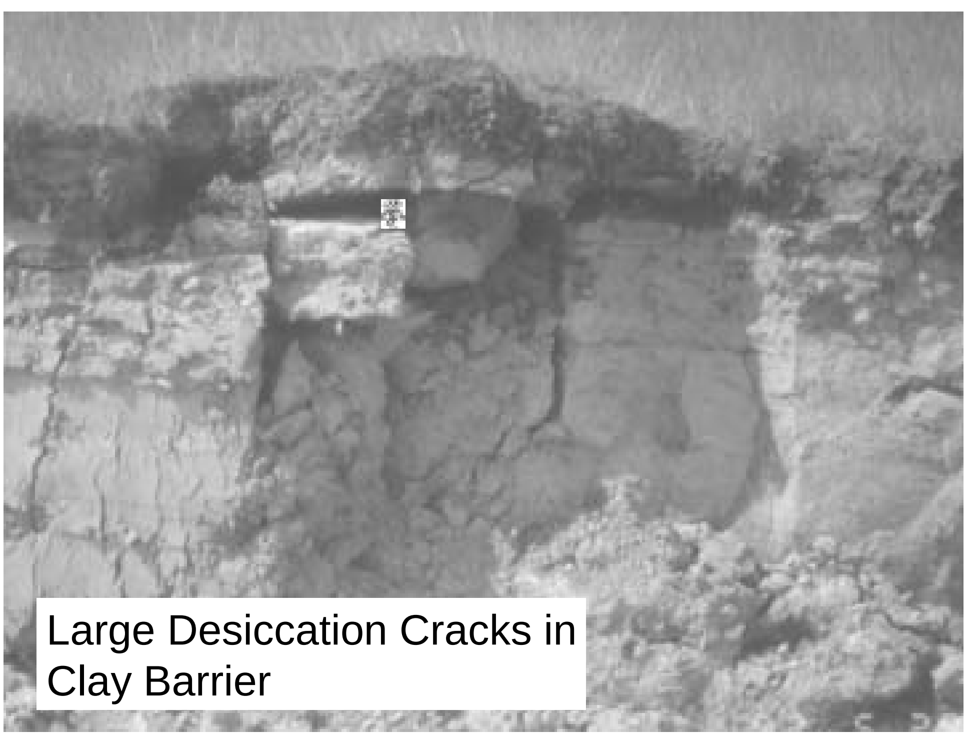
Moderately plastic glacio-lacustrine clay

Compacted 2% wet of optimum with standard Proctor

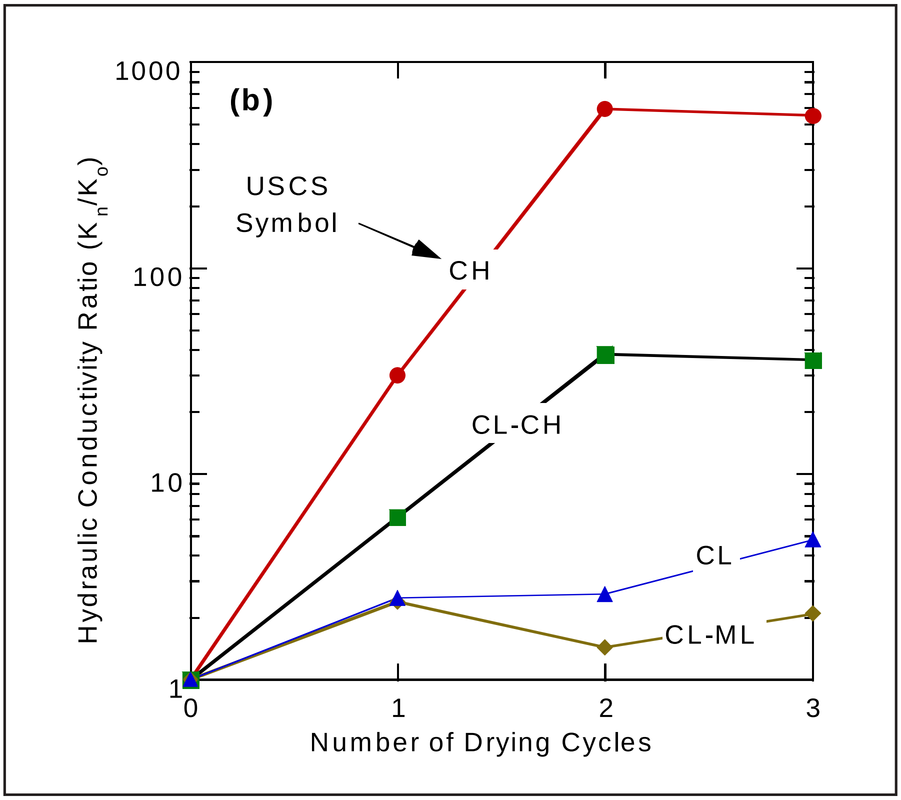


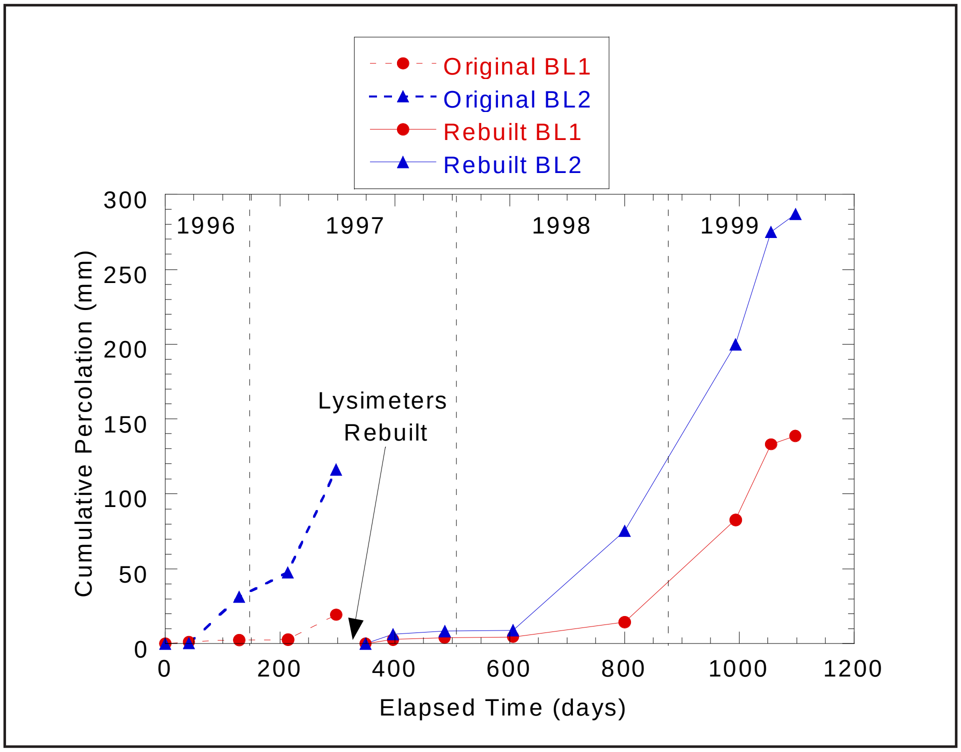
Ice Lenses

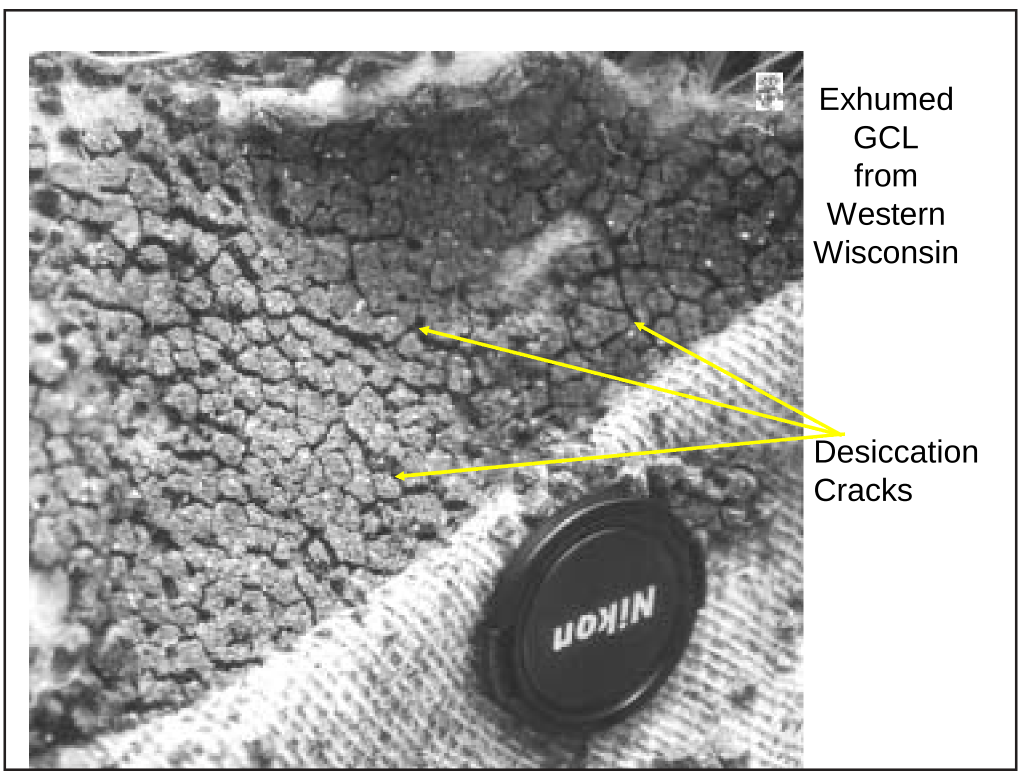




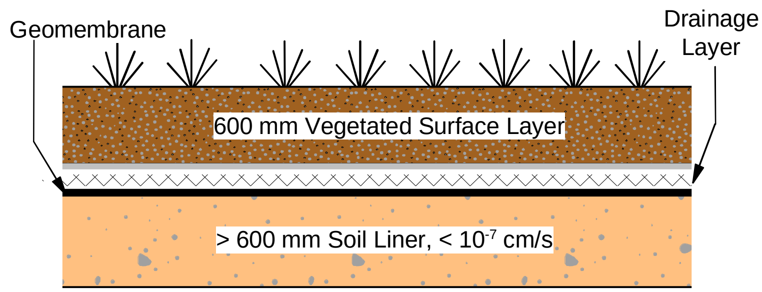
Large Desiccation Cracks in
Clay Barrier


(b)
1000
100
10
1
0
1
2
3
Hydraulic Conductivity Ratio (K_n/K_o)
Number of Drying Cycles
USCS
Symbol
CH
CL-CH
CL
CL-ML


Original BL1
Original BL2
Rebuilt BL1
Rebuilt BL2
1996
1997
1998
1999
Lysimeters
Rebuilt
Cumulative Percolation (mm)
300
250
200
150
100
50
0
0
200
400
600
800
1000
1200
Elapsed Time (days)

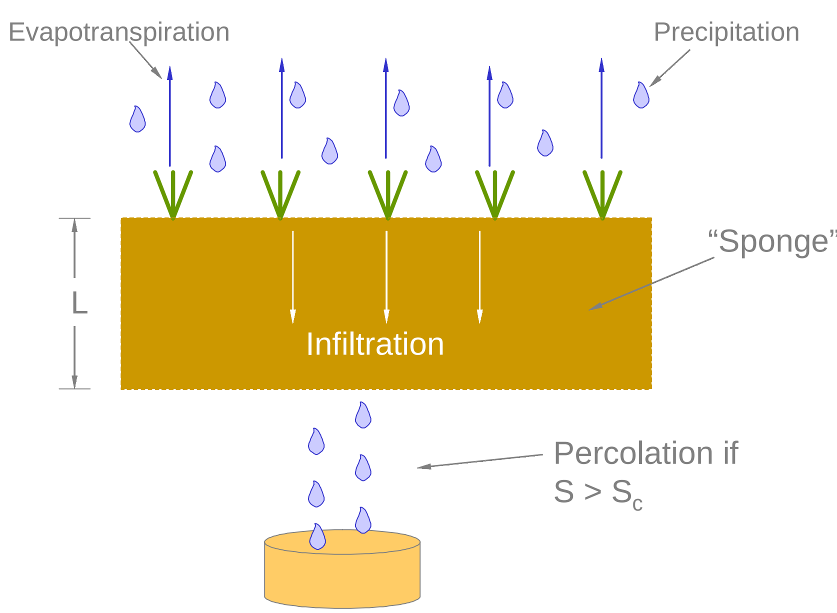

Exhumed
GCL
from
Western
Wisconsin
Desiccation
Cracks
Nikon

Conventional Covers: Composites



- Very effective (1- 3 mm/yr percolation).
- Excellent performance record
- Costly ($175,000 – 200,000 per acre)

Alternative Earthen Final Covers



Why monitor alternative covers?

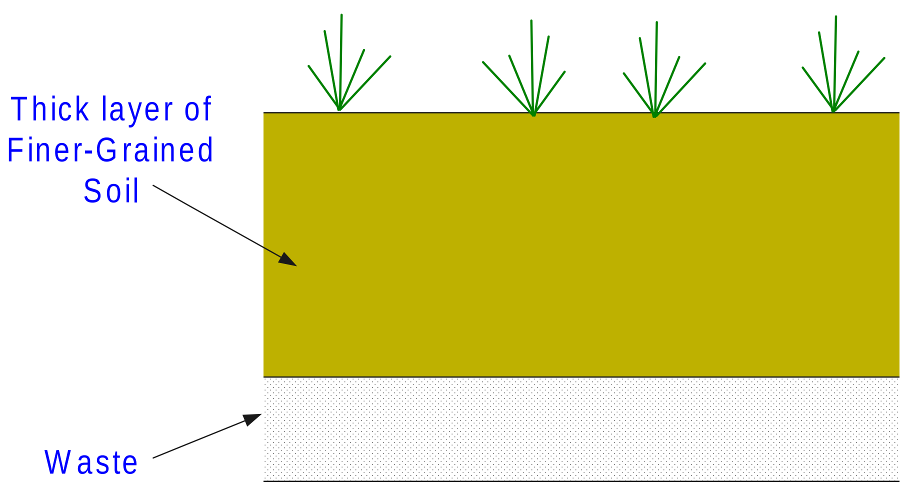
- Principle is simple, but mechanism complex

- Complex interaction between atmosphere, plants, cover surface, and flow in the cover

- Capability to make definitive predictions regarding performance currently is limited.

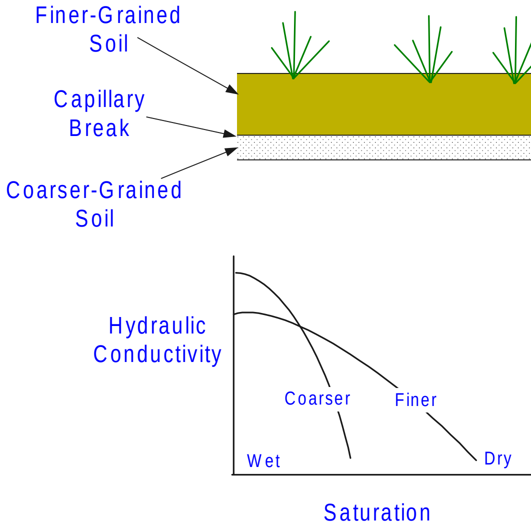
- Collect field data from a dispersed network of large-scale field test facilities to demonstrate principle and to check and refine design models.

Monolithic Barriers



Design so storage capacity of finer layer is not exceeded

Capillary Barriers



Requires:

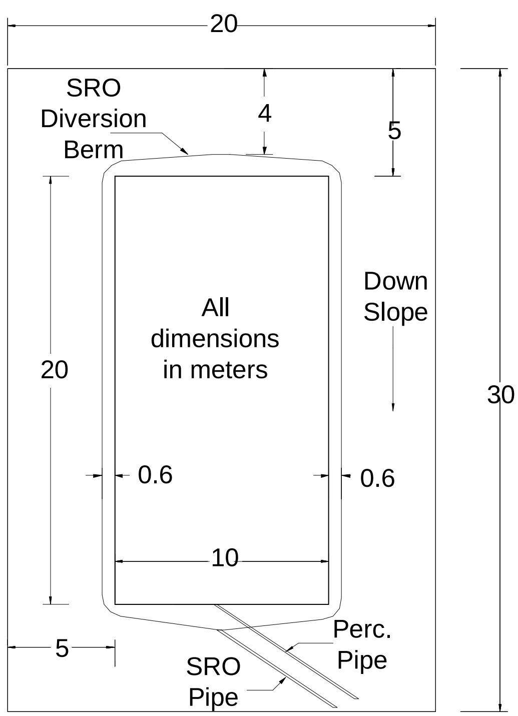
- Rigorous treatment of unsaturated flow
- Field performance data
- Understand of soil-plant-atmosphere continuum

What is Equivalency?

RCRA Subtitle D: Percolation from alternative cover must be less than or equal to percolation from prescriptive cover.

ACAP Default Equivalency Values

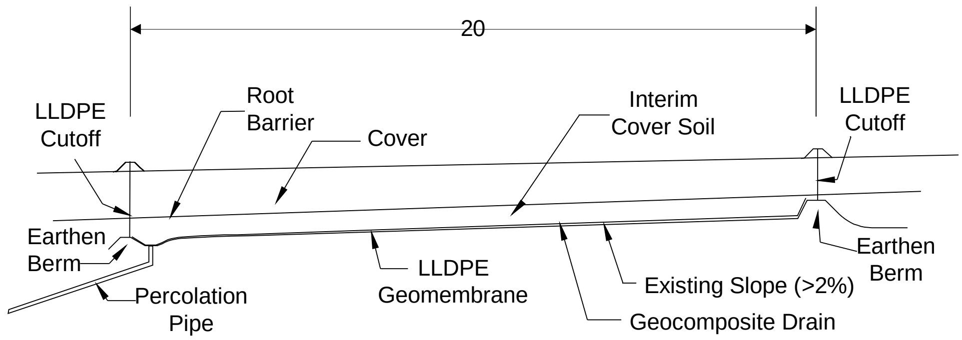
Cover	Equivalency Value (mm/yr) Humid	Equivalency Value (mm/yr) Semi-Arid
Non-Composite	30	10
Composite	3	3



ACAP
Test Section
Plan View

Large bathtub filled with cover soil and instruments.

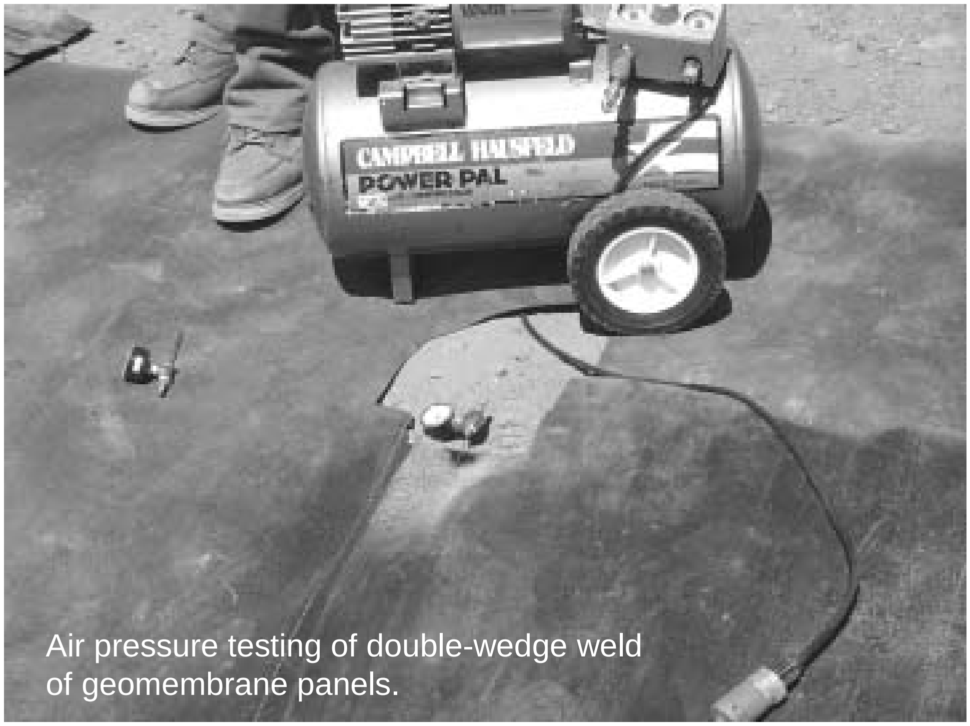
Typical Lysimeter Cross-Section



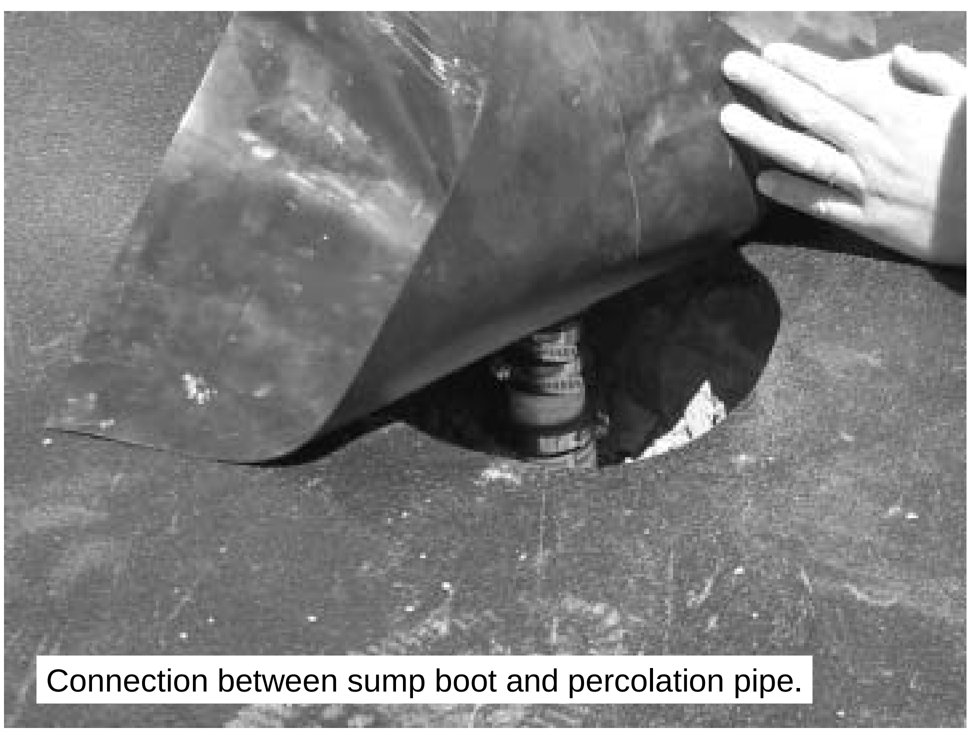
Raking surface of subgrade for geomembrane and checking compaction using drive tube method


GSE
GSE UltraFlex Textured
1.5 mm
LLDPE
Textured
Geomembrane


Aerial view of lysimeter lined with geomembrane.

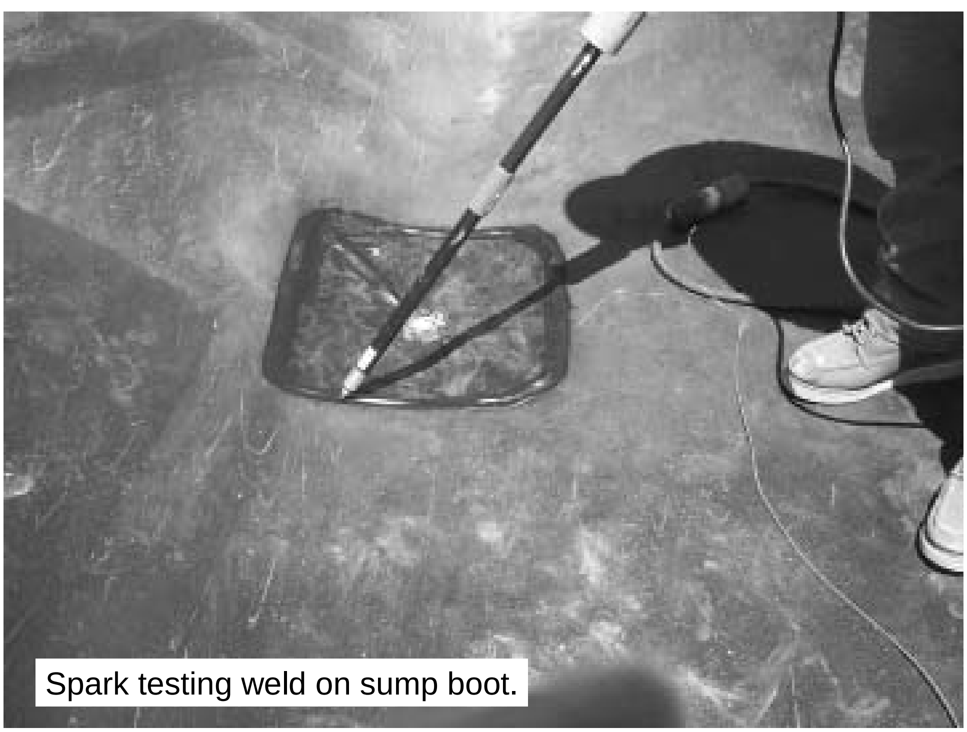


Air pressure testing of double-wedge weld of geomembrane panels.

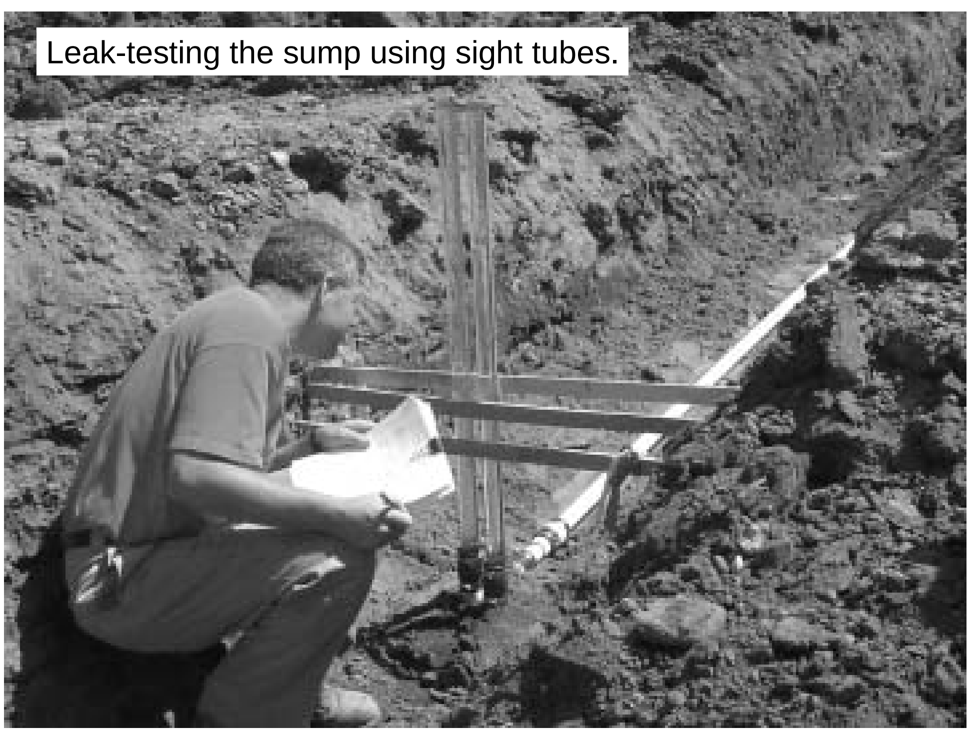


Connection between sump boot and percolation pipe.

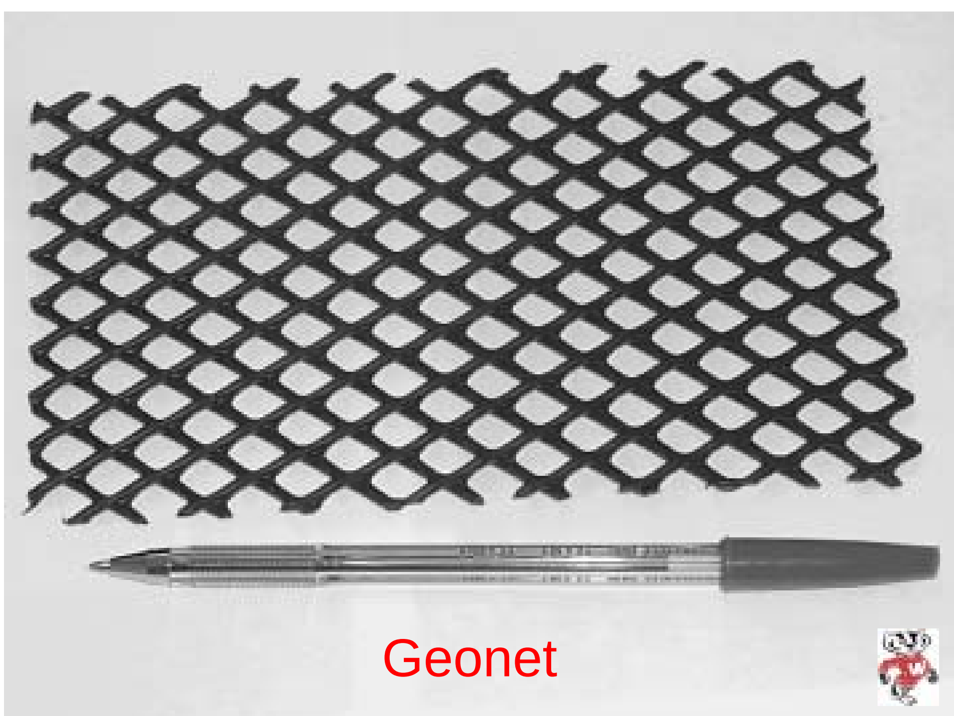
Extrusion welding sump boot.



Spark testing weld on sump boot.


Leak-testing the sump using sight tubes.


GSE
GSE FabriNet
Geocomposite
Drain
PILOT BP-S


Geonet

Installing geocomposite drainage layer above geomembrane.

Tying panels of geocomposite drainage layer.

Placing interim cover soil in bottom swale of lysimeter.

Placing root barrier.

Staking root barrier.


Completing first layer of soil above root barrier.


Corner of sidewall showing weld.

Placing anti-seep layer of bentonite along sidewall.

Trimming block sample from cover soil.

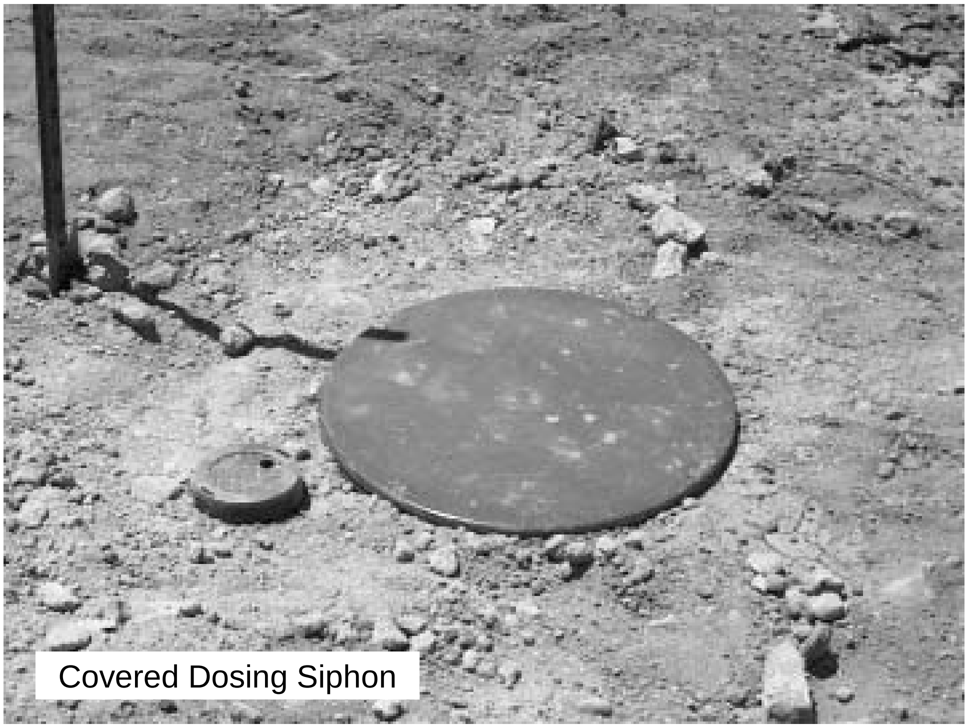
Mini-disk infiltration testing of cover soil.

Aerial view of completed test sections at Kiefer Landfill, Sacramento County, California.

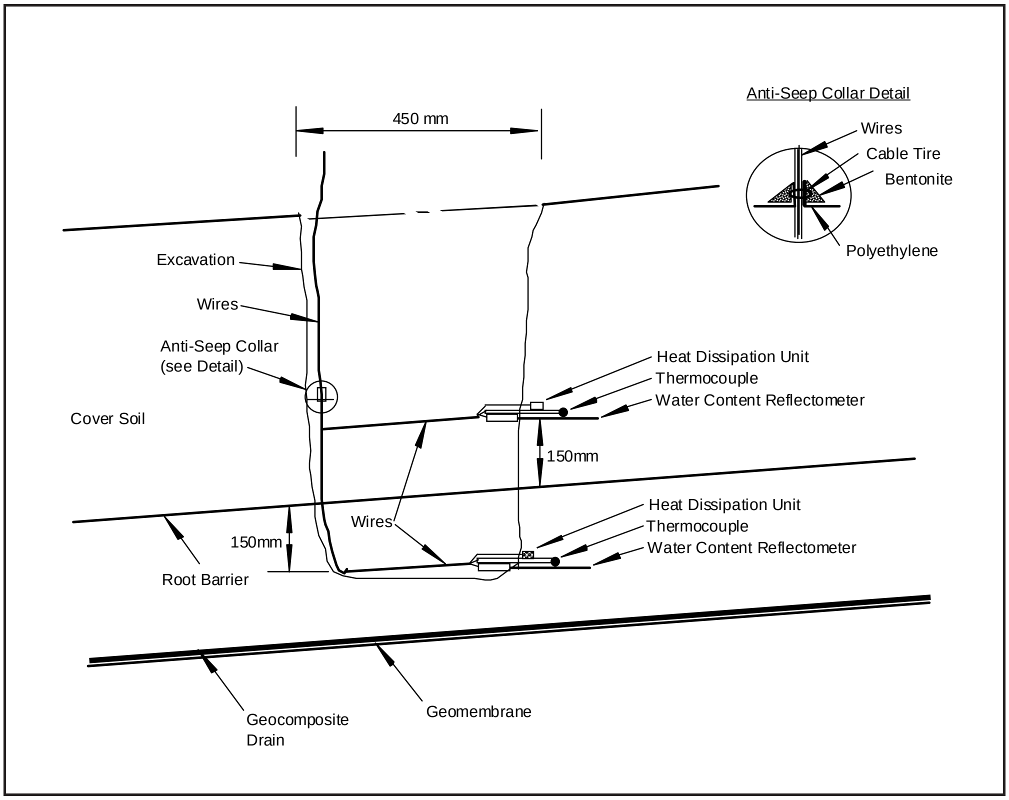
Kiefer Site:
Eight months after construction

Dosing siphon after placement on platform.

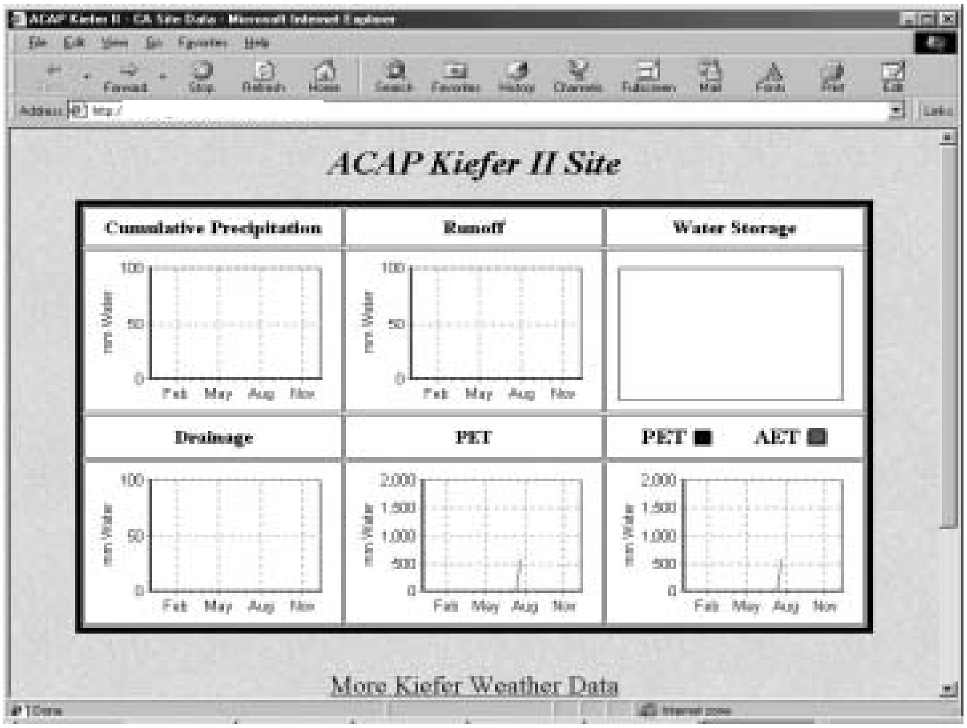
Interior of dosing siphon for percolation showing tipping bucket.

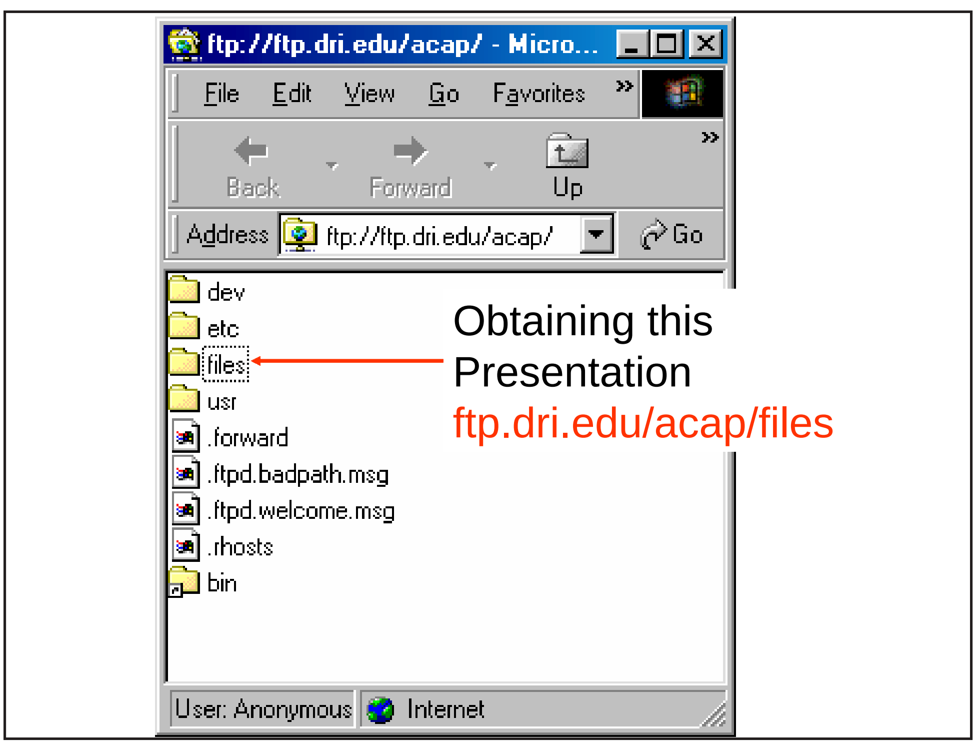

Covered Dosing Siphon


Instrument Nest



Installed weather station & datalogger.


ACAP Kiefer II Site
Cumulative Precipitation
Runoff
Water Storage
Drainage
PET
PET
AET
More Kiefer Weather Data


ftp://ftp.dri.edu/acap/ - Micro...
File Edit View Go Favorites
Back Forward Up
Address ftp://ftp.dri.edu/acap/ Go
dev
etc
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usr
.forward
.ftpd.badpath.msg
.ftpd.welcome.msg
.rhosts
bin
Obtaining this Presentation
ftp.dri.edu/acap/files
User: Anonymous
Internet

Growing a 1,000-Year Landfill Cover

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William J. (Jody) Waugh, Ph.D received a Ph.D. in Rangeland Ecology from the University of Wyoming in 1986. He has 19 years of research and applied experience evaluating and manipulating the ecology of hazardous and radioactive waste sites. He is recognized for original research on the water balance and plant ecology of evapotranspiration (ET) covers, the use of lysimetry for field measurements of soil water balance of covers, and the use of natural analogs to evaluate the ecology of covers intended to last for hundreds to thousands of years. His other research interests include retrospective environmental monitoring, phytoremediation in deserts, paleoecology, dendroclimatology, and pedogenesis of engineered soils. He has served on technology needs panels for the National Academy of Sciences, the Department of Energy, and the Environmental Protection Agency. Dr. Waugh is currently Principal Scientist with Roy F. Weston, Inc., at the DOE Environmental Sciences Laboratory in Grand Junction, Colorado, and was formerly Research Scientist at Pacific Northwest National Laboratory. He is also Adjunct Professor at the University of Arizona in Tucson and at Mesa State College in Grand Junction.

Abstract

The U.S. Department of Energy is preparing a guidance document for end-users to design long-term covers for internment of buried radioactive and hazardous waste. In some cases the covers are intended to last hundreds of years. The DOE framework for performance evaluations combines three tools: numerical modeling, field tests, and natural analog studies. Natural analog studies provide clues from present and past environments as to possible long-term changes in the performance of engineered covers. Evidence from natural analogs is needed to identify and evaluate emergent properties in the evolution of covers that cannot be captured by short-term field tests or numerical models. Natural analog data is needed to help design modeling and field tests that reasonably bound possible future changes in waste site environments. Natural analogs may also have a role in communicating the results of the performance assessment to the public, to demonstrate that numerical predictions have real-world complements.

Natural analogs exist for climate change, ecological change, and pedogenesis. Analog data can provide evidence of how a changing climate or a secondary disturbance may influence directions and rates of pedogenesis, vegetation structure and diversity, and animal community composition at a waste site. Analogs of local responses to future global climate change exist as proxy ecological and archaeological records of similar paleoclimates. Many cover designs depend on water extraction by plants. Influences of vegetation change can be inferred by evaluating plant communities representing successional chronosequences. Similarly, animal habitats like those created on waste sites can provide evidence of the potential for biological intrusion. Finally, future pedogenic effects on cover performance can be inferred from measurements of key soil properties in natural and archaeological soil profiles analogous to engineered covers.

Introduction

The typical cover design approach evaluates performance using a combination of short-term field tests and numerical models. This approach implicitly assumes that long-term changes in the performance of covers can be captured with model extrapolations based on a few years of monitoring conditions in field tests. Field test results and numerical models, alone, will not be sufficient to predict long-term performance of alternative covers. The ecology, soils, and thus the performance of an engineered cover will change in ways that cannot be predicted by short-term monitoring and numerical models. This is particularly true for alternative covers that rely on vegetation to seasonally remove precipitation stored in thick soil layers. If the U.S. Department of Energy (DOE) and others are serious about predicting long-term performance covers (hundreds of years or longer), the design process must include methods to bound reasonable ranges of change in the cover environment.

Long-Term Cover Performance Issues

This paper addressed four issues concerning the design and long-term performance of landfill covers:

*Work performed under DOE contract no. DE-AC13-96GJ87335 for the U.S. Department of Energy Grand Junction Office.

- Plant community dynamics and diversity
- Climate change
- Long-term ecological change
- Pedogenesis

Plant Community Dynamics and Diversity

Many cover designs rely on vegetation for erosion protection and soil water extraction. Changes in plant communities, particularly catastrophic losses of vegetation, will influence the performance of these covers. Changes in the plant community are inevitable. Plant communities develop and change in response to several interacting factors: propagule accessibility, climatic variability, change in soil characteristics, disturbances (such as fire), and species interactions (such as herbivory, competition, or fluctuations in soil microbe populations). Plant community dynamics are manifested by shifts in vegetation abundance, species composition, and diversity and may be accompanied by changes in rates of nutrient cycling, energy exchange, and transpiration. Consequently, plant community dynamics are complicated and effects are difficult to model and predict.

Seeding of monocultures or low-diversity mixtures on engineered covers is common. Instead, revegetation activities should attempt to emulate the structure, function, diversity, and dynamics of native plant communities in the area (Limbach et al. 1994). Diverse mixtures of native and naturalized plants will maximize water removal by evapotranspiration (Link et al. 1994a) and remain more resilient to catastrophes and fluctuations in the environment. Diverse plant communities consist of a mosaic of many species that structurally and functionally change in response to disturbances and environmental fluctuations (Tausch et al. 1993). Biological diversity is necessary for plant community stability and resilience given variable and unpredictable changes in the environment resulting from pathogen and pest outbreaks, disturbances (overgrazing, fire, etc.), and climatic fluctuations. Local indigenous genotypes that have been selected over thousands of years are best adapted to climatic changes and biological perturbations. In contrast, the exotic grass plantings common on waste-site covers are genetically and structurally rigid (Allen 1988) and, thus, more vulnerable to disturbance or eradication by single factors.

Climate Change

Current cover design paradigms and practices rely on meteorological records for performance evaluations (e.g., DOE 1989). Controlled experiments, field demonstrations, and models of water infiltration, gas attenuation, erosion, frost penetration, and biointrusion all include meteorological parameters. Meteorological data should be input only to evaluations of historical climate change, but not to evaluations of possible future changes in climate. Some performance evaluations assume that meteorological records bound reasonable ranges of future changes in climate (DOE 1989, Gilbert et al. 1988). However, climatologists generally agree that during the next decades and centuries, global climatic variation will exceed the historical record. This may happen as has occurred naturally in the past (Houghton et al. 1990; Crowley and North 1991) and/or as the lower atmosphere warms in response to increasing concentrations of anthropogenic carbon dioxide and other greenhouse gases (Hansen et al. 1988; Ramanathan 1988).

Ecological Change

Plants and animals can have profound influences, both positive and negative, on the performance of engineered covers. Without human interference, over time, ecological development will take place on all earthen covers. Ecological succession is a directional change through time in the plant and animal species that will occupy a cover. Ecological succession may alter the functional performance of a cover in ways not initially anticipated. As the plants and animals change, so also may key performance parameters such as infiltration, evapotranspiration, water retention, soil loss, gas diffusion, root penetration, burrow depths, and burrow volume. It will be important to know, for example, how changes in the plant community inhabiting a cover may influence soil water movement, evapotranspiration, and the water balance of a cover.

The ecology of a site will change in response to climate, to soil development, and to disturbances such as fire, grazing, or inadvertent cultivation (e.g., Allen 1988; Betancourt et al. 1990; Boone and Keller 1993; Laundre and Reynolds 1993). Even in the absence of large-scale disturbances, seasonal and yearly variability in precipitation and temperature will cause changes in species abundance, diversity, biomass production, and soil water extraction rates (Anderson et al. 1987; Link et al. 1990). In the long term, changes in the waste-site ecology may occur in ways not captured by predictive models or short-term field tests. For example, successional changes in the vegetation can create small-scale topographic patterns that foster greater heterogeneity in the soil water balance. At arid sites, desert shrub communities that are likely to develop on covers tend to trap wind-borne sediments causing a hummock-swale relief with variable soil physical and hydraulic properties (Link et al. 1994b). Similarly, at humid sites, blowdown of mature trees growing on engineered covers will create depressions for water accumulation (Suter et al. 1993).

Pedogenesis

Pedogenic (soil development) processes will change the physical and hydraulic properties of soils used as construction materials in engineered covers. Pedogenesis includes processes such as soil structural development (aggregation of fines and development of macropores), secondary mineralization and illuviation of materials causing the formation of distinct layers or horizons, and pedoturbation or natural soil mixing. Although rates and magnitudes of change vary, pedogenesis takes place to some degree in all soils (Boul et al. 1980). Rates of change are greatest following the stabilization of engineered soils as a result of the establishment of vegetation.

The evolution and architecture of macropores associated with root growth, animal holes, and soil structural development are highly relevant to the long-term performance of engineered covers. Overall, soil structural development creates preferential flow paths under saturated conditions (Collis-George 1991), causing water movement through fine-textured soil layers to behave more like coarse, gravely soils. Eluviation and illuviation (similar to emigration and immigration) of fine particles, colloids, soluble salts and oxides in an engineered cover may create secondary layers or horizons, with diverging physical and hydraulic characteristics (Boul et al. 1980). Accumulation of these materials in the macropores of sand and gravel layers in engineered covers could reduce the permeability of lateral drainage layers, increase the rate of downward redistribution of water through capillary barriers, and reduce the water storage capacity of overlying soil layers.

Pedoturbation, or natural soil mixing, caused by freeze-thaw activity, burrowing animals, plant root growth, and the shrink-swell action of expansive clays could homogenize engineered layer interfaces. Burrowing could also cast soil above gravel mulch and admixture layers intended for erosion protection, potentially accelerating soil loss. The formation of lag layers by winnowing, frost heaving, movement of soil gases during and after rain, and the shrink-swell action of expansive clays can cause the gradual movement of gravels toward the surface. Loess deposited on the surface can be transported below surface gravels in cracks that form in underlying vesicular soil, gradually elevating the gravel above the former land surface (McFadden et al. 1987).

Evaluation of Long-Term System Changes

The primary difference between near-term and long-term performance assessment is the need to define reasonable ranges of future changes in climate, ecology, and soils. Once reasonable ranges of long-term changes in covers systems have been defined, the sensitivity of the system to these ranges of conditions should be evaluated. Furthermore, long-term performance assessment methods and risk assessment methods must be closely coupled. Any proposed design modification or cost increase arising from an evaluation of long-term system changes must be justified by a reduction in risk to human health and the environment.

Three conformable approaches for evaluating the effects of long-term system changes on cover performance are recommended: predictive models, monitoring existing covers, and natural analogs.

Predictive Models

Numerical models of soil-water movement, erosion, and gas diffusion engender an understanding of the complexity of environmental processes acting on engineered covers and, if verified, can be used to estimate responses of designs to myriad conditions. However, verification studies only require models to reproduce short-term monitoring data. The most widely used model, HELP (EPA 1994), has been applied repeatedly as the primary cover design tool with little or no data to back the reliability of predictions. Therefore, long-term predictions using models are implicitly based on the assumption that near-term conditions of material properties, ecology, and climate—processes that drive contaminant transport—will persist. Future modeling studies should focus on estimates of performance over a range of possible future conditions of cover systems.

Monitoring Existing Covers

Field demonstrations and monitoring of existing covers, although expensive, provide the only direct measures of performance and are needed to test the credibility of models. DOE has made a considerable investment in research facilities and in existing, operational covers that encompass a diversity of designs and that exist in a broad range of environmental settings. Many existing research facilities were conceived to address near-term performance issues, as well as model verification, but monitoring has been repeatedly discontinued, and complete monitoring data sets are rare.

Because the performance of many existing covers has not been monitored, we have few means for evaluating the efficacy of designs. The DOE Uranium Mill Tailings Remedial Action (UMTRA) Project is an exception. UMTRA embodies most of the United States operational experience with the design and construction of engineered covers intended to last hundreds of years. DOE's Long-term Surveillance and Maintenance (LTSM) program recently created the Long-Term Performance (LTP) project to evaluate how changes in UMTRA disposal cell environments, both ongoing changes and projected changes over hundreds of years, may alter cover performance. This project was created not only to improve site inspections, but also to support development of design guidance for the next generation of covers at DOE weapons sites, and to support the preparation of new cover design guidance by EPA (DOE 2000).

Natural Analogs

Natural analog studies provide clues from present and past environments as to possible long-term changes in engineered covers (Waugh et al. 1994). Analog studies involve the use of logical analogy to investigate natural materials, conditions, or processes that are similar to those known or predicted to occur in some component of an engineered cover system. As such, analogs can be thought of as uncontrolled, long-term experiments. Evidence from natural analogs is needed (1) to identify and evaluate emergent properties in the evolution of engineered covers that cannot be captured by short-term tests or numerical models and (2) as input to the development of modeling and field tests that reasonably bound possible future changes in waste site environments.

Natural analogs exist for climate change, ecological change, and pedogenesis (Waugh et al. 1994). Analog data will provide evidence of how climate change or a secondary disturbance (e.g., fire) can influence directions and rates of pedogenesis, vegetation structure and diversity, and animal community composition at a single location through time. The interaction of these components and the generation of feedback loops, by definition the ecology of the engineered cover, can dramatically affect its long-term performance. Analogs of local responses to future global climate change exist as proxy ecological and archaeological records of similar paleoclimates. Many cover designs depend on water extraction by plants. Influences of vegetation change can be inferred by measuring water extraction parameters in plant communities representing successional chronosequences. Similarly, animal habitats like those created on waste sites can provide evidence of the potential for biological intrusion. Finally, future pedogenic effects can be inferred from measurements of key soil properties in natural and archaeological soil profiles analogous to engineered covers.

Conclusions

Public acceptance of plans to leave residual waste in place will depend largely on public confidence in the long-term performance of engineered covers. Engineered covers are central to perceptions of in-place disposal, yet long-term performance data are nonexistent, and short-term performance data and model predictions are largely experimental. The limited amount of monitoring data suggests that after a few years many existing covers for hazardous wastes are not meeting design and performance objectives, largely because of unanticipated ecological effects. The design and construction of long-term covers throughout the DOE complex will be very costly, but postconstruction maintenance costs may be much greater than installation costs if covers begin to degrade after a few years.

Performance assessment of engineered covers is commonly an exercise of trying to create confidence by using numerical simulations to extrapolate long-term performance from short-term field tests. In contrast, data from natural systems, past and present, should be used in the performance assessment to bound possible future changes in waste site environments. Evidence from these natural analogs is needed to physically simulate changes in engineered covers that cannot be captured by short-term field tests. Natural analogs will also have a role in communicating the results of the performance assess-ment to the public. Evidence from natural analogs will help demonstrate that numerical simulations have real-world complements.

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Growing a 1000-Year Landfill Cover

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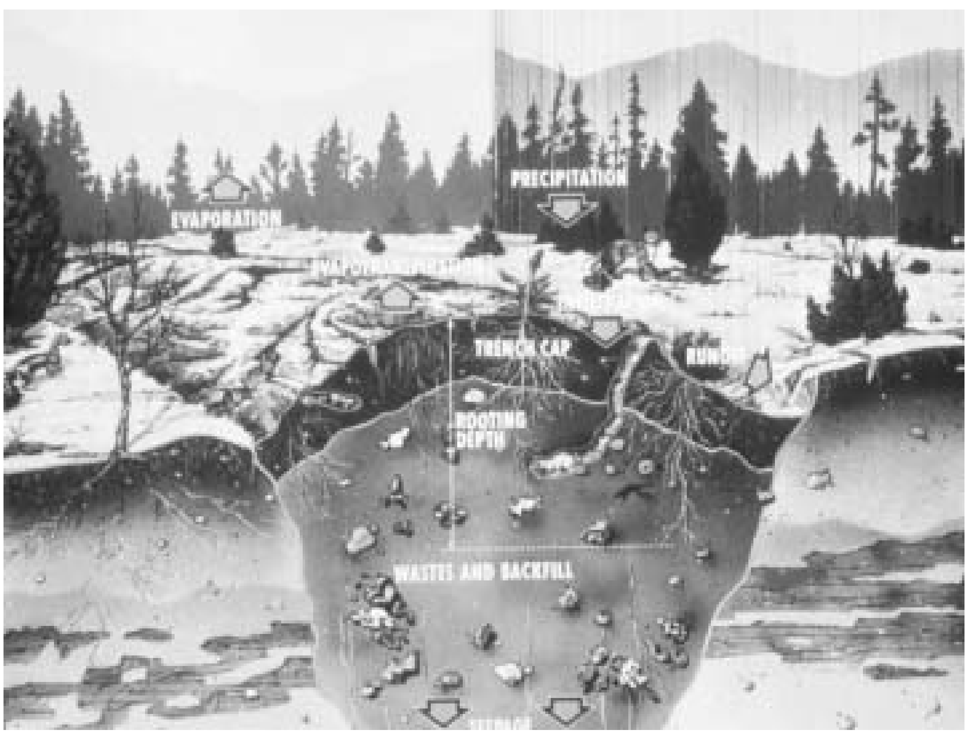
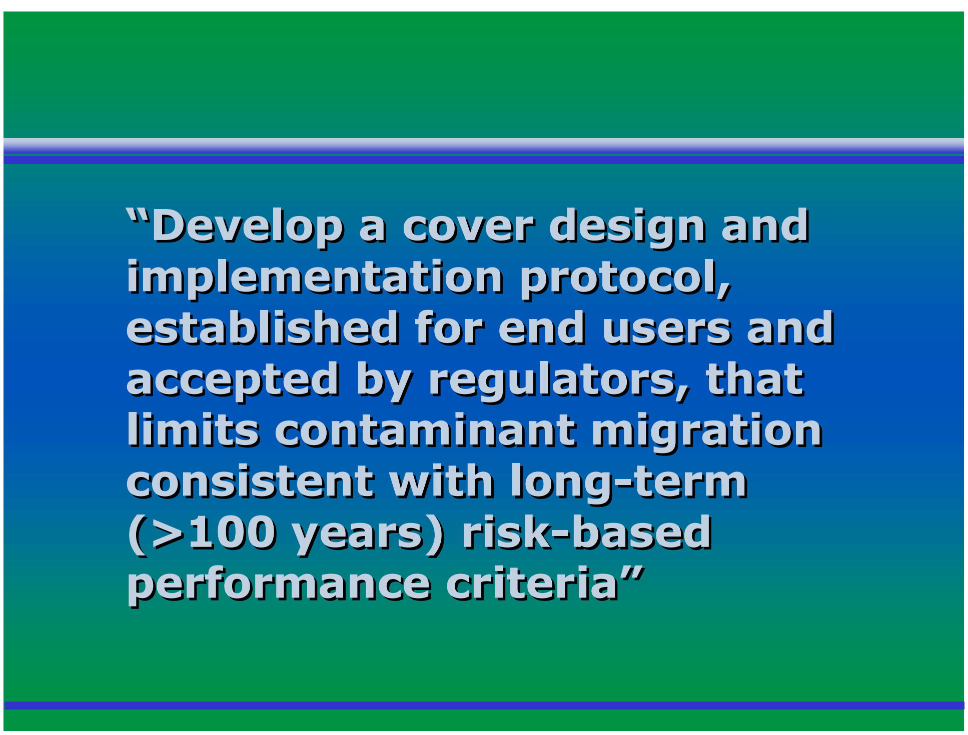
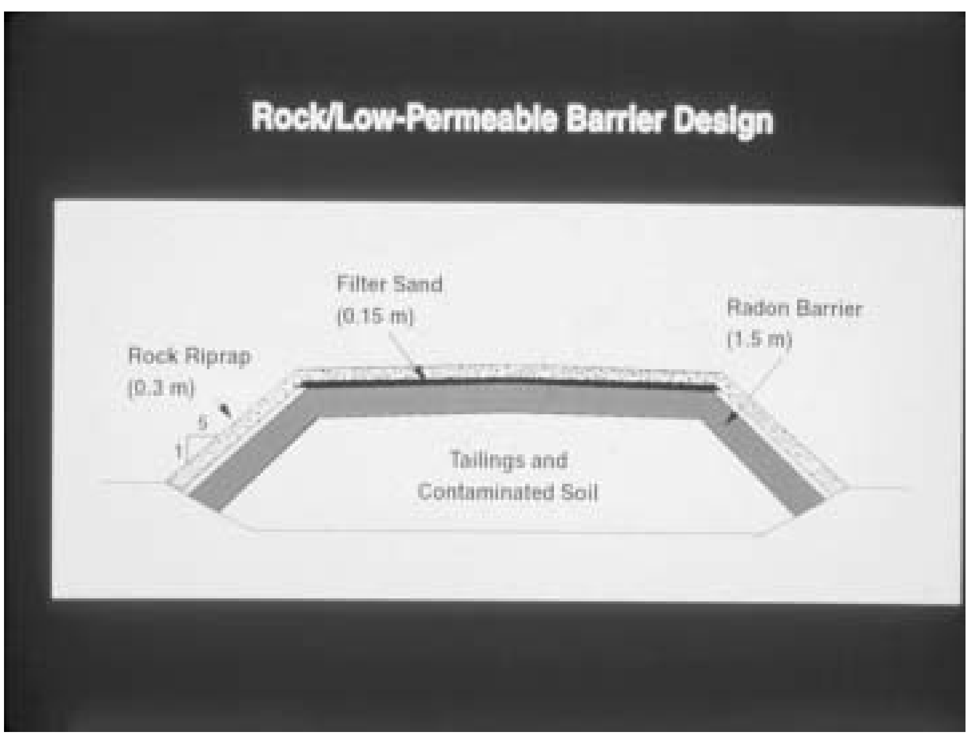
U.S. Department of Energy
Grand Junction Office
Grand Junction, Colorado

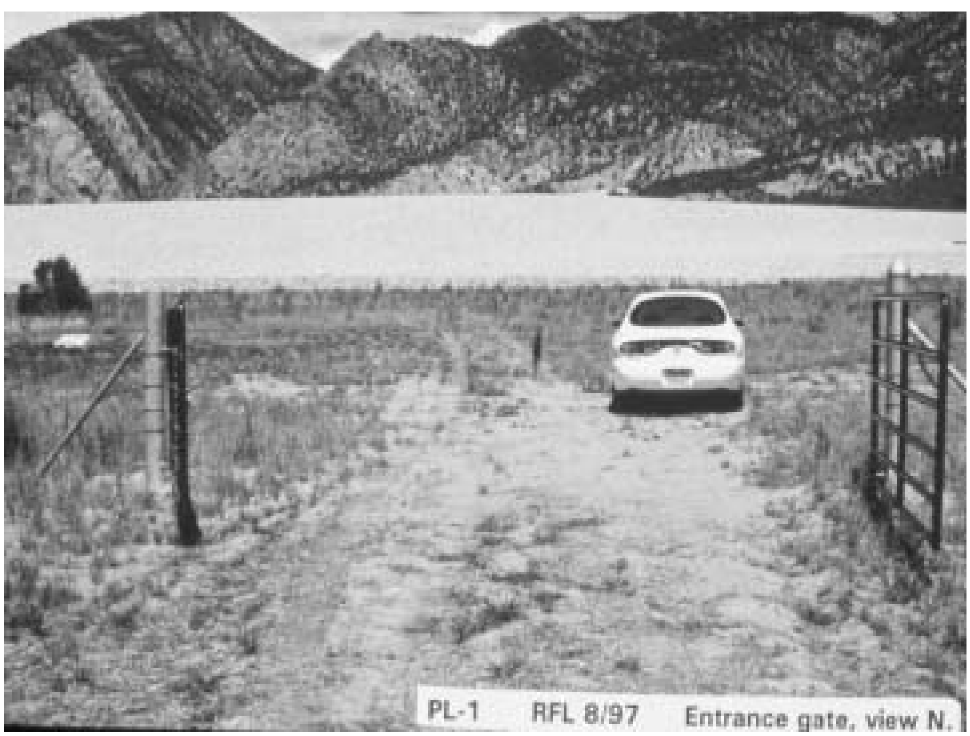
*Operated for DOE by Roy F. Weston, Inc., under DOE contract no. DE–AC13–GJ87335 with MACTEC Environmental Restoration Services.



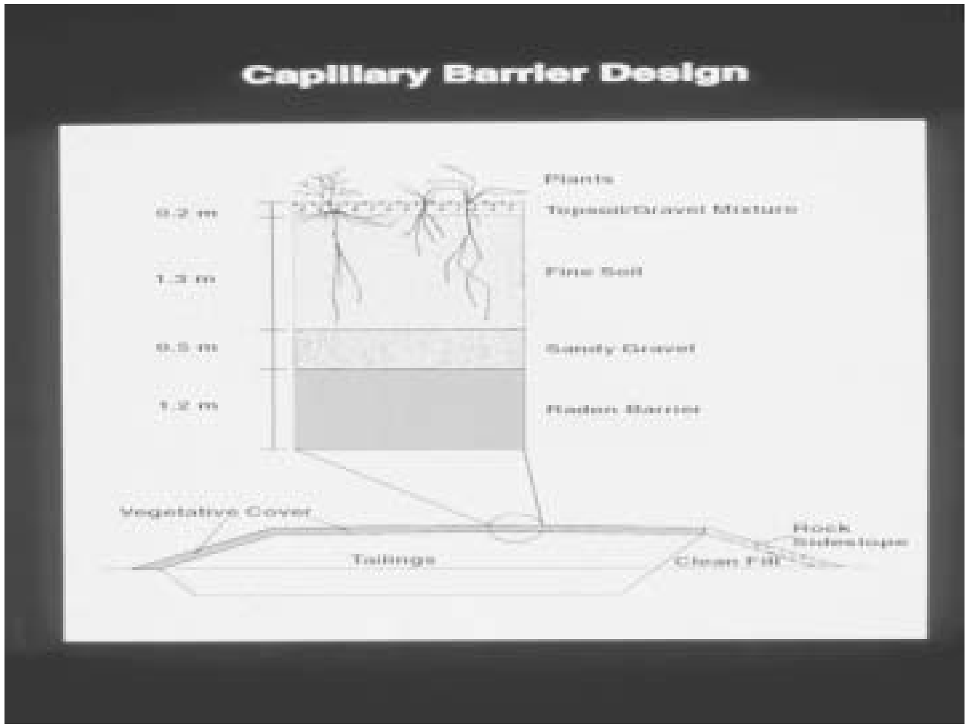

"Develop a cover design and implementation protocol, established for end users and accepted by regulators, that limits contaminant migration consistent with long-term (>100 years) risk-based performance criteria"

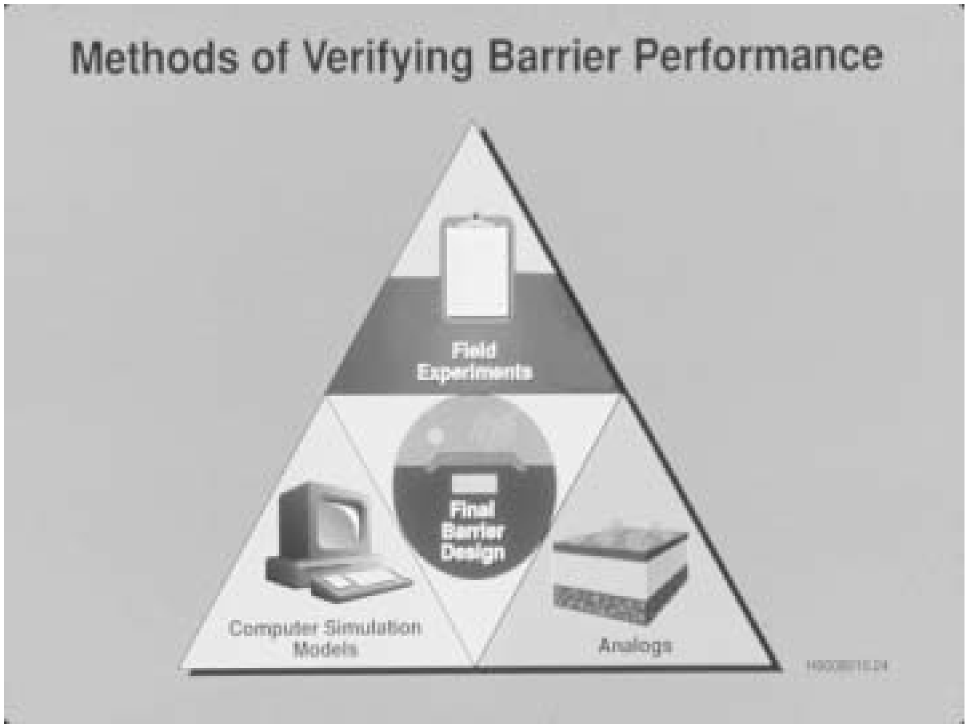

Uranium Mill Tailings
Disposal Sites


Rock/Low-Permeable Barrier Design
Filter Sand
(0.15 m)
Radon Barrier
(1.5 m)
Rock Riprap
(0.3 m)
5
1
Tailings and
Contaminated Soil


PL-1 RFL 8/97 Entrance gate, view N.


PL-23H LOW 8/94 Panorama from SMK-2, view NW


Capillary Barrier Design
Plants
0.2 m
Topsoil/Gravel Mixture
1.3 m
Fine Soil
0.5 m
Sandy Gravel
1.2 m
Radon Barrier
Vegetative Cover
Rock
Sideslope
Tailings
Clean Fill



Cover Analog Studies

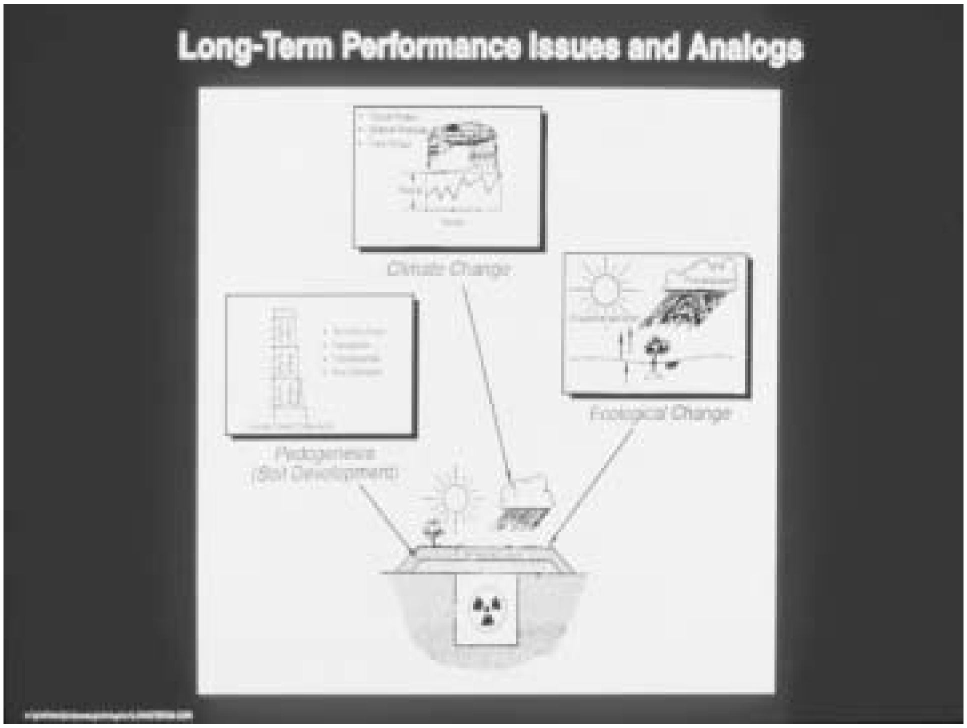
Definition

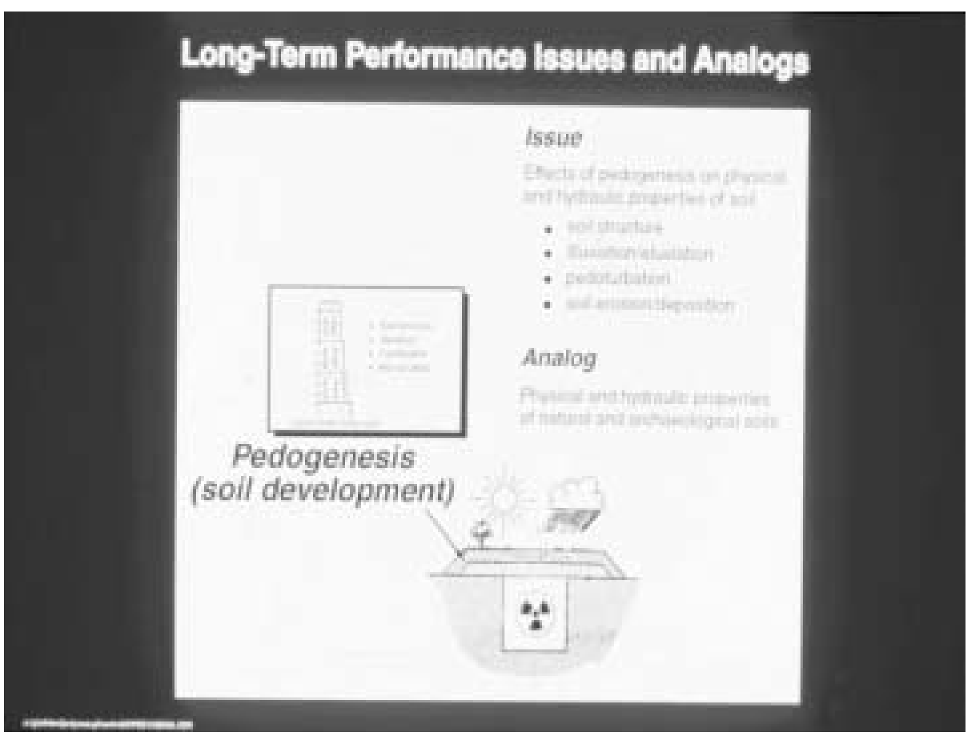
Evaluation of natural and archaeological settings that are similar in some respect to processes known or predicted to occur during the design life of landfill covers.

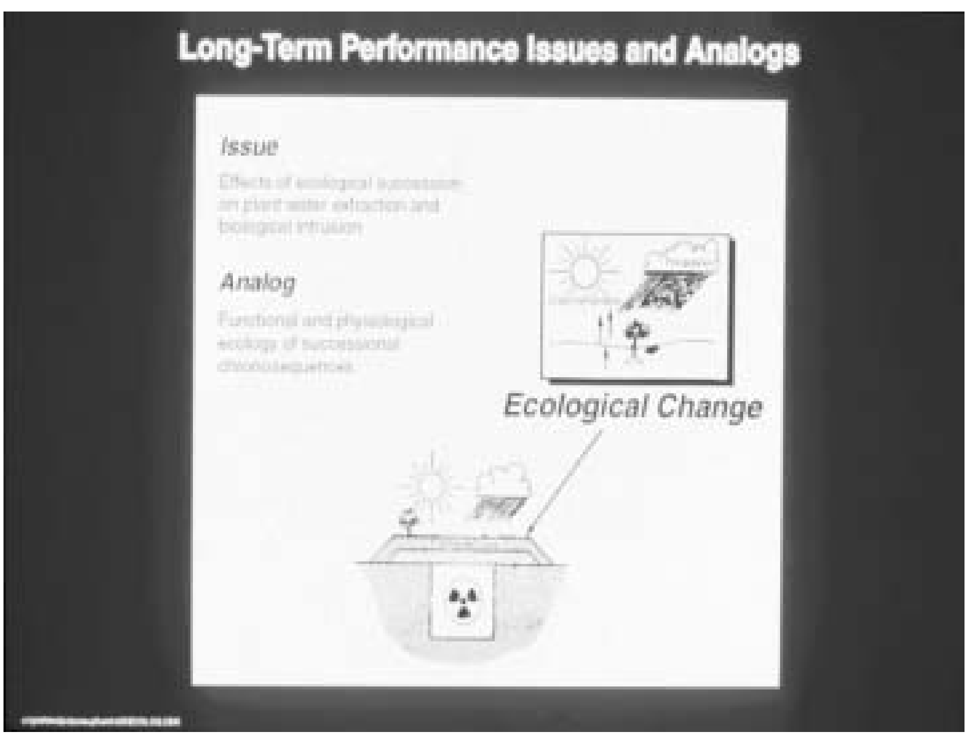
"Secrets of the past provide clues for the future"

Needs for Cover Analog Data

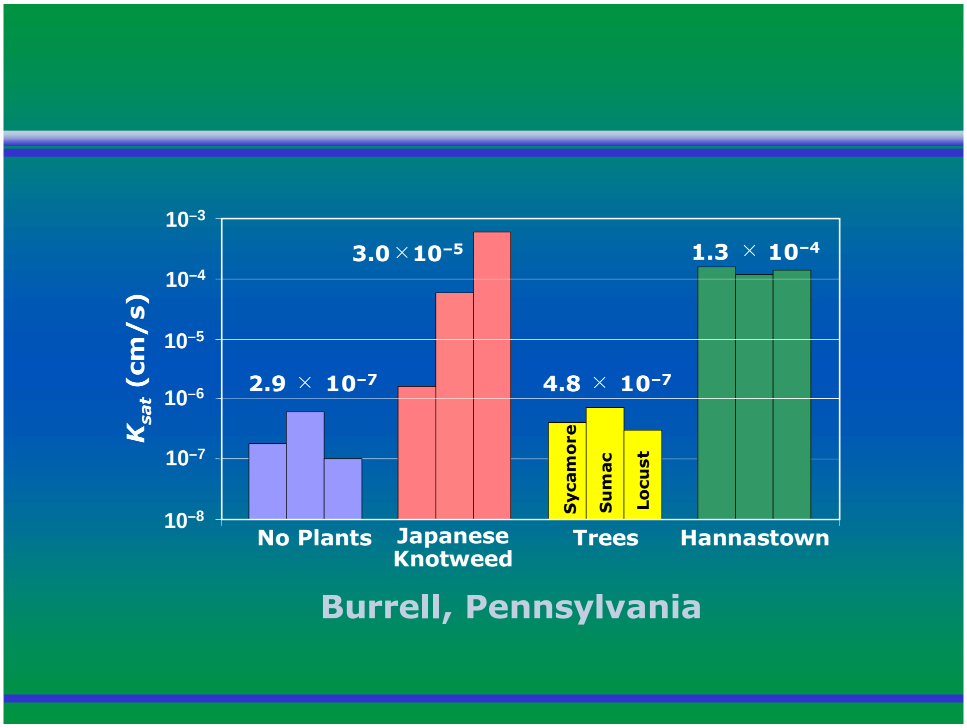
- Discern emergent attributes in the evolution of landfill covers
- Form hypotheses and select treatments for short-term field (e.g., lysimeter) studies
- Define reasonable ranges of values for model input parameters
- Demonstrate to stakeholders that numerical predictions have real-world complements


Long-Term Performance Issues and Analogs
Climate Change
Ecological Change
Pedogenesis
(Soil Development)


Long-Term Performance Issues and Analogs
Issue
Effects of pedogenesis on physical and hydraulic properties of soil
soil structure
illuviation/eluviation
pedoturbation
soil erosion/deposition
Analog
Physical and hydraulic properties of natural and archaeological soils
Pedogenesis
(soil development)


Long-Term Performance Issues and Analogs
Issue
Effects of ecological succession on plant water extraction and biological intrusion
Analog
Functional and physiological ecology of successional chronosequences
Ecological Change


BP-2
8-5-96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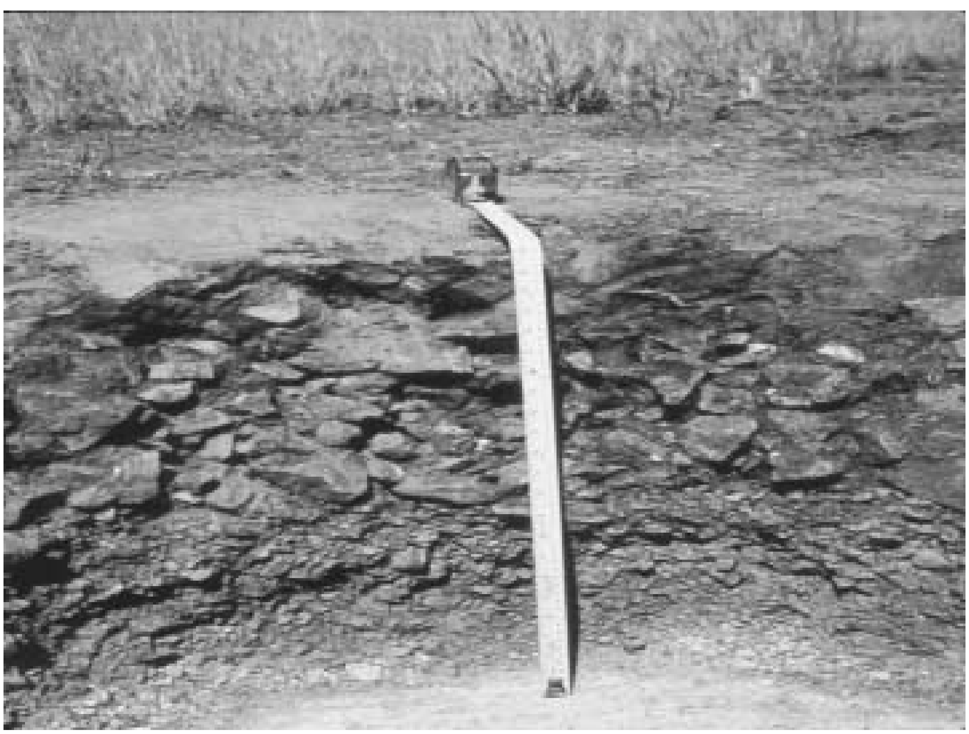
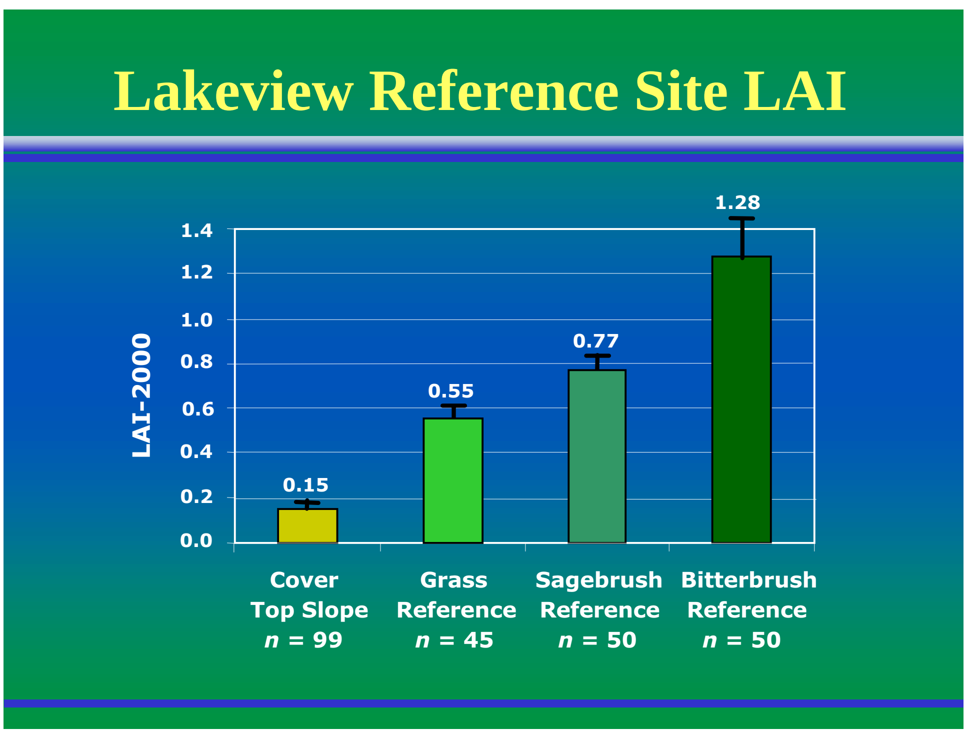
Sumac
Locust
No Plants
Japanese Knotweed
Trees
Hannastown
Burrell, Pennsylvania





Lakeview Reference Site LAI
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1.0
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0.6
0.4
0.2
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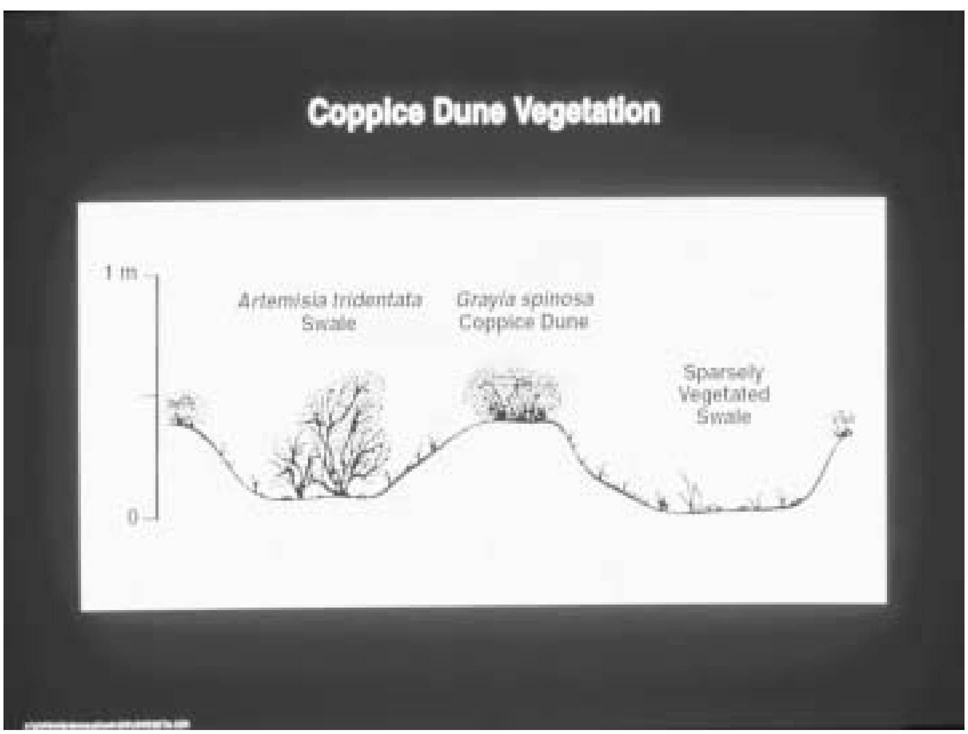
Coppice Dune Vegetation
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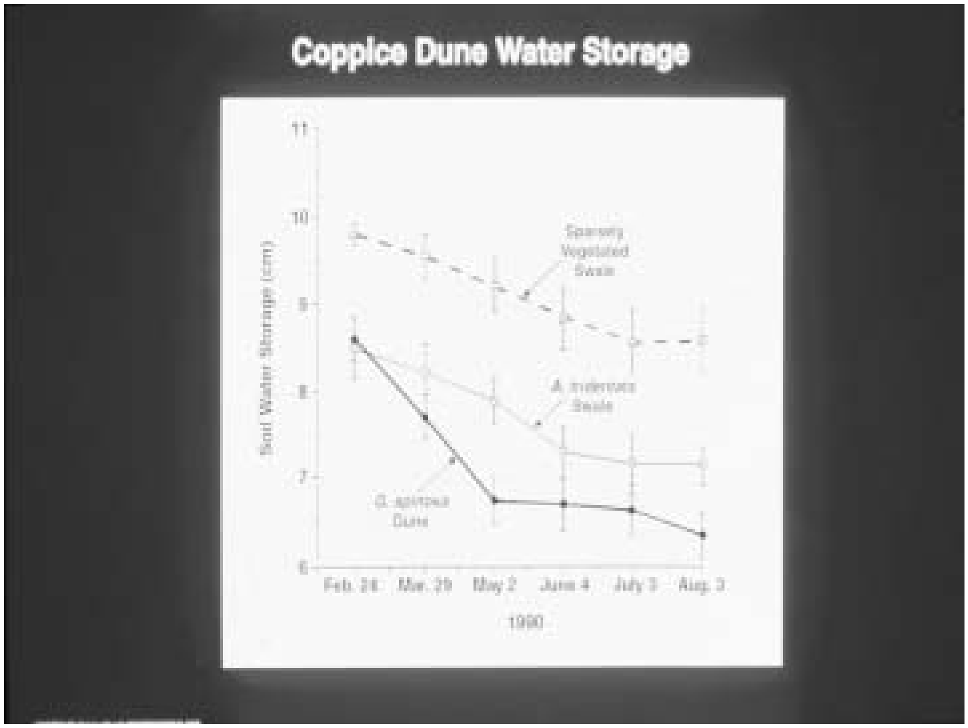
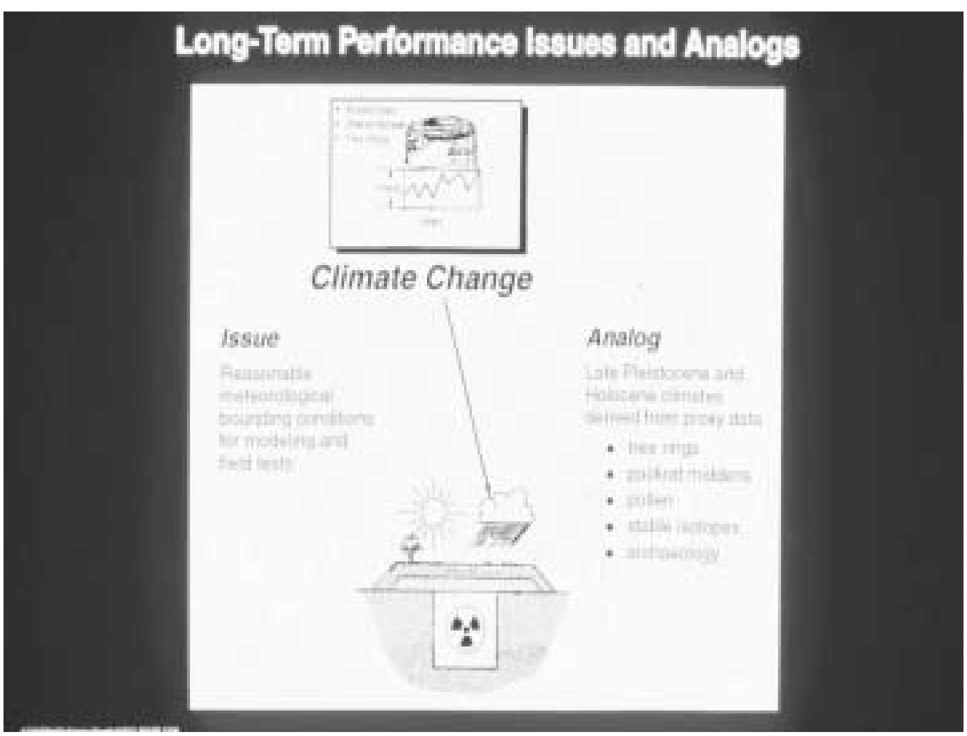
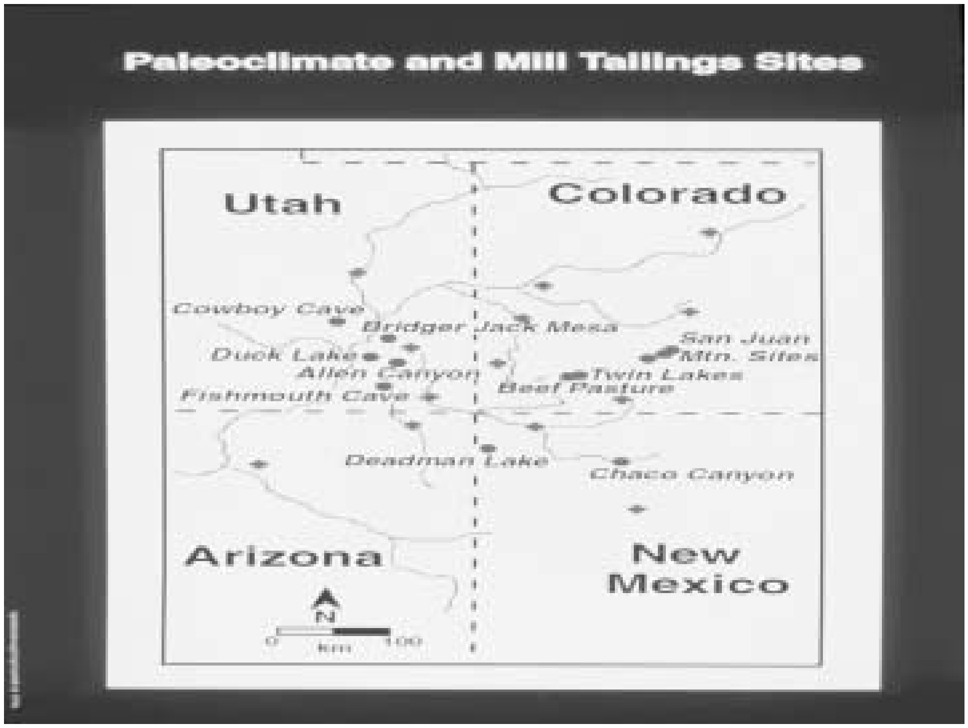
Artemisia tridentata
Swale
Grayia spinosa
Coppice Dune
Sparsely
Vegetated
Swale


Coppice Dune Water Storage
Soil Water Storage (cm)
11
10
9
8
7
6
Sparsely Vegetated Swale
A. tridentata Swale
Feb. 24
Mar. 29
May 2
June 4
July 3
Aug. 3
1990


Long-Term Performance Issues and Analogs
Climate Change
Issue
Reasonable meteorological bounding conditions for modeling and field tests
Analog
Late Pleistocene and Holocene climates derived from proxy data
• tree rings
• packrat middens
• pollen
• stable isotopes
• archaeology


Paleoclimate and Mill Tailings Sites
Utah
Colorado
Cowboy Cave
Bridger Jack Mesa
San Juan
Mtn. Sites
Duck Lake
Allen Canyon
Twin Lakes
Fishmouth Cave
Beef Pasture
Deadman Lake
Chaco Canyon
Arizona
New
Mexico
N
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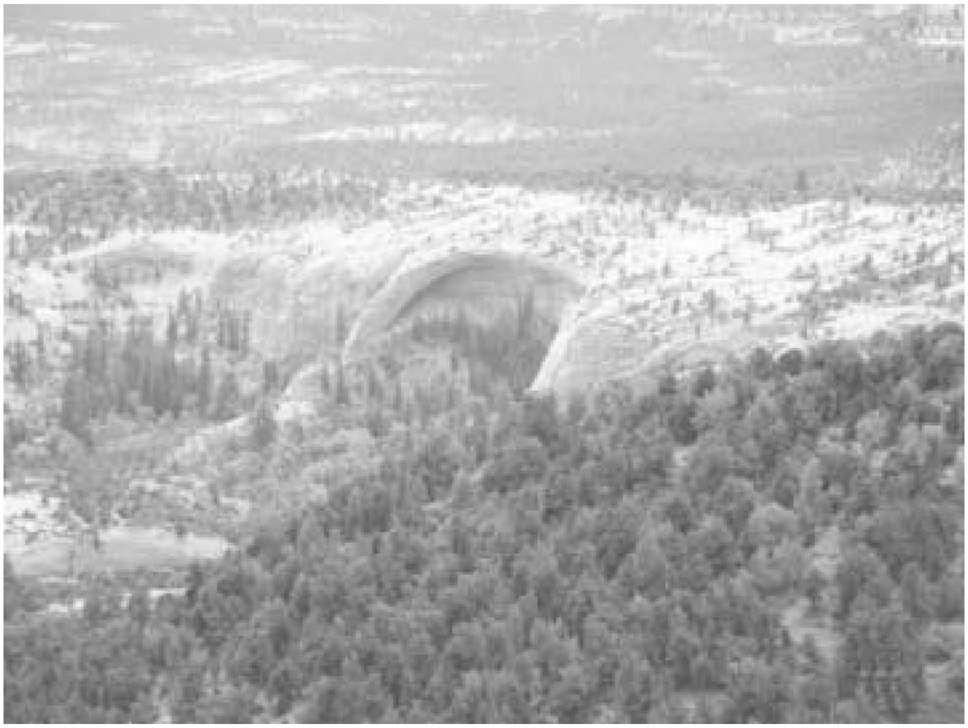

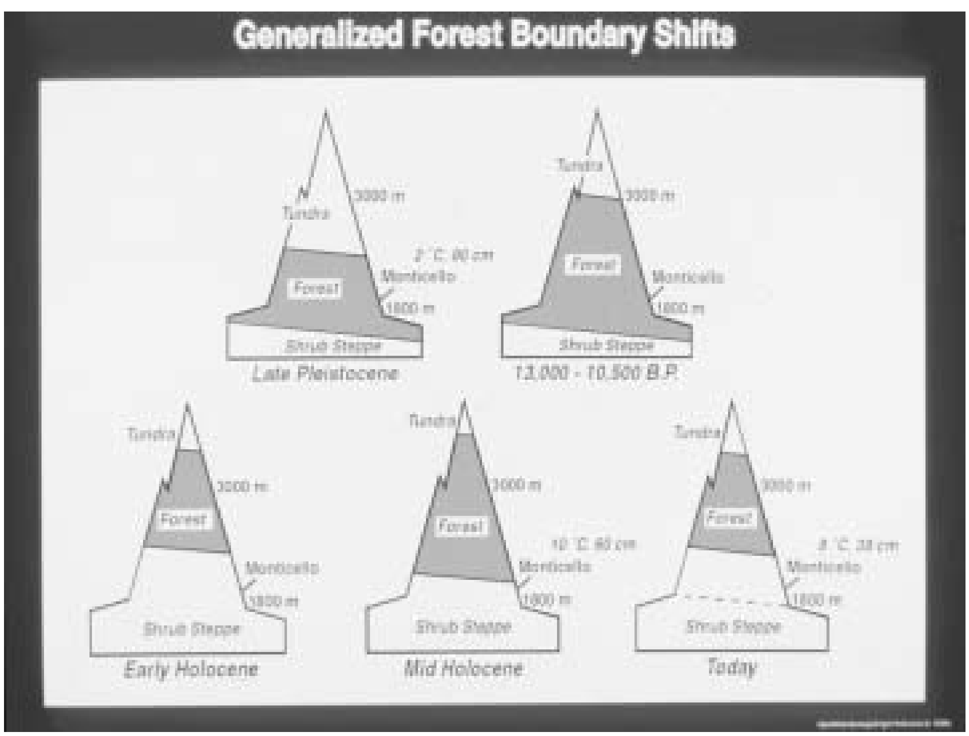
Generalized Forest Boundary Shifts
Tundra
3000 m
Forest
Monticello
1800 m
Shrub Steppe
Late Pleistocene
Tundra
3000 m
Forest
Monticello
1800 m
Shrub Steppe
13,000 - 10,500 B.P.
Tundra
3000 m
Forest
Monticello
1800 m
Shrub Steppe
Early Holocene
Tundra
3000 m
Forest
Monticello
1800 m
Shrub Steppe
Mid Holocene
Tundra
3000 m
Forest
Monticello
1800 m
Shrub Steppe
Today

Parting Thoughts

- Cover components will not function—and must not be designed—independently
- 1000-year cover performance cannot be extrapolated from initial conditions—changes in physical and ecological attributes are inevitable

Parting Thoughts (continued)

- Projections of long-term performance require a coupling of monitoring, modeling, and analog studies
- Designing covers to endure environmental change could save DOE billions in stewardship costs over the long term

VEGETATIVE COVERS

Tree Covers for Containment and Leachate Recirculation

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Ecolotree @ aol.com
For more information: www.Ecolotree.com

Eric Aitchison is an environmental engineer and project manager at Ecolotree, the oldest phytoremediation company in the U.S. Eric has worked on over 25 phytoremediation projects, and is experienced in design, site preparation, site installation, maintenance, and reporting. Eric also coordinates greenhouse experiments to evaluate phytoremediation potential at various sites.

Eric obtained a BS degree in civil engineering from Iowa State University and a MS degree in environmental engineering from The University of Iowa. His MS research evaluated the potential for phytoremediation of 1,4-dioxane by hybrid poplar trees. Eric has experience in consulting as an environmental engineer with Shive-Hattery, Inc., and as a researcher with The University of Iowa.

Abstract

The Ecolotree® Cap (E-Cap) is a patented crop system that reduces water percolation into the ground. The E-Cap grows tall poplar trees with deep root systems planted into specially prepared soils. E-Caps pump water from the cover soils, thus dehydrating the soil during the growing season and creating water storage capacity for the dormant winter months. Plants take up this water for growth or release it into the atmosphere by transpiration. E-Caps have been installed as alternative covers at 17 landfill sites in nine states. Applications include municipal solid waste landfills, industrial landfills (fly ash, casting sand), construction debris landfills, and Superfund hazardous waste landfills. The E-Cap has been approved and installed as final closure over old pre-subtitle D landfills in Pennsylvania, Tennessee, and Washington.

E-Caps can reduce long-term liability and minimize post-closure operation and maintenance ,costs. Communities are planning to use E-Caps at landfills for managing municipal sludges (biosolids, lime stabilization sludges, leaf litter, wood waste, and snow removal debris), and as recreational parks. The multiple benefits to wildlife habitat, greenhouse gas cycling, greening of a former eyesore, and reduction in costs help to make the E-Cap a technology worth the investment.

Ecolotree recently participated in the US EPA Alternative Cover Assessment Project (ACAP) at a landfill in Georgia. This project will provide valuable data with regards to the performance of an E-Cap verses a traditional clay cover.

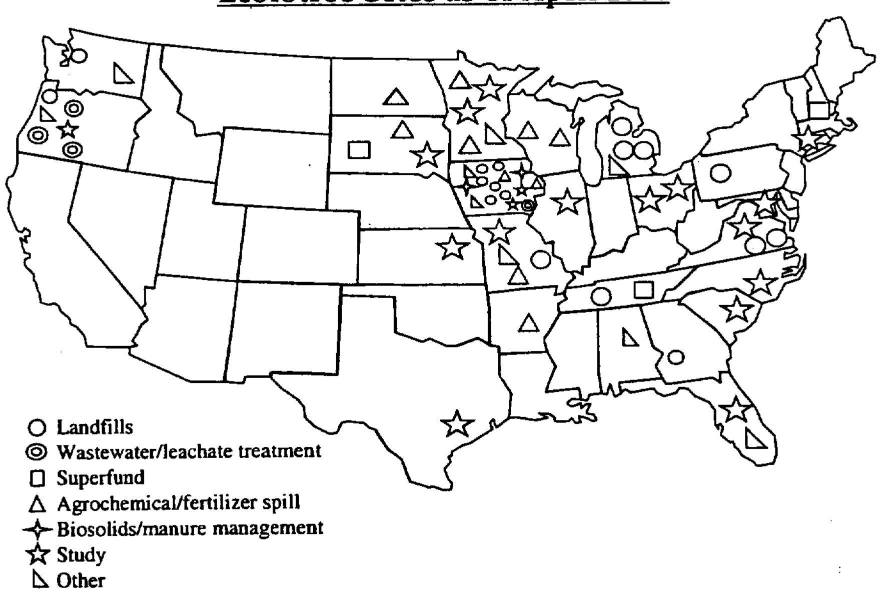
Wastewater and leachate have been successfully irrigated onto E-Caps at four sites. The vegetation takes up a significant portion of the water (up to 10,000 gallons/acre/day in summer months for 3-year old poplars), thus providing a wastewater/leachate sink. Contaminants, such as ammonium, nitrate, BOD, and BTEX compounds, are removed by 1) direct uptake into plants, 2) sorption to roots and soil organic matter, and 3) enhanced microbial degradation in the root zone. Irrigation rates can be adjusted to ensure that the desired performance standards are achieved. At the Great River Regional Waste Authority Landfill in Fort Madison, Iowa, 6 million gallons of leachate are being irrigated annually onto a 6-acre E-Cap. The E-Cap had a payback of two years when considering the previous cost of hauling the leachate to a wastewater treatment plant.

Tree Covers for Containment and Leachate Recirculation

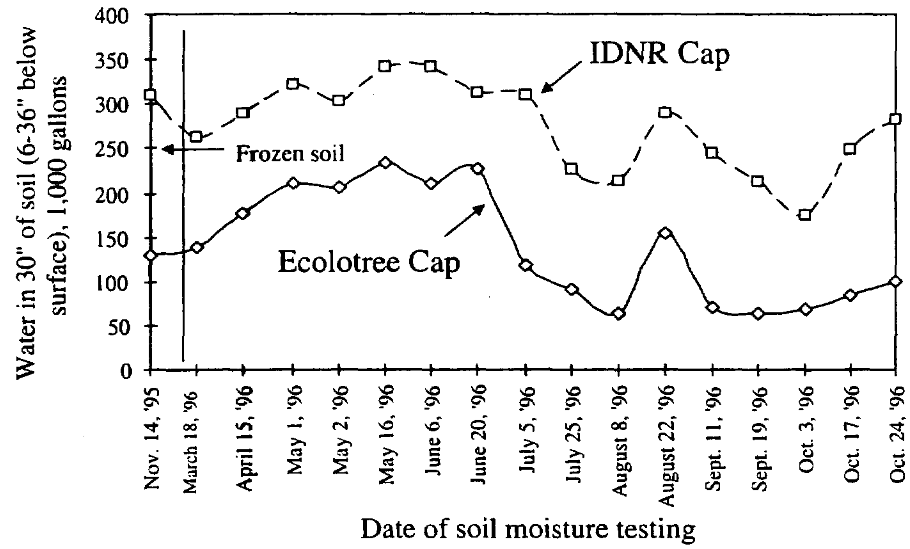
Phytoremediation: State of the Science Conference
May 1-2, 2000

Eric Aitchison, Ecolotree® Inc.
www.Ecolotree.com

<u>Ecolotree Sites as of April 2000</u>



Poplars dehydrated soil at the Bluestem Landfill (Cedar Rapids, Iowa) more than the traditional IDNR cover.



Ecolotree® Cap over Construction Debris Landfill:

Lakeside Reclamation Landfill - Beaverton, Oregon

- Planted in 1990 - 3 acres with 11,000 hybrid poplars
- > 90% survival
- 5-8' of vertical growth per year
- Roots have penetrated cover soil and rooted into waste
- Owner has received regulatory permission for full-site tree capping

Leachate Irrigation onto Ecolotree® Buffer:
Riverbend Landfill - McMinnville, Oregon

- Designed to treat 7 MGY of ammonium-rich leachate
- Installed in 1992-93 - 17 acres with 35,000 hybrid poplars
- 4th year of operation - 860,000 gallons/acre irrigated; 450 lbs N/acre removed
- Roots zone extended 7 feet below surface
- Worms dragged leaf matter to 7 feet below surface
- Soil moisture monitored by Time Domain Reflectometry
- CH2M HILL and Ecolotree received the 1994 Engineering Excellence Award from Oregon CEC and a national top 25 project award from National Society of Professional Engineers

Wastewater Treatment with an Ecolotree® Buffer:
City of Woodburn (Oregon) Wastewater Treatment Plant

- 10-acre demo (17,000 trees) planted in 1995; expanded to 90 acres in 1999
- Goal = tertiary treatment of wastewater for removal of thermal energy and ammonium
- Conservative design - water and nutrients irrigated to match plant uptake; treat 1.5 million gpd during summer months
- CH2M HILL and Ecolotree received the 1996 Engineering Excellence Grand Award by Oregon CEC

Leachate Irrigation onto an Ecolotree® Buffer:
GRRWA Landfill - Fort Madison, Iowa

- Designed to treat 7 MGY of MSW leachate; interim cap over Subtitle-D liner
- Regulatory agency very cooperative: approval 3 days after design submittal
- Installed in 1997-98 - 6 acres with 6,800 hybrid poplars
- Has provided the owner a payback of 2 years
- Organic waste will be applied between the tree rows
- Stanley Consultants and Ecolotree received the 1999-2000 Grand Conceptor Award for Engineering Excellence from the Iowa CEC

Conclusions

- Ecolotree® Caps and Buffers use poplar trees and a grass understory for containment and leachate/wastewater treatment.
- Vegetative systems offer numerous benefits to landfills:
    - Effective and economical
    - Acceptable by the neighboring community
    - Noise and visual barriers
- The data collected to date has supported the effectiveness of hybrid poplars for containment and treatment; more data is coming.

“

EPA Draft Guidance on Final Landfill Covers

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1200 Pennsylvania Avenue, NW Washington D.C. 20460

Andrea McLaughlin has a B.A. in Environmental Policy from Hood College in Frederick, Maryland. She has worked in both the private sector and with EPA on policies related to the management of hazardous wastes for 14 years.

Andrea is an Environmental Protection Specialist with EPA’s Office of Emergency and Remedial Response, where she has worked on Superfund landfill policy issues for approximately ten years. Prior to joining Superfund, Andrea developed proposed and final rules restricting the land disposal of hazardous waste for EPA’s Office of Solid Waste. Andrea is currently responsible for the development of a policy directive related to the use of alternative covers on Superfund Landfills, and is developing guidance on methods for assessing landfill gas emissions and health risks at Superfund Landfills.

Ken Skahn has a B.S. in Civil Engineering from the University of Illinois. Ken is registered both as a Professional Engineer and Structural Engineer in the State of Illinois. He has 25 years experience with EPA, 5 years with the Corps of Engineers, and 5 years in private practice as a consulting engineer. He has been closely involved with establishing EPA’s landfill regulations and policy for 13 years.

Ken is currently employed by EPA as an Environmental Engineer. For the past 10 years he has been working on design, construction, and post-remediation issues for the Superfund program at EPA’s headquarters in Washington, DC. He is the Superfund Program’s liaison to the Corps of Engineers as well as its landfill capping expert. He is currently leading a team in a revision of EPA’s landfill capping guidance that will include discussion of alternative cover designs.

Abstract

EPA is currently developing two guidance documents related to final landfill covers that are regulated under the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The first document, “Use of Selected Alternative Covers at CERCLA Municipal Landfills,” is specific to Superfund landfills, and provides guidance on how alternative covers may be considered as remedial alternatives in the CERCLA remedy selection process. Generally, the regulatory mechanism for approval of an alternative design will involve a demonstration of technical equivalence. This policy directive will explain what is meant by an “equivalent standard of performance” based on CERCLA and the National Contingency Plan (NCP). In addition, this guidance will identify factors (e.g., climatic conditions, landfill gas generation, and ground-water protection) that should be evaluated when determining whether or not consideration of an alternative landfill design is appropriate on a site-specific basis. This guidance is expected in January 2001.

The second guidance, “Technical Guidance for RCRA/CERCLA Final Covers,” provides an update to the previous U.S. EPA guidance on this subject, “Design and Construction of RCRA/CERCLA Final Covers,” EPA/625/4-92/025 (1991). In comparison to the scope of the 1991 guidance, this document has been expanded to address a number of new topics. In particular, this guidance addresses how technical equivalence may be demonstrated for alternative landfill designs, including capillary barriers and evapotranspirative barriers. The guidance also provides information on cover system design, design criteria development, new types of geosynthetics (such as geosynthetic clay liners), special design issues, lessons learned from the closure of existing landfills, performance monitoring of closed landfills, and maintenance of cover systems to achieve the required design life. This guidance was expected in December 2001.

EPA DRAFT GUIDANCE ON LANDFILL COVERS

Phytoremediation State of the Science Conference

May 2, 2000

Overview

- EPA LIQUIDS MANAGEMENT STRATEGY
- NEW EPA GUIDANCE
- STATUTORY/REGULATORY FRAMEWORK (RCRA/CERCLA)
- EQUIVALENCE DEMONSTRATION

EPA Liquids Management Strategy

- **TWO GOALS OF STRATEGY ARE TO:**
  - **MINIMIZE LEACHATE GENERATION BY KEEPING LIQUIDS OUT OF LANDFILL; AND**
  - **DETECT, COLLECT, AND REMOVE LEACHATE AS GENERATED**

Draft Landfill Guidance

- **TWO EPA GUIDANCE DOCUMENTS BEING DEVELOPED:**
  - **"TECHNICAL GUIDANCE FOR RCRA/CERCLA FINAL COVERS"**
  - **"USE OF SELECTED ALTERNATIVE COVERS AT CERCLA MUNICIPAL LANDFILLS"**
- **IMPLEMENT LIQUIDS MANAGEMENT STRATEGY**

Draft Landfill Guidance *(cont.)*

- "TECHNICAL GUIDANCE FOR RCRA/CERCLA FINAL COVERS"
  - UPDATE TO 1991 RCRA GUIDANCE
  - INCLUDES ALTERNATIVE DESIGN AND MATERIALS
- "USE OF SELECTED ALTERNATIVE COVERS AT CERCLA MUNICIPAL LANDFILLS"
  - ADDRESSES SUBTITLE D CLOSURE

RESOURCE CONSERVATION AND RECOVERY ACT (RCRA)

- SUBTITLE D CLOSURE CRITERIA (40 CFR 258.60)
  - INFILTRATION LAYER MUST HAVE:
    - » PERMEABILITY LESS THAN OR EQUAL TO PERMEABILITY OF BOTTOM LAYER, OR
    - » PERMEABILITY NO GREATER THAN 1 X 10^{-5} cm/sec, WHICHEVER IS LESS

RCRA SUBTITLE D *(cont.)*

- DIRECTOR OF APPROVED STATE MAY APPROVE ALTERNATIVE COVER THAT INCLUDES:
  - INFILTRATION LAYER THAT ACHIEVES EQUIVALENT REDUCTION IN INFILTRATION (1 X 10^{-5} cm/sec)

RCRA SUBTITLE D *(cont.)*

- RCRA PROGRAM DELEGATED TO STATES
- SOME STATES MORE STRINGENT
- MANY STATES WILL HAVE PROVISION FOR ALTERNATIVE COVERS
  - SHOULD INCLUDE 1 X 10^{-5} cm/sec STANDARD

COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION AND LIABILITY ACT (CERCLA)

- **STATUTORY REQUIREMENTS**
  - **ALL REMEDIES MUST MEET OR WAIVE APPLICABLE OR RELEVANT AND APPROPRIATE REQUIREMENTS (ARARs)**
  - **RESPONSE ACTIONS MUST BE PROTECTIVE**

CERCLA *(cont.)*

- **ARARS ARE:**
  - **ANY STANDARD, REQUIREMENT, CRITERION, OR LIMITATION UNDER ANY FEDERAL ENVIRONMENTAL LAW; OR**
  - **ANY <u>PROMULGATED</u> STANDARD, REQUIREMENT, CRITERION, OR LIMITATION UNDER A STATE ENVIRONMENTAL LAW**

CERCLA *(cont.)*

- **CLOSURE REQUIREMENTS GENERALLY IDENTIFIED AS ARARs BY THE STATE**
- **ALTERNATIVE COVER MAY BE USED IF:**
  - **STATE REGULATIONS INCLUDE ALTERNATIVE COVER PROVISION; OTHERWISE**
  - **ARAR WAIVER MAY BE NECESSARY**

CERCLA *(cont.)*

- **EQUIVALENT STANDARD OF PERFORMANCE ARAR WAIVER (SECTION 300.430(f) OF NCP):**

"The alternative will attain a standard of performance that is equivalent to that required under the otherwise applicable standard ....through use of another method or approach."

CERCLA *(cont.)*

- FOR ARAR WAIVER, RCRA SUBTITLE D INFILTRATION RATE MUST BE ACHIEVED
  - AT ALL TIMES (NOT AVERAGED)
- IF EQUIVALENCE DEMONSTRATED, MAY BE COMPARED TO OTHER ALTERNATIVES IN FEASIBILITY STUDY USING NINE CRITERIA

TO RE-CAP:

- ALTERNATIVE COVER IS POSSIBLE FOR CERCLA LANDFILLS IF:
  - CLOSURE IS SUBTITLE D;
  - STATE REGULATIONS INCLUDE ALTERNATIVE COVER PROVISION OR ARAR WAIVED
  - EQUIVALENT INFILTRATION RATE IS DEMONSTRATED
  - NINE CRITERIA ANALYSIS IS FAVORABLE

EPA DRAFT GUIDANCE ON LANDFILL COVERS

Phytoremediation
State of the Science Conference

May 2, 2000

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WHY REVISE EPA'S COVER GUIDANCE?

- EMERGENCE OF NEW MATERIALS
- LANDFILL GAS
- PERFORMANCE MONITORING
- LONG TERM MAINTENANCE
- ALTERNATIVE DESIGNS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WHAT WILL BE IN THE GUIDANCE?

- REGULATORY REQUIREMENTS
- DESIGN CONSIDERATIONS
- ALTERNATIVE DESIGNS
- WATER BALANCE MODELS
- GEOTECHNICAL ANALYSIS AND DESIGN
- LESSONS LEARNED
- LONG TERM MAINTENANCE

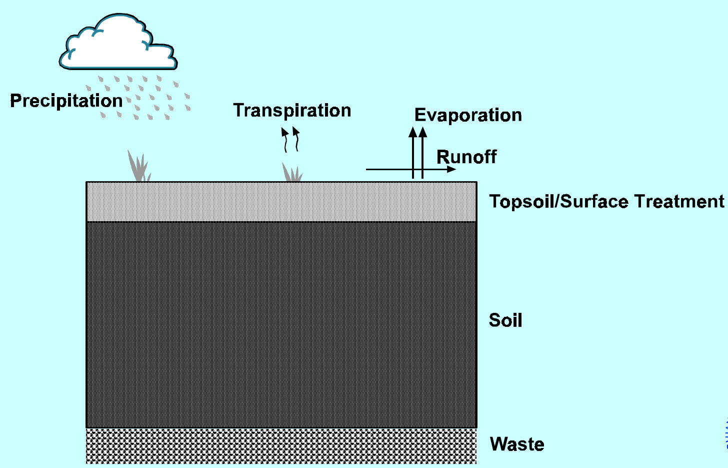
WHAT IS THE DESIGN LIFE FOR COVERS?

- HUNDREDS OF YEARS IS NOW FEASIBLE DEPENDING ON:
  - SELECTION OF MATERIALS
  - SLOPE STABILITY
  - RESISTANCE TO EROSION
  - ADEQUATE FLOW CAPACITY FOR INTERNAL DRAINAGE SYSTEM
  - LONG TERM MAINTENANCE

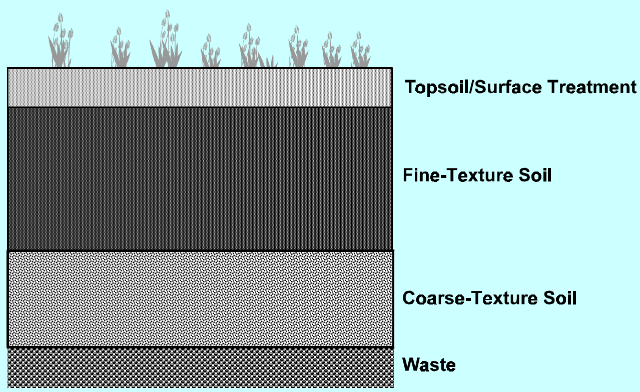
HOW DO ALTERNATIVE COVERS WORK?

- EVAPOTRANSPIRATIVE BARRIER
- CAPILLARY BARRIER

ET Barrier



Capillary Barrier



WHAT ARE THE DESIGN STEPS?

- DETERMINE IF GAS COLLECTION IS REQUIRED
- IDENTIFY CRITICAL INFILTRATION EVENTS
- CALCULATE MINIMUM STORAGE CAPACITY
- CHARACTERIZE SOIL PROPERTIES

DESIGN STEPS *(cont.)*

- CALCULATE SOIL THICKNESS (USING FACTOR OF SAFETY OF 1.5 OR MINIMUM OF 3 FEET)
- DETERMINE VEGETATION AND SURFACE TREATMENT
- ESTABLISH ADEQUACY OF DESIGN USING PREDICTIVE MODELING

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

HOW IS EQUIVALENCE DEMONSTRATED?

- SHOW THAT ALTERNATIVE COVER WILL PERFORM AS WELL AS THE SUBTITLE D COVER USING PREDICTIVE MODELING
- VERIFY BY PERFORMANCE MONITORING USING AN INSTRUMENTED TEST/VERIFICATION PAD

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WHAT ISSUES REMAIN?

- LANDFILL GAS
- APPROPRIATE PREDICTIVE MODEL
- WHAT CONSTITUTES FAILURE
- ARID ENVIRONMENT
- TREES

DEGRADATION OF ORGANIC COMPOUNDS IN SOILS

Hydrocarbon Treatment Using Grasses

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M. Katherine Banks is currently an associate professor of civil engineering at Purdue University. She received a B.S. in environmental engineering from the University of Florida, a M.S.E.E. in water resources engineering from the University of North Carolina, and a Ph.D. in civil and environmental engineering from Duke University. Dr. Banks was a member of the faculty at Kansas State University from 1989 to 1997. Her research projects focus on the use of phytoremediation for hazardous organic compunds using deep-rooted grasses. Over the past 8 years, Dr. Banks has been involved with phytoremediation field projects in California, Kansas, Virginia, Texas, and Indiana.

Abstract

Petroleum contamination of soil is a serious problem throughout the United States. Bioremediation of petroleum in soil using indigenous microorganisms has proven effective; however, the biodegradation rate of more recalcitrant and potentially toxic petroleum contaminants, such as polycyclic aromatic hydrocarbons, is rapid at first but declines quickly. Biodegradation of such compounds is limited by their strong adsorption potential and low solubility. Vegetation may play an important role in the biodegradation of toxic organic chemicals in soil. For petroleum compounds, the presence of rhizosphere microorganisms may accelerate biodegradation of the contaminants. The establishment of vegetation on hazardous waste sites is an economic, potentially effective, low maintenance approach to waste remediation and stabilization.

In a number of field trials, it has been demonstrated that phytoremediation is a viable treatment alternative for aged petroleum contaminated soil. Degradation of total petroleum hydrocarbons was found to be greater in vegetated treatments compared to unvegetated controls. The rate of remediation in the planted plots did not diminish with time; a “plateau” effect was not observed. However, there are limitations to this technology. Considerable time is needed to achieve regulated levels, depending upon the initial concentrations and the desired end points. Phytoremediation using grasses and legumes is a reasonable alternative for surface contamination but will have minimal impact below 100 cm. More information is needed concerning the plant species that are best adapted to phytoremediation. A more complete understanding of the mechanisms involved will allow for optimal selection of plants for future phytoremediation projects.

Phytoremediation of Explosives Phillip Thompson

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Steven McCutcheon and N. Lee Wolfe U.S. EPA National Exposure Laboratory Athens, Georgia

Phillip Thompson has a B.A. in Biology and an M.S. and Ph.D. in Environmental Engineering from the University of Iowa. He is a registered professional engineer in the State of Washington and has been involved in projects ranging from drinking water treatment to phytoremediation. Phillip has been an assistant professor in the Department of Civil and Environmental Engineering at Seattle University since the Fall of 1997 where he teaches He teaches courses in water supply, wastewater treatment, hazardous waste management and engineering economics. His current research interests are in the areas hazardous waste remediation and water re-use.

List of Related Publications

http://www.seattleu.edu/scieng/cee/thompson

Abstract

This research evaluated the toxicity, uptake and fate of the explosives 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in hybrid poplar trees (Populus *deltoides x* nigra, DN34). TNT was toxic to the hybrid poplar at a concentration of 5 mg/L. It also reacted quickly at the root surface where it was transformed into a number of known and unknown products, Transformation likely caused the retention of up to 75 percent of the TNT-related 14C in the root tissues. Less than 10 percent of the applied TNT was translocated to leaf tissues, all in the form of as yet defined products. The identification of these transformation products may be important to field-scale phytoremediation efforts.

RDX uptake and fate was quite different than that of TNT. Over 60 percent of the applied RDX bioaccumulated in leaf tissues as parent compound. The transformation of RDX was very slow with only small fractions of degradation in leaf tissues overtime periods of months. The accumulation of RDX in leaf tissues may be a concern with regard to leaf litter transport and consumption by herbivorous species. Since the rate of contaminant removal from soil is a function of concentration, the timeframe for phytoremediation to achieve near-pristine conditions will vary from several years to many decades. A discussion of this and other design-related questions will be included.

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Phytoremediation of Explosives Contamination

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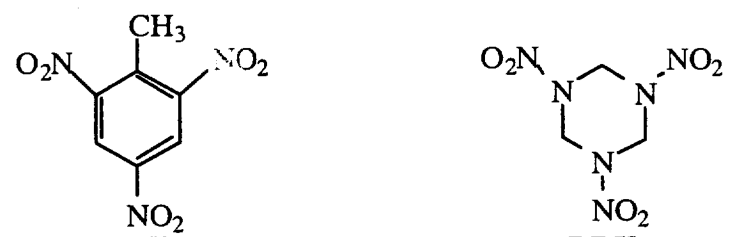
Seattle University, Seattle, Washington

Steven McCutcheon and N. Lee Wolfe
U.S. EPA National Exposure Laboratory
Athens, Georgia

TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) are two of the most commonly used explosives in the world. Liquid wastes containing TNT and RDX are generated at ammunition production facilities as a result of cleaning operations. Historically, these waste streams were discharged to lagoons that subsequently were released into local streams (Higson, 1992). Although this method of disposal is no longer practiced, thousands of acres across the United States are still highly contaminated (Funk et al., 1993). For example, TNT and RDX have contaminated several acres of land at the Iowa Army Ammunition Plant (IAAP) at Middletown, Iowa.

The chemical structures of TNT and RDX are shown in Figure 1. The dimensionless Henry's constants have been estimated to be 1.5×10^{-9} and 1.5×10^{-5} for RDX and TNT, respectively. Physical and chemical properties of the two explosives are presented in Table 1.



TNT (2,4,6-trinitrotoluene) **RDX (1,3,5-trinitro-1,3,5-triazine)**

Figure 1: The chemical structures of TNT and RDX

Table 1: Some physical and chemical properties of TNT and RDX

Explosive	Molar Mass, g	Water Solubility at 25• C, mg/L	Log Vapor Pressure at 25• C, Torr	Log K_{ow}
RDX	222.0[a]	59.0[c]	-8.3[b]	0.9[e]
TNT	227.0[a]	100.1[b]	-3.9[d]	1.9[e]

a = Budavari, 1990; b = Spanggord, 1996; c = Chen, 1993; d = Lange's Handbook of Chemistry; e = Haderlein, 1996

A number of approaches have been used to remediate TNT and RDX contamination including carbon adsorption, incineration, and microbial bioremediation (Kaplan, 1990). Incineration and carbon adsorption are widely accepted treatment methods, but they are both generally very expensive (Funk et al., 1993). Microbial transformations of TNT and RDX also have limitations in that mineralization is rarely achieved. Since existing treatment technologies are inadequate or too expensive, alternatives such as phytoremediation should be considered.

This research evaluated the potential for using poplar trees to remediate TNT and RDX contamination at the IAAP. It was hypothesized that 1) the poplar tree hybrid (*Populus deltoides × nigra* , DN34) has the intrinsic ability to translocate and transform TNT and RDX from water and soil 2) these explosives are not toxic to the tree and 3) sorption to IAAP soil controls the bioavailability of TNT, RDX and any transformation products. The information gathered from these laboratory studies was used to develop a finite difference model.

The sorption of RDX, TNT, and the TNT metabolites 4-amino-2,6-dinitrotoluene (4-ADNT) and 2-amino-4,6-dinitrotoluene (2-ADNT) to the organic-rich (f_{oc}=0.019) soil from the IAAP was evaluated to understand the potential transport and bioavailability of these chemicals. Soil-chemical equilibria were achieved in less than 24 hours for all compounds except for TNT which exhibited slow sorption for several days. The mobility and bioavailability were determined to be RDX>TNT>2-ADNT>4-ADNT based on linear sorption distribution coefficients (K_d). The values obtained for RDX and TNT agreed well with those found in the literature. Coefficients determined for 2-ADNT and 4-ADNT were an order of magnitude larger than predicted by empirical relationships and are new contributions to the literature with respect to organic-rich soils.

Hydroponic experiments with the hybrid poplar revealed that radiolabeled RDX and TNT behave quite differently in terms of uptake, transport and fate. The removal of RDX from solution was slow as demonstrated by the increase of RDX concentrations in hydroponic solution over time and the low transpiration stream concentration factor (TSCF) of 0.16$\pm$0.06 (n=9). RDX was taken-up from soil more quickly relative to TNT due to its greater availability (weaker sorption).

RDX-related radiolabel was distributed throughout/plant in similar proportions for experiments lasting from 2 to 26 days. The largest amounts (60 percent of that taken-up) of label were found in leaf tissues with the remainder being equally distributed between root and stem tissues. Mass balances for RDX showed a linear decrease in recovery over time that could not be explained through the capture of $^{14}CO_2$ or volatile organics. An average of 85 percent of the absorbed RDX-related radiolabel was extracted from plant tissues, and radiochromatograph analysis demonstrated that no RDX transformation had occurred. In uptake experiments, there was a fraction of radiolabel that could not be extracted with the acetone procedure. It is thought that this fraction was bound residue, a transformation product of RDX in the plant. Recent preliminary results by researchers at the University of Iowa have suggested that previously unrecovered radiolabel is in the form of formic acid (Just, 2000).

Contrary to RDX, the removal of TNT from hydroponic solution by poplar was quite rapid and was a result of both uptake to stems and leaves and root-mediated transformation. One unidentified polar product was detected in the hydroponic solutions while at least three unknowns (all more polar than TNT) were detected in root extracts. These compounds did not appear to be mobile within the plant as they were not detected in xylem tissues or leaves. Small amounts of transformation products 4-ADNT, 2-ADNT and 2,4-DANT were detected in all plant tissues except for the leaves where polar unknown(s) comprised the only detectable ^{14}C products. In all, these transformation products comprised about ten percent of the radioactivity taken-up by the plant and about 20 percent of the extractable label. On average, only 50 percent of the TNT-related label was extractable by organic solvents such as methanol or acetone.

The majority (about 70 percent) of the TNT-related radiolabel taken-up remained immobilized in root tissues for periods ranging from two to 42 days. This immobilization may reflect the transformation to 4-ADNT and 2-ADNT, compounds which are generally less mobile in the environment. The remaining absorbed radiolabel was equally distributed to the stem and leaf tissues. The fortuitous separation of secondary xylem and phloem tissues showed that there was 10 times the label contained in the xylem and the transport of radiolabel to the phloem from the leaves was possible. The removal of TNT from solution was quick and the TSCF for TNT was estimated at 0.46 ± 0.19 (n=18).

Phytoremediation of organic wastes requires the evaluation of toxicity of contaminants to plant species. The common method of measuring phytotoxicity is based on declines in biomass production, a destructive endpoint. Results indicated that plant toxicity can also be estimated by measuring the transpiration of exposed plants. Gravimetric measurement of transpiration is a simple technique and can be a useful means of complementing data from other toxicity tests such as overall growth rate. Hydroponic, bench-scale experiments showed that TNT removal from solution by hybrid poplar cuttings can be rapid, and that TNT concentrations greater than or equal to 5 mg/L were toxic to the cuttings; whereas 1 mg/L doses had no observed adverse-effects in 21 day tests. Therefore, the poplar hybrid has a tolerance for TNT that is greater than duckweed (Schott, 1974) and similar to yellow nutsedge (Leggett and Palazzo, 1986). A comparison between bench-scale and pilot-scale experiments suggested that the laboratory approach used for much of the poplar research at the University of Iowa was valid for estimating phytotoxicity at larger scales. The pilot-scale experiment established that a 5 mg/L TNT was not toxic for acute (<14 days) exposures, but there were indications that prolonged exposure would be detrimental. There appears to be only a small scale-up difference between the large greenhouse-grown trees and the small lab-grown cuttings. The poplar hybrid showed no signs of toxicity when exposed to concentrations of RDX up to 21 mg/L for up to 14 days.

Results from this research were used to develop a finite difference model for the estimation of cleanup times. The model assumed a uniform volume of contamination (50 mg/kg TNT and 20 mg/kg RDX) with an area of 0.4 hectares (one acre) and a depth of three meters. Model inputs included the use of experimentally determined TSCF values and partition coefficients. It was also assumed that 650 trees would be planted per acre and these trees would maximally transpire 15 gallons of water per day. Over a 180-day growing season, the total amount of transpiration would be on the order of 10,000 liters. Model results indicated that the half-life for RDX would be approximately five years and for TNT it would be fifteen to twenty years.

Since the time to cleanup for the remaining TNT and RDX contamination at IAAP are relatively long, explosives uptake by poplar may be less important than the tree's hydraulic capacity to protect groundwater. Another concern may be the translocation of RDX to the leaves of the tree and the subsequent consumption by deer, hence monitoring of leaf tissue for RDX is recommended.

Future research needs include determining if the formation of volatile products is a major fate pathway for TNT and especially RDX. This may involve the development of a capture-system that is both efficient and capable of mimicking natural growing conditions. The identification of the unknown transformation products would also broaden our understanding TNT fate.

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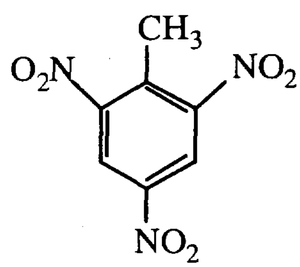
Phytoremediation of Explosives

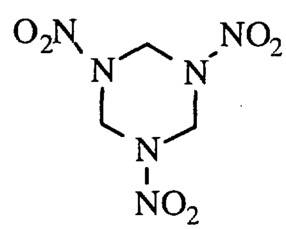
Phillip L. Thompson,
Seattle University

Steven C. McCutcheon
and N. Lee Wolfe
U.S. EPA NERL

2 May 2000



TNT
(2,4,6-trinitrotoluene)

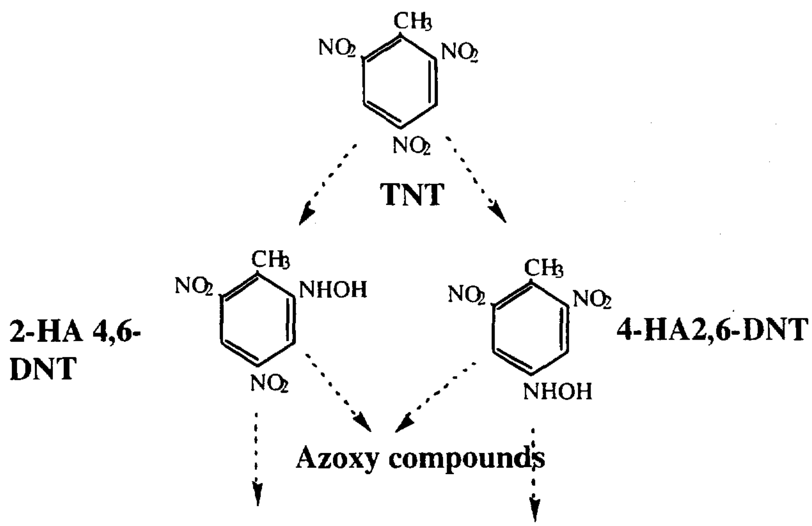


RDX
(1,3,5-trinitro-1,3,5-triazine)

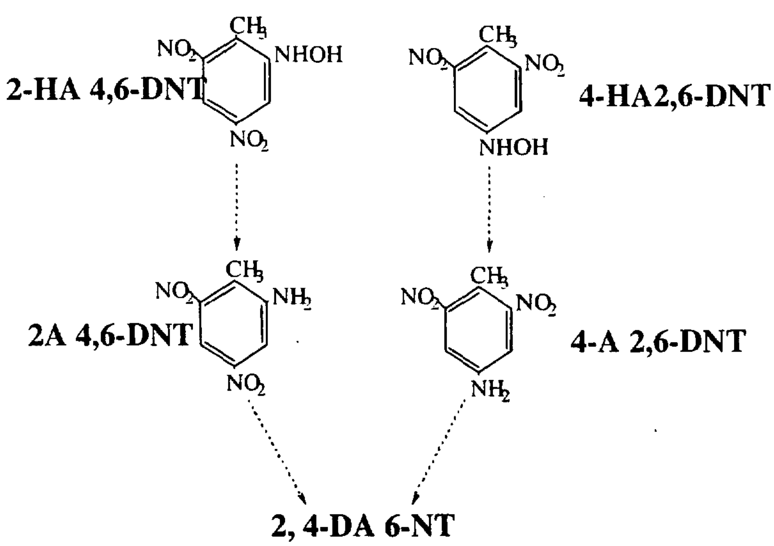
Log K_{ow} = 1.9
Solubility = 100 mg/L at 25°C

Log K_{ow} = 0.9
Solubility = 40 mg/L at 25°C

Metabolic pathways for TNT



Metabolic Pathways continued.

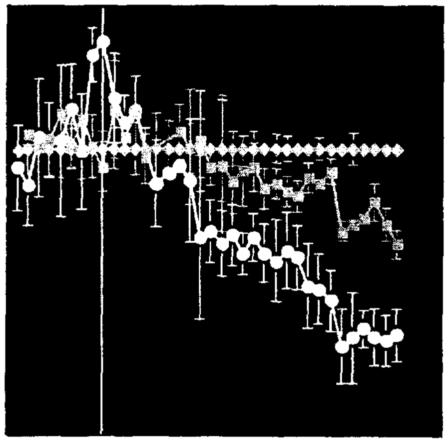


Uptake by Terrestrial Plants

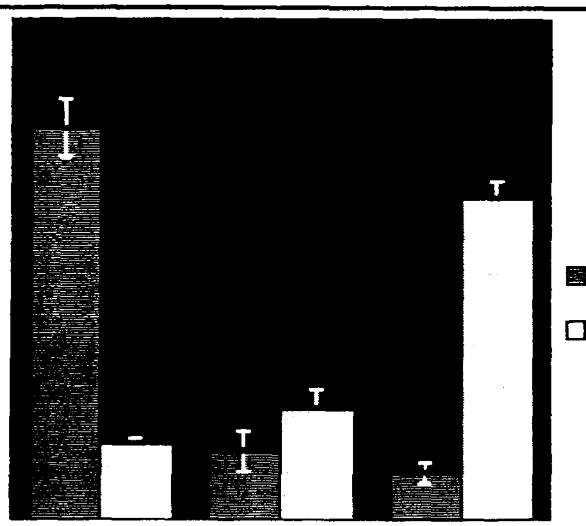
- Yellow Nutsedge
- Bush Bean, Maize, Wheat
- Poplar
- Grasses (tall fescue, switchgrass)

TNT Toxicity

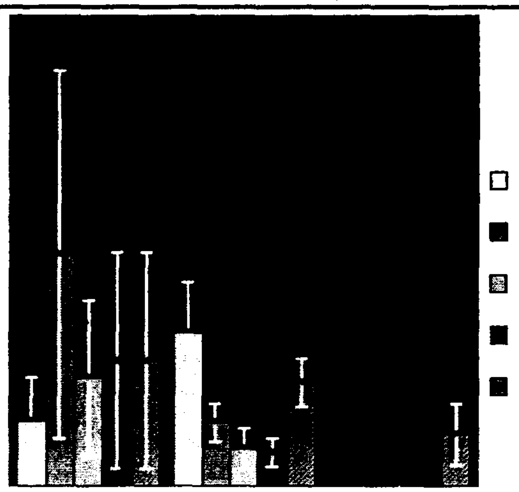
- Yellow Nutsedge - 5 mg/L
- Poplar - 5 mg/L
- Tall fescue - 30 mg/L
- Switchgrass - 15 mg/L
- Common Bean - 500 mg/kg



Translocation of TNT and RDX

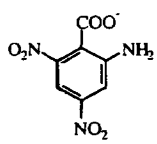


Metabolism of TNT

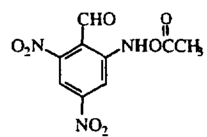


Possible Novel Products

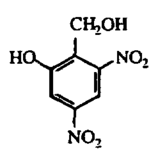
2-amino-4,6-dinitrobenzoate



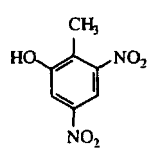
2-N-acetoxyamido-4,6-dinitrobenzaldehyde



2,4-dinitro-6-hydroxybenzaldehyde



2,4-dinitro-6-hydroxytoluene



Fate of RDX

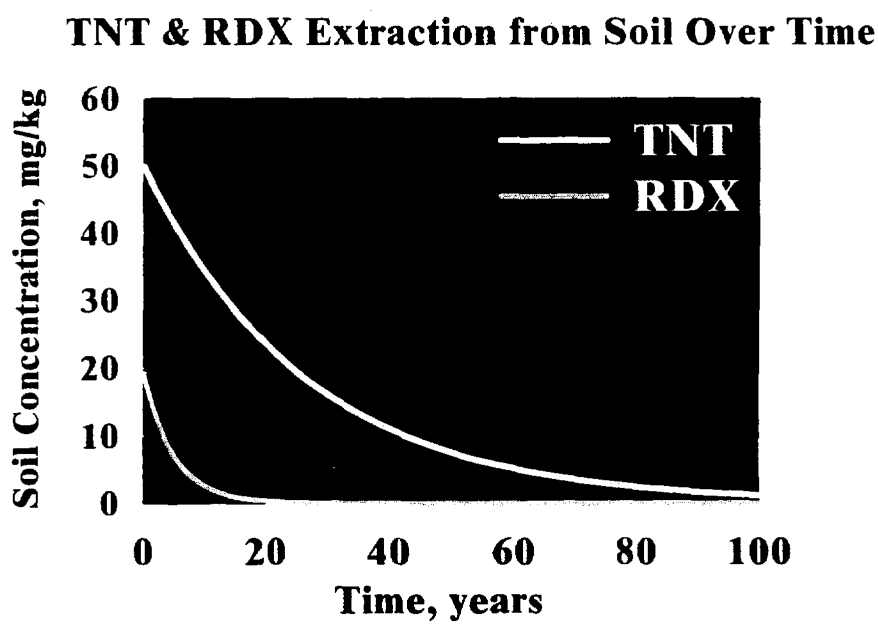
- No significant transformation in short-term (7-d) studies
- 8-30% degradation to unknown products in bush bean after 60-d
- Transformation under field conditions questionable due to detection of RDX in foliage of native plants
- Leaf litter issues...

Design of Terrestrial Systems

- Needs:
  - Toxicity Assessment
  - Uptake = eTC
    - TSCF (e, uptake efficiency)
    - Anticipated Water Use (Forestry Literature)
    - Porewater Concentration
      - Soil Concentration, K_D

Model Assumptions

- 1 acre of contamination, 3 meters deep
- Bulk Density of 1500 kg/m^3
- Porosity = 0.3
- Homogeneous Contamination
- Instantaneous Desorption of Contaminant
- K_d = 5.3 L/kg
- 1500 Trees per acre
- 600 Gallons of Annual Transpiration per Tree
- Microbial influence negligible



Model Results & Implications

- Depends Greatly on Soil Concentration
- Time to complete clean-up: years to decades

Uncertainties

- How will natural conditions affect RDX concentrations in the leaves?
- How will microbial/mycorrhizal associations affect the overall system?
- Effect of Co-contaminants?
- True timeframe

Future Concerns

- Toxicity of plant tissues, bioavailability of residues and RDX.
- Design of systems for long-term efficacy.

Case Study: Union Pacific Railroad

Felix Flechas

REGULATORY CONSIDERATIONS FOR IMPLEMENTATION OF PHYTOREMEDIATION

Felix W. Flechas, P.E.

USEPA, Region VIII

Denver, Colorado

Remedy Evaluation Criteria For Waste Sites

- Protection of human health and the environment
- Compliance with applicable rules and regulations
- Attainment of clean-up standards
- Control sources of releases
- Long-term effectiveness and permanence
- Reduction of toxicity, mobility or volume through treatment

Remedy Evaluation Criteria *(continued)*

- Short-term effectiveness
- Implementability
- Cost
- Community acceptance

Functionality

- Treatment?
- Immobilization?
- Containment?

Functionality *(continued)*

- Waste Cover : Containment or Treatment

Timing Issues

- Demonstrable Progress
- Technical Impracticability
- Baseline Data Needs
- Achievement of Clean-up Goals

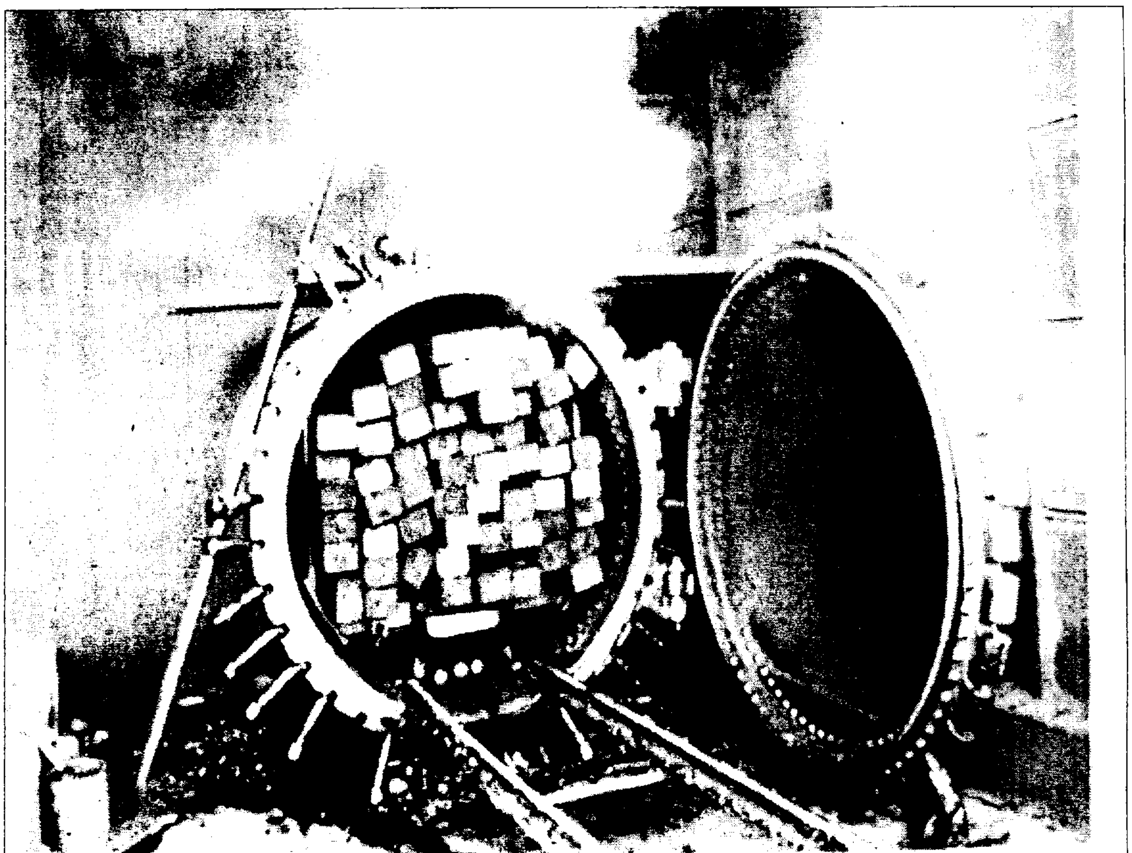
Ecological Considerations

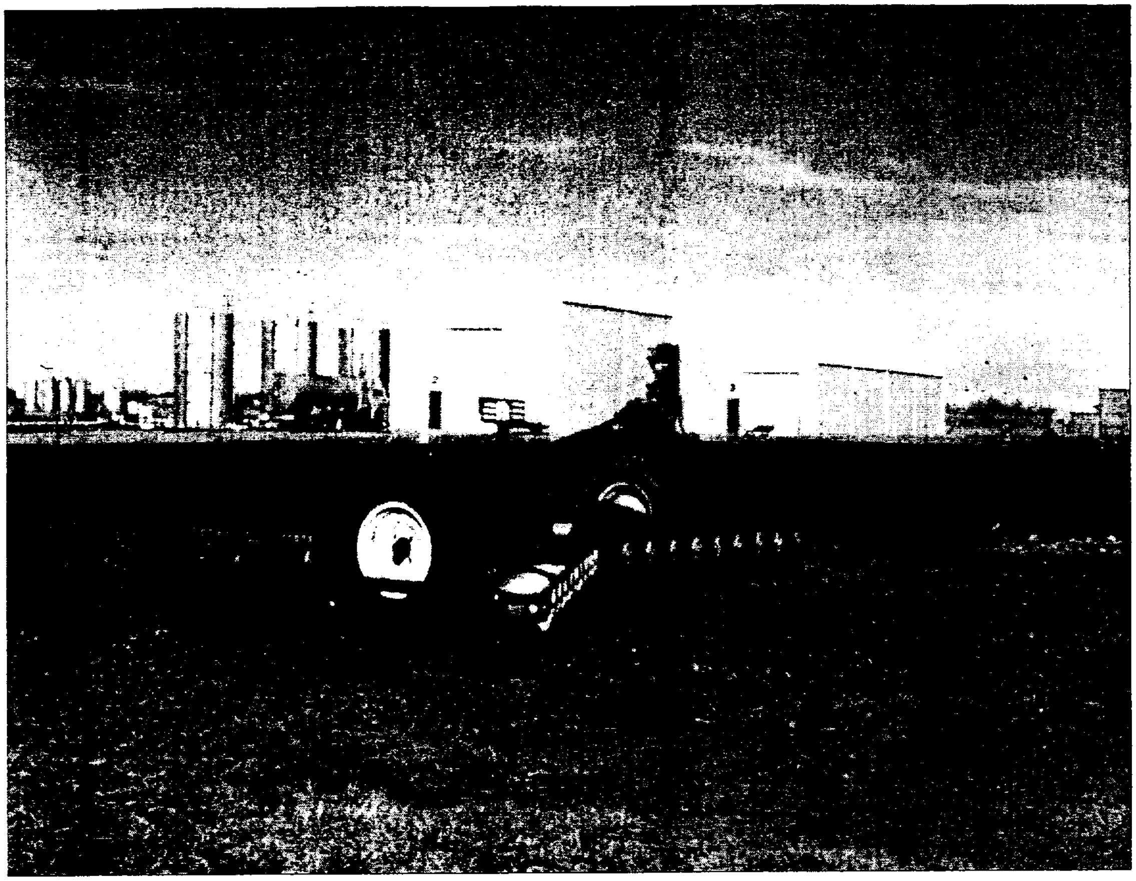
- Baseline Ecological Assesment
- New Exposures

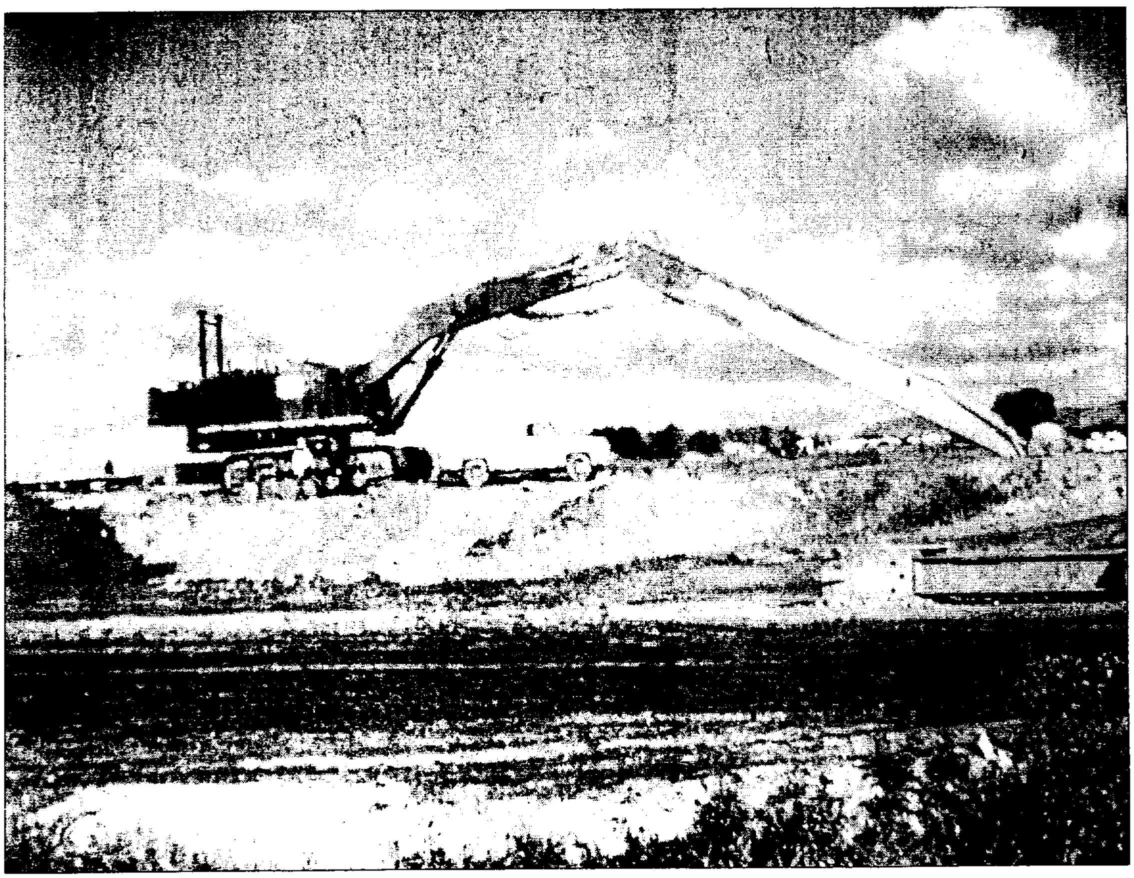
Community Acceptance

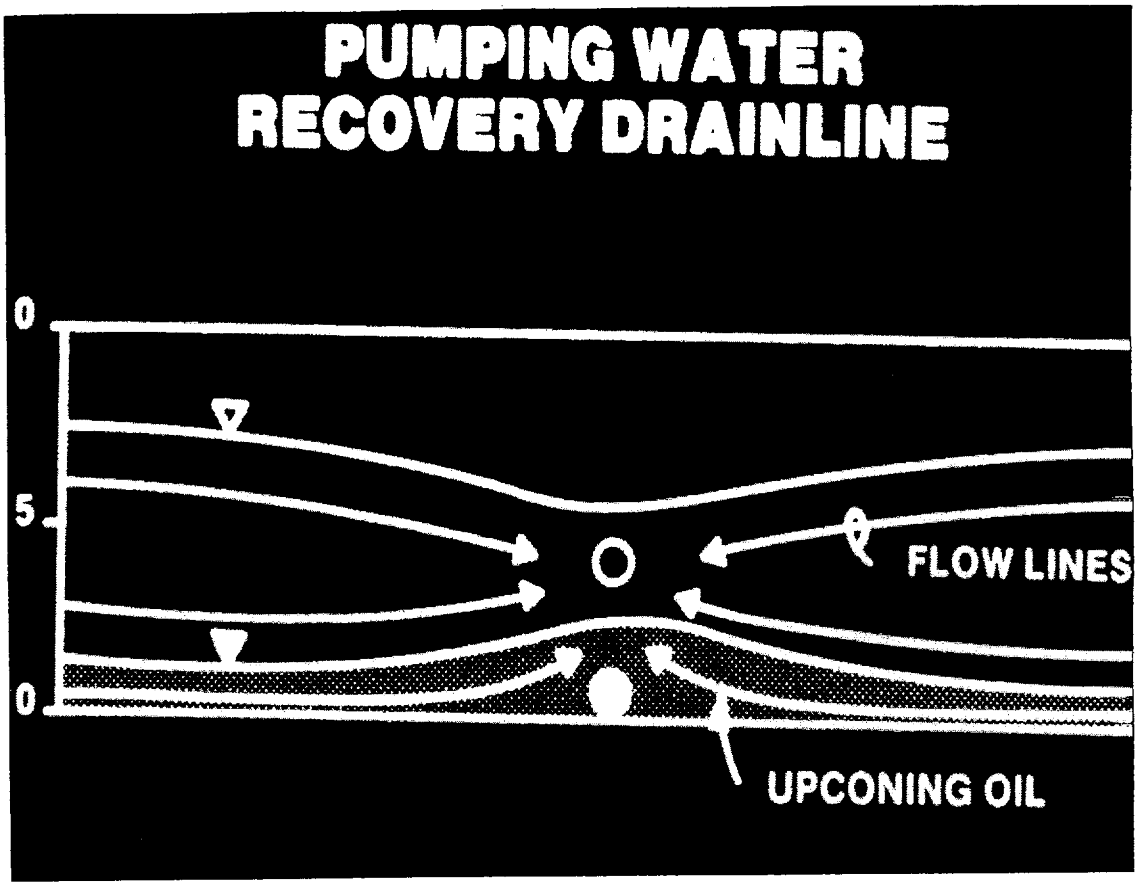
- Community Perception of Phytoremediation
- Parks and Recreation
- Ultimate Landuse

CASE STUDY OF PHYTOREMEDIATION IMPLEMENTAION AT A WOOD TREATMENT SITE








PUMPING WATER RECOVERY DRAINLINE
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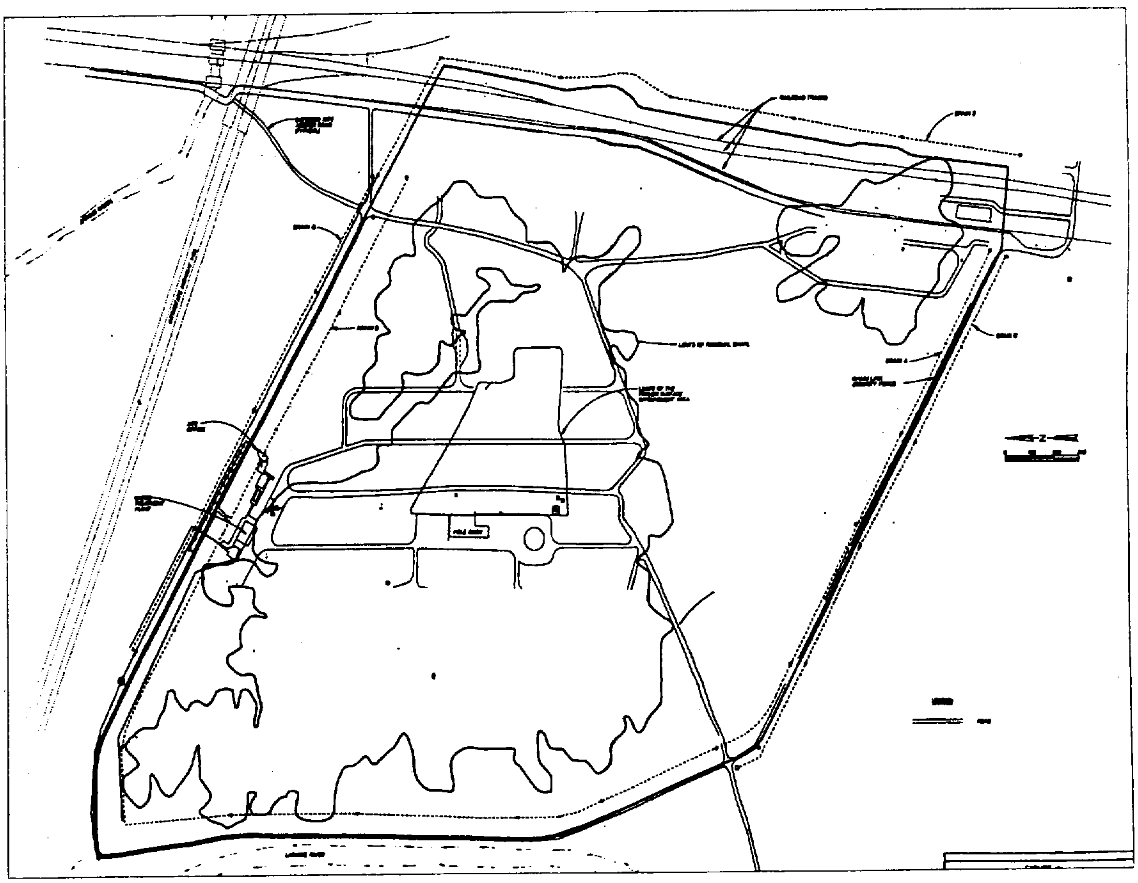
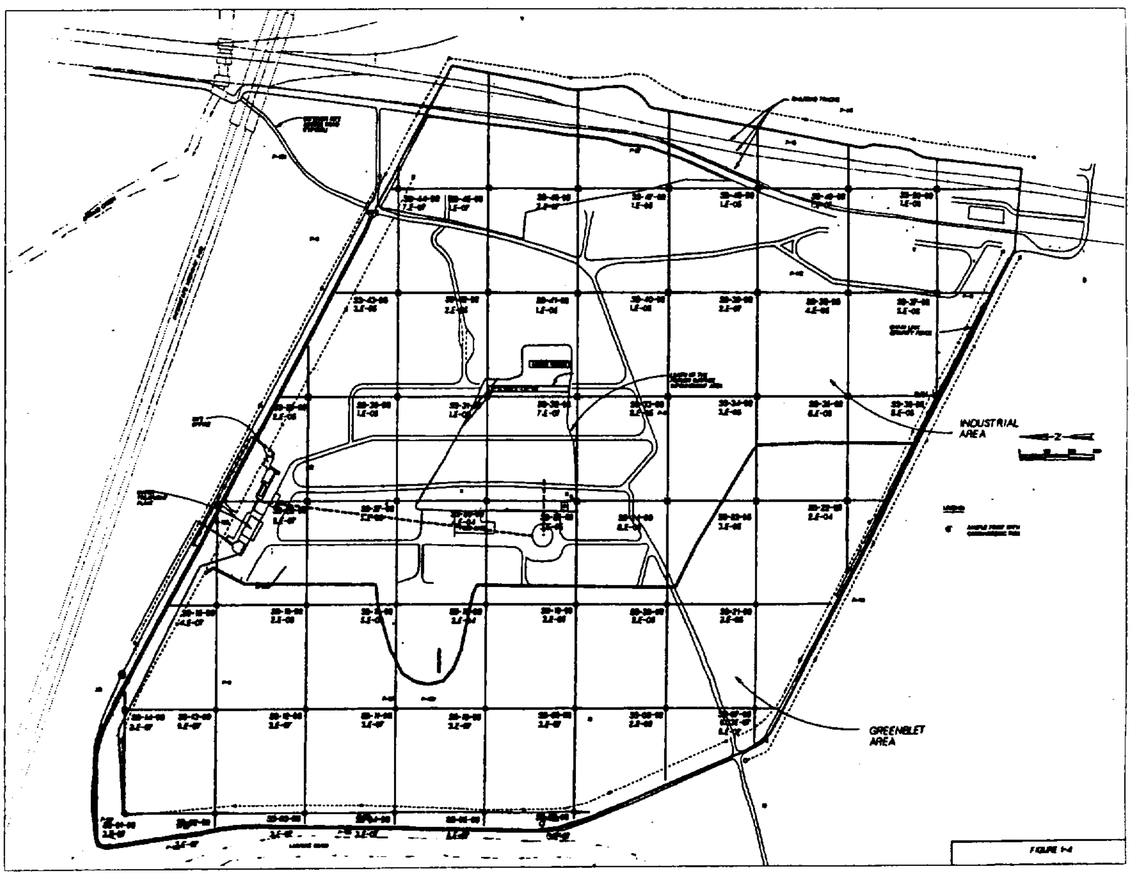
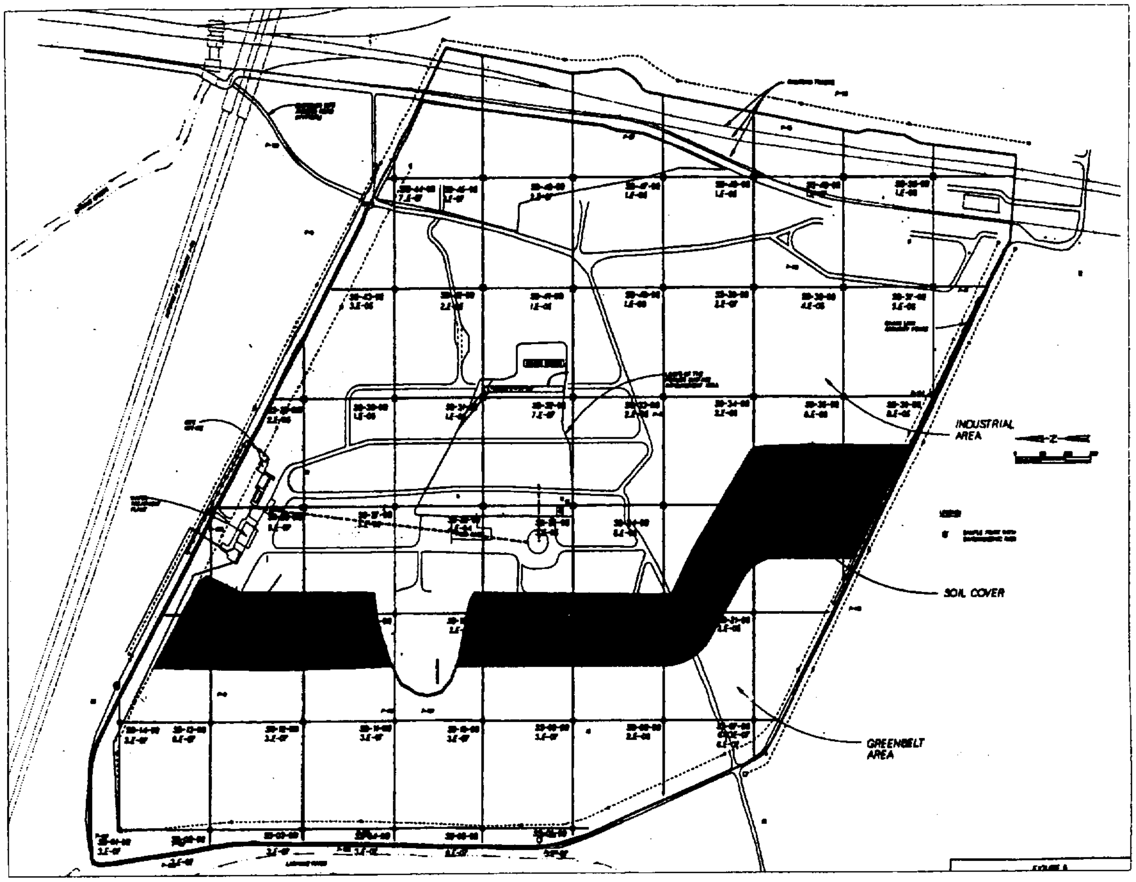
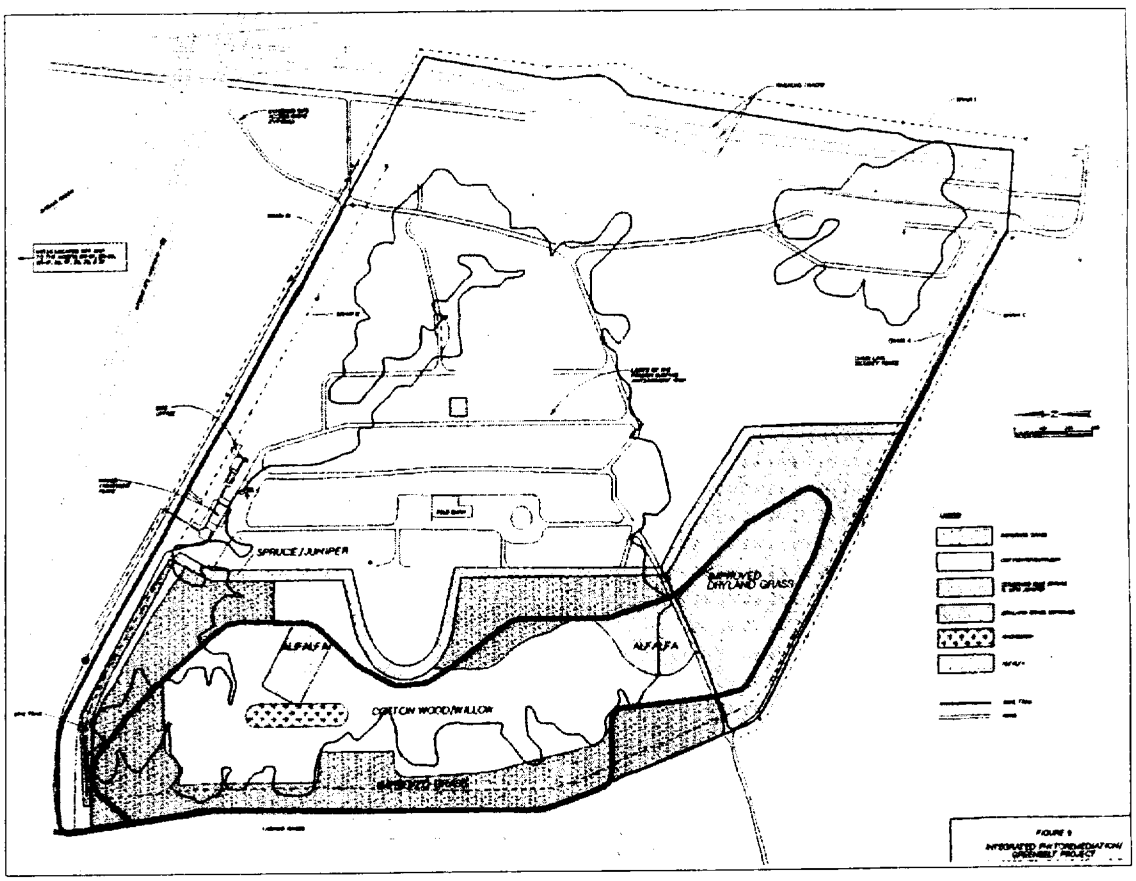
FLOW LINES
UPCONING OIL




A
B


INDUSTRIAL AREA
GREENBLET AREA
FIGURE 1-4


INDUSTRIAL AREA
SOIL COVER
GREENBELT AREA


SPRUCE/JUNIPER
IMPROVED DRYLAND GRASS
ALFALFA
ALFALFA
COTTON WOOD/WILLOW
FIGURE 9
INTEGRATED PHYTOREMEDIATION/ GREENBELT PROJECT

Phyto Project: Performance Criteria

- Plant Survival and Growth
- Establishment and Increase in Vegetative Cover
- Reduction in GW Extraction Rate
- Increase in Soil Oxygen Levels with Depth
- Beneficial Site Use
- Plant Rooting into Contaminated Zones
- Increasing Soil Organic Matter
- Decrease in PNAs and PCP

Phyto Project: Performance Criteria *(continued)*

- Advancement Toward Site Restoration Goals

Phytoremediation in Alaska and Korea

Charles Reynolds

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Education:

BS Soils Science, University of Maryland
MS Soil Chemistry, University of Maryland
Ph.D. Soil Microbiology, University of Arkansas
Postdoctoral Research. Numerical Modeling of Soil Enzymatic Processes, NCSU

Research Focus:

Cold region soil microbial processes, including:
(1) Using microbial characterization to evaluate field-bioremediation processes
(2) Low input/natural attenuation strategies such as rhizosphere enhancement and nutrient optimization
(2) Influence of freezing and cold temperatures on microbial phenomena that govern chemical fate in soils.

Editorial Service:

Invited Editor, Journal of Soil Contamination, Special Cold Regions Remediation Issue, In Preparation.
Associate Editor, 1999 – present. Journal of Environmental Quality
Editorial Board. 1998 – present. International Journal of Phytoremediation

Recent Projects:

ESTCP Project #1011 - Field Demo. of Rhizosphere-Enhanced Trt. of Organics Contam. Soils on Native American Lands with Application to Northern FUD Sites.
SERDP Project #712 - Enhancing Bioremediation Processes in Cold Regions
Army EQT Project - Bioremediation Processes in Cold-Adapted Soil Systems

Selected Recent Publications Related to Soil Microbiology / Bioremediation:

Reynolds, C. M. and D. C. Wolf. 1999. Microbial based strategies for assessing rhizosphere-enhanced phytoremediation. Environmental Technology Advancement Directorate (ETAD) of Environment Canada - Phytoremediation Technical Seminar, May 31-June 1, 1999. Calgary, Alberta, CA. Pp. 125-135.

Miyares, P. H., C. M. Reynolds, J. C. Pennington, R. B. Coffin, T. F. Jenkins, and L. Cifuentes. 1999. Using stable isotopes of carbon and nitrogen as in-situ tracers for monitoring the natural attenuation of explosives. CRREL Special Report 99 – 18.

Reynolds, C. M., C. S. Pidgeon, L. B. Perry and B. A. Koenen, D. Pelton, H.L. Nichols and D.C. Wolf. 1999. Using Microbial Community Structure Changes to Evaluate Phytoremediation. Fifth International Symposium, In-Situ and Onsite Bioreclamation. April 19-22, San Diego CA. Battelle Press. 5(6):33-38.

Reynolds, C. M., D. C. Wolf, T. J. Gentry, L. B. Perry, C. S. Pidgeon, B. A. Koenen, H. B. Rogers, and C. A. Beyrouty. 1999. Root-based Treatment of Organic-Contaminated Soils in Cold Regions: Rationale and Initial Results. *Polar Record.* 35:33-40.

Phytoremediation in Alaska and Korea

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US Army Engineer Research and Development Center - Cold Regions Research and Engineering Laboratory
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DoD has numerous sites that have been contaminated by previous operations. Many sites are relatively remote, many are in cold climates, and frequently, treatment alternatives are limited. Cost effective and defensible treatment options are needed.

In earlier laboratory research, we have shown a positive rhizosphere effect on enhancing remediation of petroleum compounds. For the compounds we monitored, the magnitude of the rhizosphere effect was greater for the more recalcitrant compounds than for the readily degraded compounds. In field research conducted in Alaska, we observed greater remediation using grasses and fertilizer than either grasses alone, fertilizer alone, or a control treatment. We also observed that the vegetation and fertilizer treatment both increased microbial numbers and influenced microbial diversity relative to the control treatment.

Our initial data from a series of field demonstrations that are still underway will be presented. These data suggest that vegetation has a beneficial effect on lowering the concentration of extractable petroleum compounds in the soil and that the effect is differentially dependent on the nature of the contaminant. Additionally, our initial data suggest that there are fertilization – vegetation interactions that can influence remediation of heavier PAHs, and thus may offer low-cost implementation and management alternatives.

Research and field demonstrations were supported by 1.) Army Environmental Quality Technology (EQT) program, work units BT-25-EC-B06 and AF , 2.) Environmental Security Technology Certification Program (ESTCP) Project # 1011, 3.) HQ PACAF/CE, and 4.) Strategic Environmental Research and Development Program (SERDP), project #712.

Status of Phytoremediation Demonstrations at Remote Locations: Alaska and Korea

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Abstract

Contaminated soils at installations built by the U.S. Department of Defense may present human and environmental health risks. Many installations are remote, are relatively inaccessible, or have limited infrastructure. The United States has many individual areas of petroleum-contaminated soil at formerly used defense (FUD) sites located in cold regions. The expenses to mobilize and demobilize cleanup efforts coupled with short treatment seasons result in high costs and restrict treatment options. Rhizosphere-enhanced biotreatment—a low-cost, easily implemented treatment technology that relies on stimulating indigenous microorganisms—overcomes many of the limitations and may stimulate degradation of more complex compounds. Wider application is held back by limited defensible data that show advantages relative to natural attenuation. Our field data from several sites suggest that vegetation and nutrients enhanced degradation of more recalcitrant polyaromatic hydrocarbons relative to natural attenuation or nutrient additions without plants, but these differences can be masked by the chemical monitoring techniques that are routinely used. We have measured increases in bacterial diversity that occur concomitantly with decreases in contaminant concentrations and suggest that soil microbial community structure changes may provide a biological method of monitoring phytoremediation progress, completion, or both.

Introduction

In cold regions, low temperatures, the brevity of the treatment season, or both reduce treatment rates. Site monitoring often is difficult because of the remote locations of many sites, the inherent heterogeneity of contaminant distribution, and the accumulation of numerous small contaminant releases that have occurred in the general area. Phytoremediation may be an attractive treatment option for these sites, yet our knowledge and experience with using phytoremediation to treat contaminated soils, especially in cold regions, is imperfect. These specifics combine to limit application of phytoremediation.

With almost any treatment technology, there is a compromise between treatment costs and treatment times. Treatment costs, although site specific, tend to be inversely related to treatment times. The magnitude of savings is site specific, but, in general, implementing phytoremediation can be a relatively low-cost option. Although phytoremediation systems can be inexpensive to implement and maintain, there is an inherent trade-off of longer treatment times than would be required for more costly technologies (Figure 1).

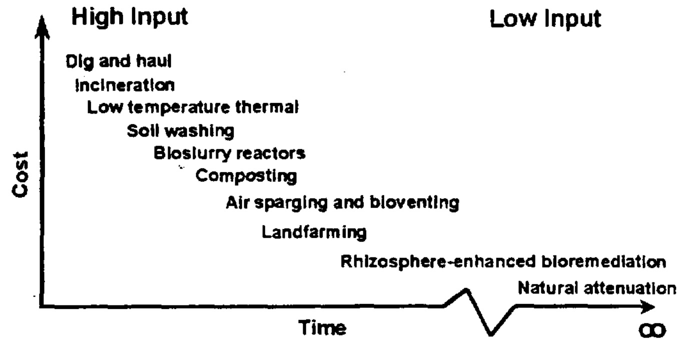

Figure 1. Relative Costs and Treatment Times for Selected Remediation Options.

Many traditional treatment technologies are sufficiently aggressive so that treatment times are relatively predictable and monitoring during the process is not necessary. Sampling and analysis can be done before and after the treatment, and target contaminant concentrations can be confirmed after the estimated treatment time has passed. The other extreme, natural attenuation, is increasingly viewed as an acceptable treatment for groundwater contaminated with benzene, toluene, ethyl benzene, and xylene (BTEX). Treatment rates and times in contaminated groundwater often can be realistically predicted because there is a database of groundwater chemistry from past monitoring of plumes and because groundwater systems are mixed and subsurface conditions, including temperature, are relatively constant, thereby reducing sample heterogeneity and facilitating monitoring. By contrast, rhizosphere-enhanced phytoremediation is suited to relatively shallow contamination of less mobile, and typically more recalcitrant, contaminants. Much of the treatment zone that is defined by the rooting depth is subject to temperature and moisture fluctuations and is generally not well mixed. These conditions can result in longer treatment times.

Understandably, acceptance and use of phytoremediation may be delayed because of longer treatment times and the uncertainty of achievable rates and endpoints. To overcome these uncertainties, requirements to increase spatial sampling density, temporal sampling frequency, or both may be imposed. Additional monitoring requirements increase overall treatment costs and can counteract many of the benefits of using phytoremediation. Although we are gaining experience in using phytoremediation at a number of sites, we are somewhat limited in our ability to effectively predict success.

For widest application, new technologies should be usable over permafrost without destroying permafrost integrity and should withstand or recover from freezing and freeze-thaw cycling. In the past, conventional remediation techniques modified for operation in the cold have proven to be expensive due to mobilization-demobilization, precautions for working over permafrost, and operation in cold or freezing conditions. There is convincing evidence from both laboratory and field studies showing that phytoremediation can be effective for treating contaminated soils. Although the majority of these studies were conducted in temperate climates (Anderson *et al.*, 1993; Aprill and Sims, 1990; Cunningham and Ow, 1996; Cunningham *et al.*, 1996; Reilley *et al.*, 1996, Schwab *et al.*, 1995; and Wiltse *et al.*, 1998), some were conducted in a subarctic climate (e.g., Reynolds *et al.*, 1999). From these studies the operative mechanisms for phytoremediation appear to be largely contaminant dependent. For many organic contaminants, especially petroleum compounds, the generally accepted phytoremediation mechanism is enhanced microbial activity in the rhizosphere, which in turn accelerates the rate of degradation of contaminants. Plant-produced compounds may serve as co-metabolites for more recalcitrant compounds, and this may result in lower contaminant concentration endpoints than can be obtained without plants (Fletcher *et al.*, 1995). We propose that a potential tool for evaluating phytoremediation, monitoring endpoints, or perhaps predicting long-term success of phytoremediation may be based on changes in the soil microbial ecology. We hypothesize that changes in the microbial ecology may be more apparent than subtle changes in contaminant concentrations and, therefore, provide a practical monitoring or confirmation tool (Figure 2). The objective of our research has been to conduct proof-of-concept evaluations for low-input, rhizosphere-enhanced bioremediation techniques for treating contaminated soils in cold regions. If successful, the potential benefits of these techniques would include reduced costs, applicability to cold and remote sites, operation over permafrost, and freedom from massive infrastructure requirements.

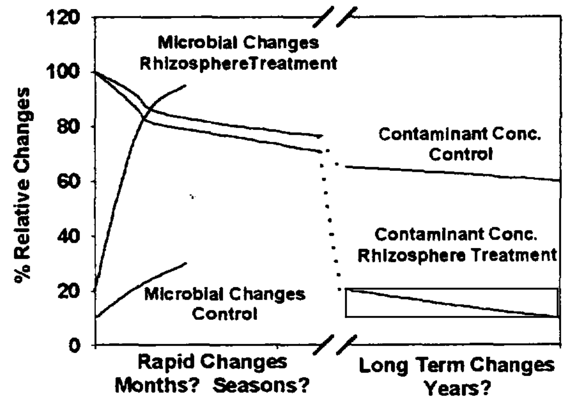

Figure 2. Theoretical Changes in Soil Microbial Characteristics and Contaminant Concentrations during Phytoremediation.

Limits to Bioremediation

Ideally, contaminant concentrations from bioremediation would approach zero, similar to the lower curve in Figure 3. In field situations this seldom happens, and decreases in contaminant concentrations often follow a path similar to the upper curve shown in Figure 3. These idealized curves illustrate two common field occurrences: typical bioremediation rates may be slower than ideal, and final contaminant concentrations tend to reach an asymptotic limit, or residual concentration, that is non-zero.

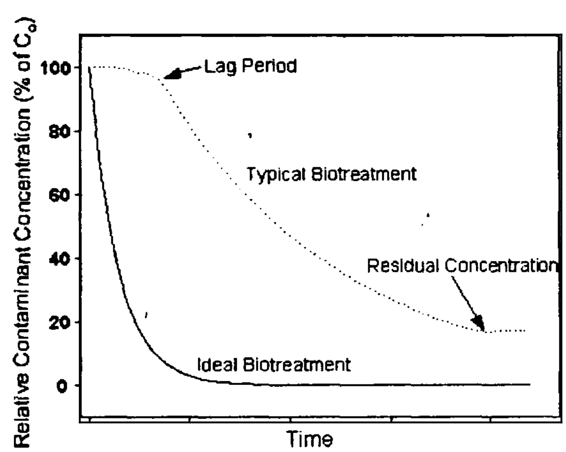

Figure 3. Typical versus Ideal Results from Bioremediation.

A number of phenomena potentially limit treatment rates and final concentrations attainable by bioremediation. As soil moisture and temperature change in a field soil, conditions for microbial activity—and the resulting biotreatment—fluctuate between inhibitory and favorable. Following the onset of favorable conditions, there is usually a lag period before significant microbial activity commences (Figure 3). Consequently, decreases in contaminant concentrations are not instantaneous but are somewhat delayed relative to favorable changes in soil conditions. The length of the lag phase, although well documented and routinely observed in laboratory incubations, is difficult to predict in field soils. Moreover, not all contaminants in the soil are bioavailable (Alexander, 1994). In cold regions, these limitations are exacerbated by low temperatures and relatively brief bioremediation seasons.

The challenges in developing low-cost remediation technologies include 1) lowering the asymptotic value or, practically speaking, the residual or endpoint contaminant concentration, 2) increasing the process rates sufficiently so that the treatment is applicable in the relatively short summer seasons available in cold regions, and 3) accomplishing these in a cost-effective manner. At a field site, the annual biotreatment rate can be improved by either increasing the degradation rate during the operational season, which would result in a steeper slope to the "typical" curve on Figure 3, or lengthening the season, which can be done by soil heating or by reducing the lag period. Exploiting the rhizosphere effect may accomplish both.

Rhizosphere-Enhanced Bioremediation

Rather than expending energy and resources to create near-optimum soil conditions in an *ex-situ* vessel, an alternative approach is to exploit the natural cycles in soils. We are capitalizing on naturally occurring processes that are enhanced in the rhizosphere—the zone of soil that is influenced by the plant root. For petroleum-contaminated soils, the objective is not increased plant uptake but increased microbial numbers and activity and the exploitation of that increased microbial activity to enhance biotreatment.

During both growth and senescence, plants release carbon compounds through their roots and into the soil. Microbes use many of the compounds released from plant roots as energy and carbon sources. This phenomenon, the rhizosphere effect, has been well documented (Curl and Truelove, 1986). The rhizosphere effect results in increased microbial numbers, activity, and, in all likelihood, microbial regeneration.

To optimize survival and growth, microbes maximize their efficiency of carbon metabolism by preferentially using readily available compounds before using more resistant compounds. In general, there is a negative correlation between the complexity of a compound and the percentage of soil microorganisms that have the capability to metabolize the compound. Simple compounds are readily metabolized by many microorganisms. More complex compounds, such as many environmental contaminants, are metabolized by a smaller percentage of the total microbial population. However, given sufficient time and conditions, the soil microbial community may adapt to better use the carbon sources that are available. Adaptive processes include natural selection for microorganisms capable of using a carbon source, stimulation of the entire population, or production of specific enzymes (Alexander, 1994). Maintaining a large and active soil microbial population would, in theory, facilitate faster biotreatment rates, lower residual contaminant concentrations, and increased efficacy of degradation for a wider range of organic compounds.

Rhizosphere effects may promote regeneration or turnover of the soil microbial population and may increase biotreatment rates by decreasing the time for microbial acclimation or adaptation to new carbon sources (contaminants) (Alexander, 1994). The increased microbial activity has the potential to enhance biotreatment of contaminated soils. Other benefits also may accrue. Because roots explore increasing volumes of soil as plants grow, there may be a reduction in mass transfer limitations. In some cases, roots may release specific compounds that are analogs of contaminants, thereby inducing production of enzyme systems capable of degrading similar contaminants (Fletcher and Hedge, 1995).

Materials and Methods

Results presented herein are from a series of laboratory and field studies. In general, we have investigated the effects of vegetation and nutrient additions on remediating petroleum-contaminated soils. We have completed an initial field study and also have ongoing field demonstrations at several other sites.

Initial field study. Our initial field study in interior Alaska was conducted at the Permafrost Research Facility in Fairbanks, Alaska.

Southern coastal Alaska site. This site is located on the southern panhandle of Alaska. The climate is wet and relatively mild by cold-regions standards. The area receives a high annual precipitation averaging 155 inches a year, with an average temperature of 45.9°F.

Interior Alaska site. The site is about 250 miles west-northwest of Fairbanks and 350 miles northwest of Anchorage. Interior Alaska is cold and somewhat dry. Precipitation and surface winds are generally light with a mean annual precipitation of about 12 inches. Temperature variations between winter and summer can be extreme, with a mean annual temperature of 27°F.

Northern Alaska site. The site is 6 miles southwest of the northernmost point in Alaska and is bordered by the Chukchi Sea to the west, the Arctic Ocean to the north, and the Beaufort Sea to the east. The climate is very cold and dry; temperatures range from −19°F in February to 40°F in July. The average annual precipitation is 14.6 inches. High relative humidity (90–95%) in the summer leads to foggy conditions about 25% of the time. Ground-based inversions are common in the winter and can concentrate airborne pollutants in low-lying areas when not dissipated by wind. The site's location between the Aleutian low-pressure system and the polar high-pressure system creates continual surface winds, predominately easterly and generally strongest in the fall and early winter.

Overseas sites: We have several studies ongoing in the Republic of Korea. These sites have longer and warmer summers than the interior and northern Alaska sites.

General Approach

We typically have used a time-series sampling approach for both field and laboratory studies and have used these samples to monitor changes in petroleum concentrations. In some studies, we have concomitantly characterized the microbial populations by different indices, including species richness (*d*) and the Shannon-Weaver diversity index ($\overline{H}$).

For most of our work, we have used grasses, including Arctared red fescue (*Festuca rubra*) and annual ryegrass (*Lolium multiflorum*). These have been chosen for their cold hardiness and rapid growth, respectively. Both grasses have extensive root distribution and tolerance to low-fertility soils. In field studies, seeds were planted each spring to account for winter kill. We have fertilized only at the beginning of the experiment by hand-broadcasting commercially available agricultural fertilizer. To limit the number of trips to a site, we have surface-applied fertilizer at fairly high rates that approached the maximum fertilizer rate that we could use without inhibiting microbial activity by inducing osmotic stress in the soils (Walworth *et al.*, 1997). We reasoned that this approach could readily be used at remote field sites at minimal cost. After the initial fertilizer application, no further fertilizer was added.

For microbial characterization, soil samples were serially diluted and plated on 0.1-strength tryptic-soy agar to determine viable numbers of bacteria (Zuberer, 1994). For each soil sample characterized, we evaluated between 50 and 100 randomly chosen isolates from dilution plates having between 30 and 300 colonies. Bacterial isolates were identified to the species level by characterizing their fatty acid methyl ester (FAME) profiles following the procedures outlined by Sasser (1990) and Sasser and Wichman (1991) in which fatty acid (FA) profiles are identified by comparison to a bacterial reference library (MIDI, 1995). Isolates that we could not identify using the library were given an internal laboratory identifier and added to the library. Unknown isolates having fatty acid profiles distinctively different from other unknowns were treated as individual species. Unknowns having similar fatty acid profiles were characterized as individuals of the same, although unidentified, species.

We used two indices, species richness (*d*) and Shannon-Weaver index ($\overline{H}$).

Species richness (*d*) was defined as (Odum, 1971; Pielou, 1975):

$$d = (S-1)/\log N \qquad (1)$$

where S = number of species
N = number of individuals.

The Shannon-Weaver index ($\overline{H}$) was defined as (Shannon and Weaver, 1963):

$$\overline{H} = (C/N)(N \log N - \Sigma n_i \log n_i) \qquad (2)$$

where C = 2.3
N = number of individuals
n_i = number of individuals in the i^{th} species.

The diversity index $\overline{H}$ incorporates terms for the total number of individuals and the number of members of each species within the community.

Soil total petroleum hydrocarbon (TPH) was extracted by sonication with CH_2Cl_2. Anhydrous Na_2SO_4 was added to the soil during extraction as a drying agent. Extracts were analyzed by gas chromatography using flame ionization detection (GC-FID).

Chemical Monitoring Approaches

Various analytical methods can be used to characterize petroleum compounds in the soil. For example, total petroleum hydrocarbon (TPH) data are expressed as a concentration of mass of petroleum per mass of soil. Although this approach measures an integrated value of the total amount of petroleum products present, we cannot distinguish among specific compounds or changes in composition due to degree of weathering or degradation from a single numerical value. We have therefore used TPH in conjunction with more advanced methods to determine contaminant degradation and the time-related depletion of specific fractions. The subsections below briefly describe these approaches.

Total Petroleum Hydrocarbons

We used high-resolution gas chromatography using flame ionization detection (HRGC/FID). This method is based on integrating relative amounts of petroleum compounds as they differentially elute from a chromatographic column. Integrating the area under the curve and between two defined retention times provides a measure of TPH. TPH data are generally provided as a single, numeric concentration value, such as mg/kg or ppm; thus, much of the data contained in the chromatogram is lost because a numeric TPH value gives no qualitative information about the distribution of fractions. Nonetheless, when monitored over time, TPH data can show, in general, if concentrations of petroleum products are decreasing. To rely mainly on TPH as a monitoring tool, you must assume homogeneity of initial concentrations.

Depletion Monitoring with a Selected Biomarker: α,β-Hopane

Spatial heterogeneity of contaminant concentration makes it difficult to measure treatment effects. For a site that is contaminated with a relatively *uniform composition* of contaminant, bioremediation effectiveness can be calculated by expressing decreases relative to a compound that is relatively non-degradable. These recalcitrant or stable compounds are often referred to as "biomarkers." As different fractions of the total suite of petroleum degrade, the relative concentration of the recalcitrant fraction, or biomarker, increases. The compound α,β-hopane (hopane) is often chosen as a biomarker because it appears in many petroleum compounds and it degrades very slowly. The high resolution gas chromatograph–mass spectroscopy (HRGC/MS) method used for polycyclic aromatic hydrocarbons (PAHs) is used to quantify hopane.

Using this technique, the percent loss of an individual or suite of compounds, such as TPH, can be calculated as follows:

Percent depletion of individual target analytes

$$\{1 - [(C_1/C_2) * (H_2/H_1)]\} * 100$$

Percent depletion of total petroleum hydrocarbons (TPH)

$$(1 - (H_2/H_1)) * 100$$

where:

C_1 = Concentration of analyte in the sample
C_2 = Concentration of analyte in the source (time zero)
H_1 = Hopane concentration in the sample
H_2 = Hopane concentration in the source (time zero).

Depletion estimate calculations are done on an oil-weight rather than a concentration-in-soil basis. Oil weights used are obtained during sample preparation.

Results and Discussion

At our completed research and demonstration site at Fairbanks in interior Alaska, we have been able to show a change in microbial community structure that occurs concomitant with decreases in contaminant TPH. Soil TPH concentrations in both the natural attenuation and rhizosphere treatments decreased relative to the initial TPH concentrations. The rhizosphere treatment had significantly lower TPH concentrations after approximately 640 days of treatment for both diesel- and crude-oil-contaminated soils. For each treatment in the crude-oil-contaminated soil, TPH concentrations decreased, but they remained greater than TPH values in the corresponding treatments in the diesel-contaminated soil.

In the diesel-contaminated soil, diversity, expressed as both species richness (d) and the Shannon-Weaver index ($\overline{H}$), initially increased after approximately 300 days for both the control and rhizosphere treatments (Figures 4 and 5). For the control treatment, $\overline{H}$ was stable at 420 and 640 days (Figure 5).

Using d and $\overline{H}$ as indicators, we showed that bacterial diversity increased after contaminant concentrations in the soil had reached relatively low levels. This effect, as well as the decrease in contaminant concentration, was greater in the rhizosphere treatment compared to the control treatment. From approximately 300 to 640 days, TPH concentrations remained above 2000 mg/kg in the control treatment but had dropped to approximately 700 mg/kg in the rhizosphere treatment after 420 days. During this time, increases in diversity, expressed as d, were relatively constant for the control treatment but accelerated for the rhizosphere treatment. Continued increases in $\overline{H}$ were seen only for the rhizosphere treatment.

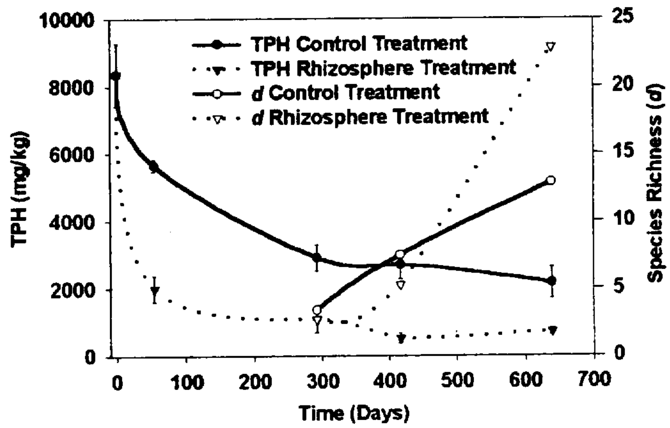

Figure 4. TPH and Bacterial Species Richness in the Diesel-Contaminated Soil during Remediation.

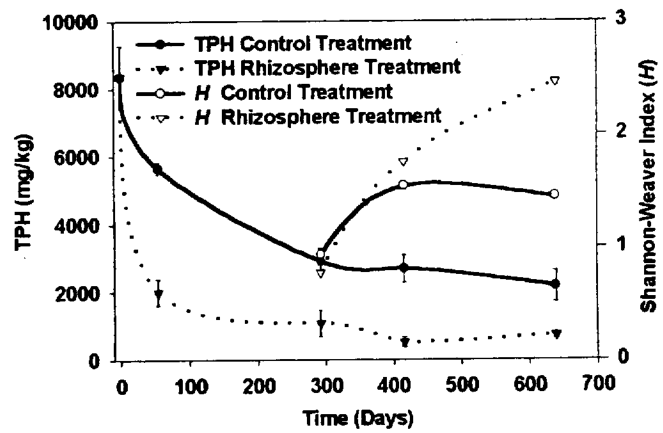

Figure 5. TPH and Shannon-Weaver Index for Bacteria in the Diesel-Contaminated Soil during Remediation.

Three relatively new sites in Alaska are still ongoing, and data are not yet conclusive. However, analysis of variance on the TPH depletion data from the northern Alaska site indicates that the plant-plus-nutrient treatment is having a greater effect (at the 20% level) than the controls, plants alone, or nutrients alone (Figure 6). These data, although not yet conclusive, are encouraging in suggesting that phytoremediation may have application in extreme climates. From our earlier work and allied laboratory studies, we believe the role of nutrients is critical (Walworth *et al.*, 1997). Additionally, there likely are plants better suited to such an extreme environment. An initial database of cold-hardy plants for petroleum remediation has recently been compiled and should soon be available (Environment Canada, 2000).

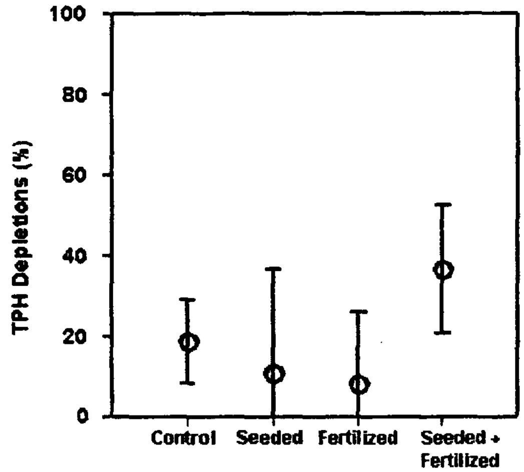

Figure 6. TPH Depletions at Northern Alaska Site.

Using a similar variant, TPH depletion data for two demonstration sites in the Republic of Korea do not show an effect for nutrients, plants, or their combination when compared against a control (Figure 7).

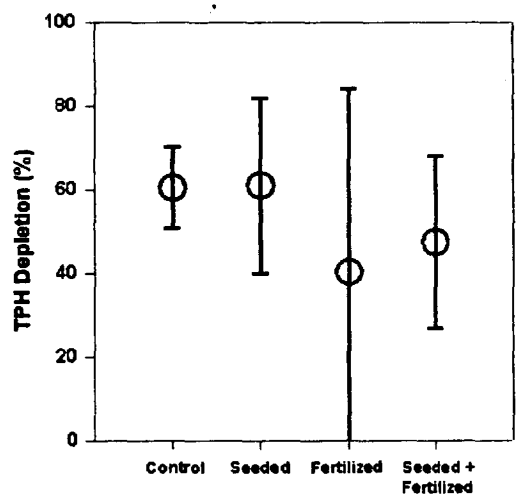

Figure 7. TPH Depletions at Korea Site 1.

However, if we capitalize on the more specific information gained from using a biomarker-based approach, we can obtain greater information from a single soil sample. Using data identified by HRGC/MS, we can plot the hopane-normalized percentage depletion for a range of compounds identified in each soil sample. The resulting data appear as a plot with percentage depletion on the ordinate and a range of compounds, generally in increasing recalcitrance, on the abscissa. As expected, as recalcitrance increases, percentage depletion of each individual compound decreases (Figure 8).

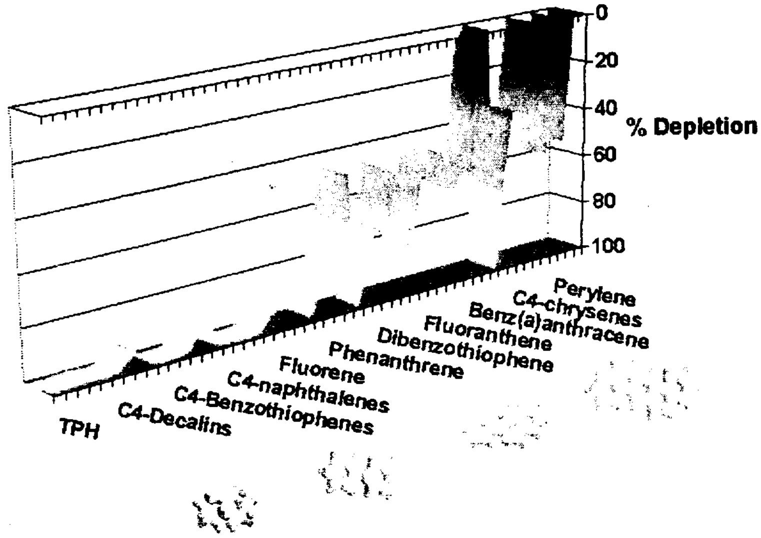

Figure 8. Two-Dimensional Depletion Data by Increasing Recalcitrance of Compounds.

For our field demonstrations, where we are following a modified Remediation Technologies Development Forum (RTDF) developed protocol (http://www.rtdf.org), we have four replications and four treatments:

1. Fertilizer and seed
2. Seed only
3. Fertilizer only
4. Control (no seed, no fertilizer).

By plotting the data for each composite sample, from each treatment, and grouping the treatments, we observe a pattern in the treatment efficacies (Figure 9).

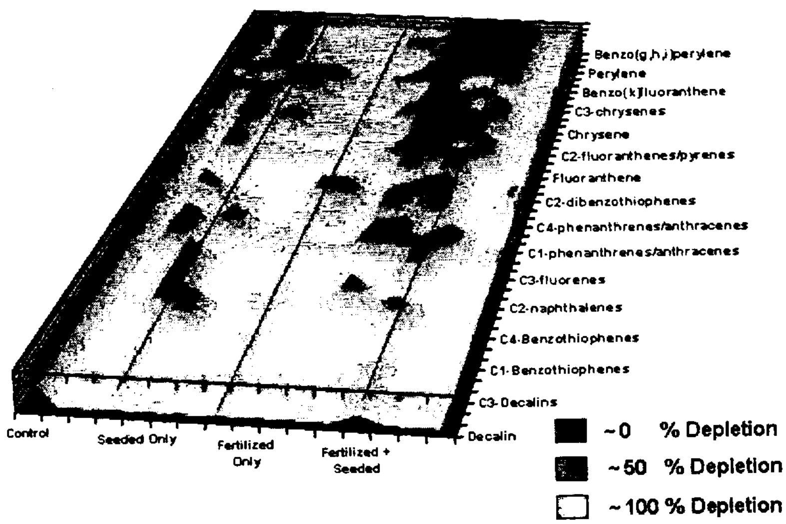

Figure 9. Three-dimensional Depletion data from Korea Site 2.

It is important to realize that, although plots are spatially grouped by treatment in the depletion-data figure above, the plots were arranged in a randomized complete block in the field. Figure 9 shows a pattern of increased percentage depletion of the more recalcitrant compounds in the vegetated (seeded) plots relative to the control and the fertilizer-only treatments. If one uses only TPH as a measurement criterion, this difference is not observable. Moreover, the data suggest that depletion of the more recalcitrant compounds may be inhibited, relative to the control, by using fertilizer alone. These data are for one treatment season and represent the results of processes that have occurred at that time. Given more time, the treatment effects may diverge or converge. We obtained similar results at another site.

Discussion and Conclusions

Ecologists use the term diversity to indicate the heterogeneity of the microbial populations within a community occupying a given habitat (Hauxhurst *et al.*, 1981). Communities with low diversities tend to be relatively specialized, which can be an indication of severe environmental stress (Hauxhurst *et al.*, 1981). When the microbial community is altered by stress, community structure and the diversity of the community change (Atlas, 1984). Generally, introducing moderate to high levels of pollutants into the habitat results in decreased microbial diversity due to toxicity of the pollutant that eliminates sensitive species. This, in turn, reduces competition and results in enrichment of tolerant populations (Atlas, 1984; Mills and Wassel, 1980; Peele *et al.*, 1981).

Crude oil and gasoline contamination have been shown to reduce species diversity (Atlas, 1984). The greatest diversity reduction was noted in an Arctic tundra pond for the more toxic hydrocarbons found in gasoline, where only one species survived and proliferated. The crude-oil amendment resulted in a gradual reduction of $\overline{H} = 4$ to $\overline{H} = 2$ over several weeks. The results indicated that petroleum hydrocarbons reduced microbial diversity and reflected fewer species but increased numbers of metabolically specialized microorganisms.

In addition to diversity, microbial communities can be characterized by productivity (Atlas and Bartha, 1993). Greater diversity generally coincides with decreased productivity, reflecting the increased interactions and complexities of a mature community that has reduced productivity. Conversely, high productivity systems are more likely to be dominated by a few species, and these selected species are likely to have more individuals that are highly productive. For contaminated soils undergoing phytoremediation, or for bioremediation in general, we may be able to use changes and stability of the microbial community structure to make inferences about the bioavailability of the remaining contaminants.

The microbial structure data we have collected to date are encouraging in suggesting a means to evaluate "completeness" of bioremediation, but we caution that they represent only two soils, and we have characterized only the bacterial component of these systems. The fungal component of most soils is generally believed to have significant contaminant degradation potential, but characterization is less mature than for bacteria.

Measurement of microbial diversity, community structure, contaminant degrader activity, and frequency of degradative genes could be combined to enhance our understanding of remediation processes (Langworthy *et al.*, 1998; Mills and Wassel, 1980; and Song and Bartha, 1990). An improved understanding of the time-dependent relationships between contaminant concentration changes and microbial community changes, coupled with improved techniques to readily characterize microbial communities, may provide a useful tool for monitoring the functioning of phytoremediation, evaluating desirable endpoints when bioavailable contaminants are diminished, or both.

Our chemical field data at two sites show that the benefits of rhizosphere enhancement—rather than being uniform for all petroleum compounds—are greater for more recalcitrant compounds. These findings are supported by our earlier laboratory studies. The practical significance of this includes:

1. Because the benefits of rhizosphere-enhanced treatment compared to non-plant-associated treatments are greater for recalcitrant compounds than for readily degraded compounds, there may be a greater cost benefit to applying rhizosphere-enhanced treatment to heavy or residual compounds than there is for readily degraded compounds.

2. Using compound-specific depletion data is a more sensitive monitoring approach for rhizosphere-enhanced remediation and may identify desirable processes that are otherwise masked by less specific analytical methods.

Acknowledgments

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POSTERS

Using Excavated Material for the Remediation of Sewage Farm Land in Berlin and Brandenburg

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Abstract

In the vicinity of Berlin, a total area of 20.000 ha has been treated with municipal wastewater for almost 100 years, resulting in changes of various soil properties and high accumulation of organic and inorganic pollutants [Blume et al., 1980; Schlenther et al.; 1996]. For many decades, constant waste water supply and arable farming prevented the leakage of contaminants into the groundwater. Since the continued irrigation of crops presented a potential risk of pollutant accumulation in the food chain, farming activities were stopped and the proposed land-use was changed to forestation. After stopping wastewater supply the groundwater level sank, which lead to rapid soil acidification and mineralization and an increase of dissolved heavy metals in the soil; - the forestation failed.

Today, due to intense mineralization of organic matter and strong soil acidification, toxic elements are being mobilized and transported into the groundwater [Hoffmann et al.; 1998; Hoffmann & Renger; 1998]. The German Federal Soil Protection Act [1998] and the corresponding Federal Soil Protection Ordinance [1999] demand that land owners take appropriate measures to prevent on-site and off-site environmental endangerment. As yet there is no economically or ecologically viable technique to remediate such wide spread and heterogeneous contamination.

The scope of our current research is to introduce a remediation technique for the fixation of contaminants in the top soil, to improve soils capacity to hold heavy metals and plant nutrients, to improve the soil water economy and to dilute the contaminants by mixing contaminated soil with dead loamy material (from a depth

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of 5-15m underground) as a precondition to a more successful afforestation attempt on former sewage farm land.

In spring 1998, a 12ha area of the sewage farm land was spread with a layer of boulder clay and marly soil (70-80% sand, 15-20% silt, 7-14% clay; pH 7.5 ($CaCl_2$); CEC 14 mmol/kg; carbonate 11%) from construction activities in Berlin, to a thickness of 20-40 cm. After 4 to 6 month of soil coverage the soil was mixed with the contaminated top soil by deep rotary tilling down to a total depth of 60-80 cm, giving a mixing ratio of contaminated soil to cover material of 1:1). After tilling, the biological soil parameters recovered quickly from the intake of new material and vast improvement of chemical and physical soil properties were achieved. The plant available water (nFK) in 10 cm depth rose from 1301/m^2 to 2001/m^2, the humus contents decreased from 3% to roughly 2%, the pH grew from 4.5 to 7.0 ($CaCl_2$), the heavy metal values were reduced by 60 to 70% (dilution) and the values of dissolved heavy metals were reduced by element specific sorption for Zn: 35.4% to 05%; Cd: 21.6% to 2.6%; Cu: 0.5% to 0.2%.

In the first year, there is already a vast change in the flora found on the remediated land. A widespread carpet of couchgrass turned into a rich plant association, which predominantly reflects the former land-use as arable farm land.

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U.S. and International Activities in Phytoremediation: Industry and Market Overview

David Glass

U.S. and International Activities in Phytoremediation: Industry and Market Overview

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Introduction. This presentation discusses the commercial aspects of phytoremediation. Included are an overview of the companies that are developing and commercializing phytoremediation in the U.S. and around the world, as well as major non-profit research groups, a brief summary of the 200-plus field uses of phytoremediation to date, and estimates of phytoremediation's market potential. Although the bulk of today's commercial market is in the United States, there are significant industrial, academic and government activities taking place in Canada, Europe, and elsewhere in the world.

U.S. Phytoremediation Industry. The U.S. phytoremediation industry consists of several dozen companies falling within discrete categories. Most visible are the dedicated phytoremediation companies, whose sole or primary remediation technology is phytoremediation. This category includes a number of companies that have been using deep-rooted trees for hydraulic control for ten years or more (that is, before the term "phytoremediation" was even coined), as well as several companies formed more recently with the specific purpose of commercializing innovative phytoremediation technologies for the remediation of either organic or heavy metal contaminants.

A related category includes other specialty companies that are diversifying into hazardous waste or wastewater phytoremediation. The most prevalent examples are companies having experience with managed or constructed wetlands, which are seeking to leverage their expertise using aquatic plants, generally for wastewater treatment, to enter phytoremediation markets. Another group of companies have used trees and other plants for other environmental purposes, such as erosion control, riparian zone buffers and other uses.

Perhaps the most active segment includes a number of the large to midsize consulting/engineering firms that have developed an expertise in phytoremediation. The number of these firms with credible phytoremediation expertise has grown significantly in the past two years, and these companies are beginning to play a dominant role in the U.S. market. These firms utilize phytoremediation as one of many remedial technologies that may be applicable to different contaminated sites.

A number of large industrial companies, principally in the oil or chemicals industry, are also active in conducting or supporting phytoremediation research. Most of these companies have been involved in phytoremediation more as site owners than as technology developers, and for the most part these companies are interested in phytoremediation for its possible use on their own contaminated sites. A number of these corporations are participating in EPA's RTDF Phytoremediation of Organics Action Team and the Petroleum Environmental Research Forum group.

Although at an early stage of its growth, the U.S. phytoremediation industry appears to be developing similarly to other industry sectors devoted to innovative remediation technologies. The dedicated companies drive much of the innovation, and dominate the market in its early days, but run the risk of seeing the market dominated over time by larger, diversified companies, once the technology is better proven and the necessary expertise more widely disseminated. In phytoremediation's case, competition is also faced from specialty companies such as nurseries, plant breeders, agricultural biotechnology companies and other firms having expertise in plant agriculture, some of which have already begun to show an interest in phytoremediation. In the past two years, competition from the specialty sector has not emerged to any significant degree, while a more formidable challenge has come from the growing number of consulting/engineering firms now servicing the phytoremediation market.

Phytoremediation Industry Outside the U.S. Commercial phytoremediation activities have been slower to develop outside the United States. However, industrial interest is developing in several countries, notably Canada and several European countries, as well as Australia and Japan.

In Europe, there are today more than a dozen small firms possessing phytoremediation expertise of some kind or to some degree. Most of them fall into the category mentioned above of "diversifying specialty companies", and derive their expertise from constructed wetlands or various agricultural specialties. However, other than treatment of wastewater or landfill leachate with willow trees or constructed wetlands, there has not been a great deal of actual commercial use of phytoremediation in Europe, and the market remains at a very preliminary stage. This is likely due to the fact that the overall remediation market is less well developed in Europe than in the U.S., although this is changing.

In Canada, although there has been significant government interest in, and promotion of, phytoremediation, this has to date translated into very little industrial activity. This replicates a trend in Canada that we have previously noted in the field of microbial bioremediation, and may simply be indicative of the smaller remediation market found in Canada today. There are also a small number of companies with phytoremediation interests in Australia, Japan and elsewhere in the world, where remediation markets are just starting to take shape.

Academic Research Activities. There are a large number of academic and public sector research laboratories conducting research in phytoremediation. Almost all the pioneering work in phytoremediation took place in academic laboratories, and today university research groups carry out valuable basic and applied research in this field. Government agencies are also responsible for large amounts of basic and applied phytoremediation research, either conducted in-house at government laboratories, military bases and research stations, or through funding of extramural research at the nation's universities. A portion of academic phytoremediation research is directed at field studies and other applied research, while another group of researchers is investigating ways of improving phytoremediation's efficacy, including creation and use of transgenic plants.

There is also a great deal of excellent research being conducted in Canada, Europe, and elsewhere in the world. Through the funding efforts of the European Union (EU) and the unifying effects of the Internet, international research collaborations and consortia have been formed, which are helping coordinate activities and reduce possible duplication of efforts. Some of these efforts have been funded by national governments around the world, and in the EU. Among these are several international research consortia funded by the EU, and the COST program, whose Action 837 brings together over 100 European scientists studying various aspects of phytoremediation.

Phytoremediation Field Activities. Phytoremediation has been carried out commercially or demonstrated at pilot scale at perhaps 200 sites in the U.S. These sites have involved contaminated soils, groundwater, wastewater and other polluted aqueous wastestreams, and have included all of the many contaminant categories to which phytoremediation is applicable. In addition to projects completed by for-profit firms, there are a number of demonstration projects underway, many of which are funded, supported, or conducted by U.S. federal government agencies. The goals of many of these projects include the generation of economic and technical data to support the efficacy of phytoremediation in specific remediation scenarios.

There have also been a number of field tests, demonstrations, and commercial remediations in Canada and Europe. Projects in Canada have generally involved either remediation of petroleum hydrocarbons or heavy metals. Research projects in Europe have focused to a large extent on heavy metal and radionuclide pollution, although there has also been limited field work on hydrocarbon contamination. Both these regions have only recently begun the transition from academic research to commercial remediation projects.

Markets for Phytoremediation. Phytoremediation's market success will be governed by many factors, not least of which are its own strengths and weaknesses. Among its greatest advantages are its low cost (although solid economic data are generally still lacking), the fact that it is a permanent, *in situ* technology, its applicability to a wide variety of contaminants, and its attractiveness to the general public. Among limitations are that some phytoremediation activities are slower than competing remedial technologies, the limitation of some applications to shallow soils or groundwater, the inherent limitations of biological systems, and regulatory unfamiliarity.

Phytoremediation faces other barriers to market acceptance as well, ones that are common to all innovative technologies. These include the need to prove efficacy and cost-effectiveness to site owners, consultants and regulators, various barriers and biases embodied in environmental laws and regulations that favor traditional technologies over newer ones, and the challenges of the changing climate for remediation in the U.S., where economic factors are replacing regulatory factors as driving forces. However, these obstacles may be mitigated by prospects for regulatory relaxation, and the possibility that the new economic climate may favor low-cost technologies that can address the riskiest portions of contaminated sites. Phytoremediation's growth may also be assisted by a number of U.S. government programs for the promotion of innovative technologies.

Phytoremediation is applicable to a number of hazardous waste and other remedial scenarios, which offer sizable potential markets. Markets for remediation of organics, metals and radionuclides from soils and water, combined with municipal and industrial wastewater treatment markets, the treatment of polluted runoff, primarily including landfill leachate, and the market for removing inorganic contaminants such as nitrate from drinking water supplies, offer a total potential market size of U.S. $33.8-49.7 billion per year.

The largest 1999 U.S. markets for phytoremediation are for treatment of organic contaminants in groundwater, with revenues estimated at $7-12 million, control of landfill leachate, approximately $5-8 million, remediation of organics in soil, estimated at $5-7 million, and remediation of metals from soil, perhaps about $4.5-6 million. Other significant markets are for removal of nonmetallic inorganics from groundwater and wastewater, and the remediation of metals from groundwater. In general, the markets involving organic and nonmetallic inorganic contaminants should see strong, steady growth in the coming years, while the markets involving metals or radionuclides are capable of dramatic growth as the technology's efficacy becomes better established.

The estimated 1999 U.S. market represents a significant increase from our estimates of 1998 revenues, and is close to a doubling of the market in one year's time. We attribute the market increase primarily to the increased number of companies now offering services in this market, particularly companies in the consulting/engineering sector, and to growing acceptance of the technology. However, our current estimates of 1999 and 2000 revenues are slightly lower than what we had previously projected for these years, which is largely attributable to the fact that phytoremediation applications for metals and radionuclides appear to have been slower to reach commercial markets than we had previously anticipated. We estimate the total U.S. phytoremediation market in 1999 to have been $30-49 million, and that the market will total $50-86 million in 2000. Growth to $100-170 million by 2002 and $235-400 million by 2005 is predicted.

Although the United States represents the largest environmental market in the world, markets for environmental goods and services, including remediation of contaminated soil and water, exist elsewhere in the world, particularly in industrialized nations. Smaller, but emerging, markets exist in developing nations, particularly in portions of Asia. The total world remediation market in 1998 was approximately U.S. $15-18 billion/year. The next largest environmental market after the U.S. is found in Europe, particularly in the European Union. With an estimated remediation market of U.S. $2-4 billion/year, it is a sizable market, with excellent opportunities for growth in the coming years as more countries upgrade their environmental laws and regulations to be in accordance with EU standards, and as more countries inventory and prioritize their contaminated sites.

Based on recent compilations of national inventories, it is now believed that there may be as many as 1.5 million potentially contaminated sites in Europe, with perhaps 28,000-61,000 of these actually proving to be contaminated. At least 5,000 sites in the latter category are located at military installations, mostly sites in Eastern Europe abandoned by the Soviet Army. The costs to remediate all these sites are estimated at U.S. $80-140 billion, using exchange rates current at the time of these estimates (the late 1990s).

Phytoremediation is already practiced commercially in Canada, Europe, and several other countries; however, the current markets outside the U.S. are believed to be small. We estimate 1999 Canadian phytoremediation revenues at U.S. $1-2 million, and European revenues at $2-5 million. Both regions show significant potential for growth in the early years of the new century.

Although there is little commercial phytoremediation activity outside these major world regions, we are optimistic about phytoremediation's ultimate international market potential. Many countries, including the former Soviet bloc countries and many developing nations in Asia and Latin America, have significant problems of improper landfilling and wastewater treatment. Although site remediation is generally not a priority in these countries, phytoremediation is capable of addressing certain of the high priority issues including wastewater treatment and control of leachate from uncontrolled dumping sites so these markets may present opportunities for phytoremediation which would not present themselves for other remedial technologies. These markets might offer opportunities for market growth later in the first decade of the 21st Century.

U.S. and International Activities in Phytoremediation:

Industry and Market Overview

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United States Dedicated Phytoremediation Companies

Firm	*Specialty*
Applied Natural Sciences	Poplar trees for treatment of organics.
Ecolotree	Poplar trees for treatment of organics.
Edenspace Systems Corp.	Plants for treatment of metals.
Phytokinetics	Poplar trees, plants and grasses treatment of organics.
Thomas Consultants	Poplar trees for treatment of organics.
TreeTec Environmental	Specialty trees for control of effluents, treatment of organics.
Verdant Technologies	Poplar trees for treatment of organics.
Viridian Environmental	Plants for treatment and recovery of metals.

United States Diversifying Specialty Companies

Constructed Wetlands

Azurea	Ecoscience	Lemna Technologies
BioConcepts, Inc.	GreenGold	

Constructed ecosystems for wastewater treatment

Sustainable Strategies	Living Technologies
Wolverton Environmental	West Wind Technologies

Revegetation, erosion control

Bitterroot Restoration	The Bioengineering Group

Bacterial bioremediation, wastewater treatment

Ios Corporation

Electrokinetic soil treatment

Lynntech, Inc.

U.S. Consulting/Engineering Firms Using Phytoremediation

Alliant Tech	ARCADIS G&M	ARM Group
August Mack	Battelle	Braun Intertec
CBRS	CH2M Hill	CoreGroup Services
CRA Services	ERM	Fuss & O'Neill
Geomatrix	GeoSyntec	Global Remediation
ICF Kaiser	IT Corporation	Key Engineering
Kingston Environ.	LJB Group, Inc.	Malcolm Pirnie
ManTech	McLaren Hart	Mitretek Systems
MSE	Parsons Engineering	Roy F. Weston
SAIC	Sand Creek	SoilQuest
TetraTech	ThermoRETEC	URS/Dames & Moore

U.S. Industrial Companies Conducting Phytoremediation Research

Alcoa	Aramco Services	Arco Chemical
BASF	BP Amoco	Browning-Ferris
Chevron	Coastal Corporation	Conoco
DuPont	Eastman Chemical	Elf Aquitaine
Exxon	Kaiser Aluminum	Mobil
Monsanto	Novartis	Occidental Chem.
Phillips	Rohm and Haas	Rhone-Poulenc
Texaco	Shell	Union Carbide
Unocal	Koch Industries	Marathon Oil

European Companies Commercializing Phytoremediation

Agritec (*Czech Republic*)	Reset SRL (*Italy*)
Hedeselskabet (*Denmark*)	Euramtecna (*Portugal*)
Rhone-Poulenc (*France*)	Battelle Europe (*Switzerland*)
BioPlanta (*Germany*)	Biotec SA (*Switzerland*)
Piccoplant (*Germany*)	Hydropol (*Slovakia*)
Consulagri (*Italy*)	VBB VIAK (*Sweden*)
Ecobios (*Italy*)	Slater (*U.K.*) Ltd.
Metapontum Agrobios (*Italy*)	OEEL (*U.K.*)
Plantechno (*Italy*)	Quest Environmental (*U.K.*)

Companies Commercializing Phytoremediation: Rest of World

Canada
Aquaphyte Remediation
CH2M Gore & Storrie
Conor Pacific
Erin Consulting
Federated Co-Operatives
Global Forestry Consulting
Harrington & Hoyle
Inspec-Sol Inc.
Jacques Whitford
Nature Works Remediation

Canada (continued)
Pollutech
Roy Consultants

Rest of World
Above Capricorn (*Australia*)
Envirogreen (*South Africa*)
HortResearch (*New Zealand*)
John Bray & Assoc. (*Australia*)
Phyto-Link(*Australia)*
Taisei Company (*Japan*)

Phytoremediation Research Proposals Funded by the European Union DG12

Bioremediation and Economic Renewal of Industrially Degraded Land by Biomass Fuel Crops (BIORENEW).
Coordinator: Dr. D. Riddell-Black, U.K. Rehabilitation of heavy metal contaminated land (Zn, Cd) using biomass fuel crops (*Salix*, *Miscanthus*, *Pharalis* and *Eucalyptus*).
An Integrated Approach to the Phytoremediation of Organic Pollutants in the Rhizosphere.
Coordinator: Dr. C. Leyval, France. Remediation of PAHs in the rhizosphere by enhancing microbial activity in mixed grass-legume systems and the symbiotic arbuscular mycorrhizal fungi and rhizobia.
In situ Remediation of Contaminated Soil by Plants (PHYTOREM).
Coordinator: Dr. S. C. McGrath, U.K. Transport and accumulation of metals (Zn, Cd, Cu) in plants and methods to enhance metal accumulation.

Phytoremediation Research in Europe

- Phytonet Internet Discussion Group.
- Several research programs funded by EU, national governments (BIORENEW, PHYTOREM, etc.).
- COST: European Cooperation in the Field of Scientific and Technical Research -- Phytoremediation Action.
- NICOLE: Network for Industrially Contaminated Land in Europe *(project withdrawn).*

Phytoremediation COST Action

- Program includes > 95 scientists from at least 18 countries, will run from November 1998 - November 2003.
- Objectives include coordination of information-sharing to promote phytoremediation, development of standardized testing protocols, improvement of scientific education and training.
- Four working groups: Organics, Metals, Metabolic Engineering, Cultivation and Utilization.

European Phytoremediation Selected Field Projects

Katowice, Poland

•Removal of lead from contaminated soil at a refinery.
(*Florida State University, Phytotech*).

Chernobyl Nuclear Reactor Site, Ukraine

•Sunflowers for rhizofiltration of uranium-contaminated water;
•Industrial hemp for radionuclide-contaminated soil.
(*Phytotech and collaborators*).

Liepzig, Germany

•Phytoremediation to clean sewage sludge. *(BioPlanta).*

European Phytoremediation Selected Field Projects

Slovakia

•Use of poplars on a contaminated plume. *(Hydropol).*

Trecate, Italy

•Remediation of crude oil contaminated soils *(Battelle Europe).*

Belgium

•Phytostabilization of heavy metal contaminated soil.
(*Vangronsveld, et al., University of Limburg*).

Several other academic field experiments

•Germany, Denmark, Poland, Czech Republic.

European Phytoremediation Selected Field Projects

Municipalities in Sweden

•Use of willow trees to treat wastewater, landfill leachate.

Sweden

•Field tests of willows on Cd contaminated soils.

Switzerland

•Field tests of willows at a Zinc landfill.

•Field tests of phytoextraction at a Zinc/Copper site.

United Kingdom

•Field tests of willows on Ni, Cd, Zn contaminated soils.

Estimated U.S. Phytoremediation Markets 1999-2005

Market Sector	**1999**	**2000**	**2002**	**2005**
Organics in groundwater	7-12	11-22	21-42	40-80
Organics in soil	5-7	7.5-10.5	10-15	20-30
Inorganics in groundwater	2-3	3-6	6.0-8.5	12-20
Metals in groundwater	1-2	2-3	3-6	7-12
Metals in soil	4.5-6.0	9-14	28-40	75-110
Radionuclides	0.5-1.0	2-4	6-12	20-40
Landfill leachate	5-8	7.5-12.0	13.5-21.5	23-35
Organics in wastewater	1-2	2-3	3-5	5-10
Inorganics in wastewater	2-4	2.5-5.0	3.5-7.0	6-12
Metals in wastewater	0.1-0.2	0.2-0.4	0.3-0.6	1.0-2.0
Other	1.9-3.8	3.3-6.1	5.7-12.4	26-49
Total	**30-49**	**50-86**	**100-170**	**235-400**

Millions of U.S. Dollars

Estimated Worldwide Phytoremediation Markets, 1999-2002

	1999	**2000**	**2002**
United States	30-49	50-86	100-170
Europe	2.0-5.0	2.1-5.5	2.5-7.0
Canada	1.0-2.0	1.3-2.5	1.5-4.0
Other	1.0-2.0	1.6-2.5	2.0-5.0
World	**34.0-58.0**	**55.0-96.5**	**106.0-186.0**

Millions of U.S. Dollars

Phytoremediation Market Trends

- U.S. market nearly doubled from 1998 to 1999.
- Much of this growth results from the companies newly entering the market (mostly c/e firms).
- Rapid growth (50 + % per year) is likely through 2001.
- Continued strong growth (30% per year) is expected 2001 to 2005.

Phytoremediation Market Sector Trends

- Remediation of organics from groundwater continues to be the strongest sector.
- Considerable ongoing work with nonmetallic inorganics in groundwater, wastewater.
- Remediation of metals from soils, radionuclides, have been slow to develop.
- Prospects for remediation of metals from groundwater, wastewater are more positive if trees can be used.

Phytoremediation Industry Trends

- The number of c/e firms with credible phytoremediation expertise is growing rapidly.
- Most dedicated phytoremediation firms are doing well and are finding plenty of jobs.
- Some dedicated phytoremediation firms have gone out of business or have been acquired.
- Involvement, interest from the industrial sector (i.e., private site owners) appears to be increasing.

International Phytoremediation Trends

- Significant research interest in Canada and Europe, commercial activities are slowly starting to develop.
- Most European research is directed at heavy metals, but overall site remediation market is mostly limited to petroleum hydrocarbons.
- History of existing uses of willows in Europe, constructed wetlands in Europe, Canada.
- Interest elsewhere in the world includes Japan, Australia, Asia.

Phytoremediation: Strengths

- Low capital and operating costs.
- Efficiency and performance are well-suited for risk-based remediation and other scenarios.
- Permanent treatment solution, capable of mineralizing organics.
- *In situ* application avoids excavation.
- Applicable to large contaminated surface areas.
- Public acceptance expected to be good.

Phytoremediation: Limitations

- Slower than some alternatives; dependent on climate, seasons.
- Generally limited to surface soils, relatively shallow aquifers (with some exceptions).
- High contaminant concentrations toxic to plants.
- Efficiencies may be too low to meet rigorous endpoints.
- Regulatory unfamiliarity.
- Lack of recognized performance data.

D. Glass Associates, Inc.

D. Glass Associates, Inc. is a consulting firm specializing in market analyses, technology assessments, and technology transfer in the fields of site remediation and environmental biotechnology. The firm has advised clients in several countries about the structure of international remediation markets, and has assisted a number of companies in the U.S., Canada, Europe, Australia, Japan and South America locate partners for innovative remediation technologies.

This presentation is adapted from D. Glass Associates' market report "***U.S. and International Markets for Phytoremediation, 1999-2000***", a comprehensive overview of international activities in phytoremediation. The company has also published "***The 2000 Phytoremediation Industry***", an industry directory that features over 70 company profiles of U.S. and international phytoremediation companies.

David Glass, Ph.D., president of D. Glass Associates, has nearly 20 years experience in various fields of biotechnology, has published several market reports on bio- and phytoremediation, and has been a featured speaker at a number of international conferences.

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INDUSTRY

RESEARCH AND FIELD WORK

COMMERCIAL MARKETS

U.S. Government Phytoremediation Activities

U.S. Environmental Protection Agency
- Internal research laboratories
- Extramural research funding
- SITE Program, RTDF Program
- Technology Innovation Office, Clu-in.com website

U.S. Department of Agriculture
- Internal research laboratories
- Extramural research funding

U.S. Department of Defense
- SERDP, ESTCP Programs
- U.S. Army Corps of Engineers Waterways Experiment Station
- U.S. Navy Naval Facilities Engineering Service Center
- U.S. Air Force Center for Environmental Excellence
- U.S. Air Force Aeronautical Systems Center
- ***U.S. Department of Energy***
- ITRD Program
- Research at national laboratories

Tennessee Valley Authority
- Environmental Research Center

Selected U.S. Soil Phytoremediation Projects

Metals and Radionuclides

Pig's Eye Landfill; **St. Paul, MN**
Cd, Zn, Pb — USDA (Chaney)

Zinc Corp. of America; **Palmerton, PA**
Zn, Cd — USDA (Chaney)

Magic Marker site; **Trenton, NJ**
Pb — Phytotech (Edenspace)

Former metal-plating site; **Findlay, OH**
Cd, Ni, Zn, Cr — Phytotech (Edenspace)

Brookhaven National Lab; **Long Island, NY**
Cs-137 — Phytotech, MSE, USDA

Organic Contaminants

Superfund site; **Portland, OR**
PAHs — Phytokinetics

Land treatment site; **Craney Island, VA**
hydrocarbons, PAHs — Kansas State Univ.

Naval Station; **Port Hueneme, CA**
petroleum hydrocarbons — Purdue University

Army test site; **Fairbanks, AK**

Selected U.S. Water Phytoremediation Projects

Fuel transfer terminal; Ogden, UT	
Fuel oil	Phytokinetics, Chevron
Naval Air Sta. Joint Reserve; Fort Worth, TX	
TCE	ESTCP, USAF, EPA
Contaminated groundwater; Tacoma, WA	
TCE	Univ. Washington
Aberdeen Proving Grounds; Edgewood, MD	
TCE, DCE, PCE, TCA	Weston, ANS
Edward Sears Properties; New Gretna, NJ	
TCE, metals	Weston, EPA, Thomas Consult.
Army Ammunition plants; Milan, TN, Burlington, IA	
TNT, RDX, explosives	Army Corps of Engineers
Municipal Treatment Facility; Woodburn, OR	
Landfill leachate	Ecolotree, CH2M HILL
Landfills; Cedar Rapids, IA	
Landfill leachate	Ecolotree, CH2M HILL
DOE site; Ashtabula, OH	
	Uranium
	Phytotech (Edenspace)
Upper Bear Creek; Oak Ridge, TN (Y-12 site)	
	Uranium
	Phytotech, SAIC, ORNL

Phytoremediation Cost Estimates

Soils	
$1-10/cu. meter	(S. Cunningham, DuPont)
$10/cu. yard	(Geraghty & Miller)
$15-20/ton	(E. Drake, Exxon)
$25-50/ton	(Phytotech)
$29-48/cu. meter	(Salt et al.)
$80/cu. yard	(R. Levine, DOE)
$96/cu. yard	(Jerger et al., IT Corporation)
$100-150/cu. meter	(R. Chaney, USDA)

Water (per 1,000 gallons treated)

$0.64	(V. Medina, EPA)
$2.00 - 6.00	(Phytotech)

Vegetative Cover (e.g. Landfill Cap, Wastewater)

$10-20,000/acre	(Christensen-Kirsh 1996, citing CH2M Hill data)
$14-30,000/acre	(EPA RTDF Action Team)

Phytostabilization Practices for Riverbank and Wetland Problems

Wendi Goldsmith and
Bill Morgante

Wendi Goldsmith is senior bioengineer with the Bioengineering Group, Inc. She has extensive experience in all phases of project design and implementation for lakes, rivers, and tidal areas. As project manager, consulting bioengineer, or horticultural advisor, she has often led interdisciplinary joint-venture design teams. She has played a key role in promoting local familiarity and acceptance of bioengineering methods, and has aided in the logistical planning for innovative projects. Evaluating change in land use and its effect on geomorphic stability, non-point source pollution, and habitat degradation has been an integral part of Ms. Goldsmith's waterways assessments and restoration projects. Ms. Goldsmith is skilled in the areas of soil science, fluvial geomorphology, landscape design, and wetland management. She also has a thorough understanding of federal, state, and local environmental regulatory policy. Current research carried out by Ms. Goldsmith includes phytoremediation study and testing as well as Brownfields redevelopment.

William Morgante is a Plant and Soil Scientist with the Bioengineering Group, Inc. His knowledge of native plants and soil genesis allows him to correctly interpret field conditions and plan complex natural resource restoration projects. He participates in site evaluation, design development, construction documentation and supervision, as well as the monitoring of bioengineering treatments for streambanks, shorelines and wetlands. Mr. Morgante is skilled at landscape design as well as delineating wetland borders through both vegetation and hydrology. He has recently carried out research relating to phytoremediation of lead-contaminated soils targeted toward the redevelopment of Brownfields.

Two Case Studies: Landfill Bank Stabilization/Leachate Collection and Salt Marsh Restoration

Poster Session Abstract

1. Cincinnati, OH, bank stabilization was required to halt erosion along a creek that threatened to uncover landfill materials. The stream bank contained an existing leachate collection system, located atop a clay soil layer overlain by highly permeable soils mixed with landfill materials. Bioengineering was utilized because of its ability to aid in stabilization, assist in leachate extraction and enhance wildlife habitat, water quality, and aesthetics.

2. Salt marsh restoration in Salem, MA, was required to remedy an area filled with lead-contaminated refuse. Fill was removed to restore former correct salt marsh hydrology, and salt marsh plant species were installed throughout site. Salt marsh vegetation was reestablished on the former fill area restoring wetland hydrology, enhancing wildlife habitat containing residual contaminants, and improving aesthetics.

Field Studies Examining Rhizosphere-enhanced PCB Degradation in the Czech Republic

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Mary Beth Leigh has a B.F.A. in dance, an M.S. in botany and is now pursuing a Ph.D. in microbiology from the University of Oklahoma. She is currently conducting field research in rhizosphere bioremediation of PCBs in the Czech Republic with an NSEP Graduate International Fellowship. She is examining the vegetation, root-associated microflora and PCB congener profiles in contaminated sites to determine the influence of plant species on microbial PCB degradation.

She has conducted root physiology and ozone research with the EPA Western Ecology Division in Corvallis, OR, as a NNEMS Fellow for two summers and for six months as plant physiologist/biochemist. She was also selected for NASA's Space Life Sciences Training Program at Kennedy Space Center, FL, and was employed in NASA's Environmental Analytical Chemistry Laboratory.

John Fletcher holds a B.S. from Ohio State University, an MS from Arizona State University, and a Ph.D. in plant physiology from Purdue University. He is a professor of botany in the Dept. of Botany and Microbiology at the University of Oklahoma in Norman, OK. During his 30 year tenure at the University of Oklahoma he and his graduate students have studied the metabolism of nonphotosynthetic plant tissues, root uptake of xenobiotics, ecological risk assessment (including PHYTOTOX and UTAB database development), and rhizosphere remediation of PCBs and PAHs. In 1997 Dr. Fletcher received a Level 1 research award from EPA's Office of Research Administration for phytotoxicity research he conducted in collaboration with persons at the EPA Laboratory in Corvallis, OR. His current research is focused on rhizosphere remediation of PAHs at a former industrial sludge basin in Texas and several PCB-contaminated field sites in the Czech Republic. Both projects are being conducted with the cooperation of industrial partners. Dr. Fletcher's professional service activities related to environmental issues include: plant editor for the *Journal of Environmental Toxicology and Chemistry*, member of the Chemical Manufacture Association's Technical Implementation Panel for Ecological Risk Assessment Research, and member of EPA's Scientific Advisory Panel for the Federal Insecticide, Fungicide and Rodenticide Act.

Abstract

Research has been initiated in the Czech Republic to determine the long-term influence of vegetation on the microbial degradation of PCBs in contaminated soil. Two sites have been secured for this study in which a variety of plant species have naturally grown for at least 10 years in PCB-contaminated soil ranging in concentration from 50-500 ppm. The oldest and largest plants present are maple (*Acer* sp.) and birch (*Betula* sp.) trees, in addition to several grasses and shrubs. The microorganisms associated with the roots of different plant species are being examined and compared to bulk soil organisms to identify plants that selectively foster the growth of PCB degraders. Initial screening studies employing a 4-chlorobiphenyl agar plate assay have identified aggressive PCB-degrading bacteria associated with rhizosphere soil. In parallel, PCB-contaminated soil from the rhizosphere of mature plants (at least 10 years old) is being examined for evidence of congener degradation.

Natural Attenuation/Phytoremediation at a Former Sludge Basin

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John S. Fletcher
Department of Botany and Microbiology
Paul R. Philip
Department of Geology and Geophysics
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Norman, OK 73019
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Paul E. Olson received a B.S. in biology from Central State University, an M.S. in biology from the University of Central Oklahoma, and a Ph.D. in botany from the University of Oklahoma under the direction of Dr. John S. Fletcher. His dissertation research focused on the role of vegetation and root-associated microorganisms in the phytoremediation and ecological recovery of former sludge lagoons contaminated with organic pollutants. Results from these studies indicated that select plant species and rhizosphere microflora have the capacity to alter site conditions, while providing the means for the sustained cleanup and restoration of soils contaminated with recalcitrant organic pollutants.

Currently, Paul E. Olson is part of a collaborative research group at Colorado State University as a postdoctoral fellow. The research group at Colorado State University, consisting of members from the Departments of Biology, Microbiology, and Chemical and Bioresource Engineering, is investigating the underlying mechanisms between plants and soil microorganisms in the enhanced dissipation of organic pollutants, including polycyclic aromatic hydrocarbons (PAHs). The overall goal of this research group includes devising plant-microbe remediation approaches that will lead to an improved bioremediation strategy for sites contaminated with organic pollutants.

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John Fletcher holds a B.S. from Ohio State University, an M.S. from Arizona State University, and a Ph.D. in plant physiology from Purdue University. He is a professor of botany in the Dept. of Botany and Microbiology at the University of Oklahoma in Norman, OK. During his 30 year tenure at the University of Oklahoma he and his graduate students have studied the metabolism of nonphotosynthetic plant tissues, root uptake of xenobiotics, ecological risk assessment (including PHYTOTOX and UTAB database development), and rhizosphere remediation of PCBs and PAHs. In 1997 Dr. Fletcher received a Level 1 Research Award from EPA's Office of Research Administration for phytotoxicity research he conducted in collaboration with persons at the EPA Laboratory in Corvallis, OR. His current research is focused on rhizosphere remediation of PAHs at a former industrial sludge basin in Texas and several PCB-contaminated field sites in the Czech Republic. Both projects are being conducted with the cooperation of industrial partners. Dr. Fletcher's professional service activities related to environmental issues include: Plant Editor for the *Journal of Environmental Toxicology and Chemistry*, member of the Chemical Manufacture Association's Technical Implementation Panel for Ecological Risk Assessment Research, and member of EPA's Scientific Advisory Panel for the Federal Insecticide, Fungicide and Rodenticide Act.

Abstract

The natural attenuation of polyaromatic hydrocarbons (PAHs) in the vadose zone of a naturally revegetated former industrial sludge basin was examined. This was accomplished by comparing the concentration of 16 PAH contaminants present in sludge collected below the root zone of plants with contaminants present at 3 shallower depths within the root zone. Chemical analysis of 240 samples from 60 cores showed that the average concentration of total and individual PAHs in the 0-30 cm, 30-60 cm, and bottom of the root zone strata were approximately 10, 20, and 50%, respectively, of the 16, 800 ppm average total PAH concentration in deep non-rooted sludge. Statistically significant differences in average PAH concentrations were observed among all strata studied and the non-rooted sludge, except for the concentrations of acenaphthene and chrysene present

at the bottom of the root zone, in comparison to sludge values. The rooting depth of the vegetation growing in the basin was dependent on vegetation type and plant age. Average rooting depths for trees, forbs (herbaceous non-grasses), and grasses were 90, 60 and 50 cm, respectively. The deepest root systems observed (100-120 cm) were associated with the oldest (12-14 year-old) mulberry trees. Examination of root systems and PAH concentrations at numerous locations and depths within the basin indicated that plant roots and their microbially active rhizospheres fostered PAH disappearance, including water insoluble, low volatility compounds i.e. benzo(a)pyrene and benzo(ghi)perylene. The reduced concentration of PAHs in the upper strata of this revegetated former sludge basin indicates that natural attenuation has occurred. This observation supports the concept that through appropriate planting and management practices (phytoremediation) it will be possible to accelerate, maximize, and sustain natural processes, whereby even the most recalcitrant PAH contaminants (i.e. benzo(a)pyrene) can be remediated over time.

Phytoremediation of Heavy Metals, Metalloids, and Organics: A Multidisciplinary Approach

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Elizabeth Pilon-Smits has a Ph.D. in biology from the University of Utrecht, The Netherlands. She worked as a postdoctoral fellow at the University of Utrecht from 1992-1994, and at UC Berkeley from 1994-1998 (in the lab of Norman Terry). Since 1998, Elizabeth Pilon-Smits is working as a tenure-track assistant professor in the biology department at Colorado State University (Fort Collins, CO). Her main topic of research is phytoremediation of selenium and heavy metals (6 years of research experience) and, more recently, of polycyclic aromatic hydrocarbons (PAHs). Other areas of expertise include plant drought tolerance mechanisms, and plant biotechnology.

Elizabeth Pilon-Smits has over twenty publications in peer-reviewed scientific journals, and two patents pending for transgenic plants with superior capacity to accumulate trace elements. Her current research is funded by NSF (CAREER) and the EPA (two projects).

Abstract

Our research centers on understanding the mechanisms by which plants and their associated microbes metabolize and accumulate environmental pollutants, with the goal to improve phytoremediation efficiency. We study phytoremediation processes at the molecular level, the whole plant level, and in the field. One of our approaches is to identify steps that are rate-limiting for the phytoremediation of different pollutants and then use genetic engineering to improve phytoremediation efficiency. We use Indian mustard (*Brassica juncea*) as a model system for studying trace element metabolism. So far, we have created transgenic mustard plants with increased accumulation of, and tolerance to, selenium and cadmium. This was achieved by overexpression of enzymes involved in the sulfate assimilation pathway and in phytochelatin biosynthesis, respectively. We are presently studying the capacity of these transgenics for remediation of a range of trace elements (As, Cr, Cu, Cd, Hg, Mn, Mo, Ni, Pb, Te, W, Zn), from synthetic substrates and from contaminated environmental substrates.

Other related research focuses on the creation and analysis of new transgenic plants for trace element remediation, and the isolation of new plant genes involved in trace element homeostasis and tolerance. Finally, we have recently formed a collaborative research group with members from the CSU Departments of Microbiology, and Chemical and Bioresource Engineering, to devise plant-microbe remediation approaches toward recalcitrant organic pollutants. Research efforts are presently focusing on the relative contributions and interactions of plants and soil microorganisms in the enhanced dissipation of polycyclic aromatic hydrocarbons (PAHs). Future research goals include implementing our findings in field trials, for the enhanced cleanup and restoration of metal- and/or organic-contaminated environments.

Growth and Contaminant Uptake by Hybrid Poplars and Willows in Response to Application of Municipal Landfill Leachate

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and
J.G. Isebrands, USDA-Forest Service
Forestry Sciences Laboratory, Rhinelander, WI 54501 (jisebrands@fs.fed.us)

Christopher J. Rog, has a B.S. in geology from Colorado State University and an M.S. in geology from the University of Minnesota-Duluth. He is a registered professional geologist in Wisconsin and Minnesota, and has worked in natural resource-related issues for 15 years on projects in the midwestern, northwestern, and southwestern United States.

Mr. Rog is currently employed by Sand Creek Consultants, Inc., as a senior hydrogeologist. Current project work has increasingly involved the use of plant-based remedies for low-level VOC, metal, and nutrient contamination in groundwater affected by landfill leachate, especially along riparian boundaries. Sand Creek Consultants, Inc., is currently engaged in a joint research agreement with the U.S.D.A. Forestry Sciences Lab exploring various aspects of the use of hybrid poplars and willows for phytoremediation at closed municipal landfills.

Jud Isebrands has a B.S. and Ph.D. in forestry and forest science with a minor in statistics from Iowa State University, Ames, IA. He has worked at the USDA - Forest Service, Forestry Sciences Laboratory, Rhinelander, WI, for 32 years, first as a tree physiologist and then as project leader of a research team on ecophysiological processes.

His primary research focus is on the effects of climate change on forests and the environmental effects of trees and forests including biomass for energy, riparian buffers, and phytoremediation. He is presently the U.S. representative to the International Poplar Commission and serves on their executive committee. He is the author of over 150 scientific papers and book chapters and an active reviewer on national scientific panels on forestry issues.

Abstract

Phytoremediation is an emerging technology that is a cost-effective and environmentally sound approach for many municipal landfill cleanups. Two of the most common tree species used in phytoremediation are poplars (*Populus* spp.) and willows (*Salix* spp.); both exhibit rapid growth rates and ease of vegetative propagation. More information is needed on the proper choice of tree clones for phytoremediation because soils, climate, and contaminants vary with sites. In this study we examined the phytoremediation potential of 10 northern poplar and willow clones in response to applications of Rhinelander, WI, municipal landfill leachate in a replicated factorial experiment.

Our objectives were to compare seasonal: 1) plant growth, 2) hydrological uptake, 3) volatile organic compound (VOC) removal, and 4) inorganic macro- and micro-ion removal for the 10 clones growing across four experimental treatments (i.e., with and without contaminated water, and with and without trees).

Trees were grown from cuttings in landfill soil in 600 plastic tanks, and watered weekly with applications of either municipal water (control), or leachate ground water (contaminated) during the 1999 growing season; other tanks were treated similarly without trees. VOCs of the influent and effluent were monitored periodically, leaves were collected in October, and plant components (i.e. stems and roots) harvested in December for micro- and macro-ion analysis. Our results showed that height and volume growth of the poplar and willow clones growing in contaminated water were not significantly different from the controls. There were growth differences among the clones - 2 poplar and 2 willow clones performed the "best." Tanks with trees took up 3 times the quantity of water when compared to tanks without trees indicating significant hydrologic uptake. Contaminant VOCs from the Rhinelander landfill were removed at a rate similar to the evaportranspiration rate including 2-butanone (MEK), cis-1,2 dichloroethene, tetrahydrofuran, benzene, and vinyl chloride. Significant quantities of some trace metal ions were removed by the trees; e.g., boron and zinc were found in leaves of some clones at concentrations much higher than most northern plants. Moreover, there were significant differences among clones in leaf concentrations of macro-ions such as magnesium and calcium that are suggested as contributing to ion toxicity in receiving waters near landfills. Our overall results suggest that certain poplar and willow clones have much potential for successful phytoremediation at the Rhinelander landfill.

Aqueous Phase Phytotreatment of Munitions Victor Medina

Victor F. Medina
Assistant Professor of Civil & Environmental Engineering
Washington State University, Tri-Cities.

Victor Medina has a B.S. in Geology from the UCLA and an M.S. and Ph.D. in Civil Engineering from the University of Southern California. He has worked for three years as an environmental consultant, and served a two-year post-doctoral research fellowship through the National Research Council at U.S. Environmental Protection Agency National Exposure Research Laboratory in Athens, GA.

Victor is currently an assistant professor of Civil and Environmental Engineering at Washington State University Tri-Cities. His phytoremediation research has focussed on the treatment of munitions both in water and soil. More recently, he has begun work on treatment of metals in conjunction with the Army Corp of Engineers. He has four papers in print or press in refereed journals on the topic of phytoremediation. Other research Dr. Medina is currently involved with includes water quality issues in irrigation systems and issues involving tank wastes at the Hanford Nuclear Reservation.

Abstract

This poster will summarize research to treat munitions in the aqueous phase using phytoprocesses. Results of batch experiments will cover the effect of plant type, plant density, temperature, and TNT concentration. Batch treatment of RDX and HMX will also be presented. Continuous flow reactors treating TNT will also be presented and will include data covering variations in influent concentration and flow rates. Problems in treating aminodinitrotoluenes (ADNTs) will be discussed. Preliminary results investigating toxic levels of TNT on parrotfeather, a plant commonly used for treatment, will be shown. The development of new approaches using exudates, minced plants and slurried plants will also be presented.

Measuring Evapotranspiration in Hybrid Poplars

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Paul R. Thomas founded Thomas Consultants, Inc., in 1989. He has a B.S. in geology from Marshall University and twenty one years of professional consulting experience. He has served as principal consultant for remedial actions at major industrial facilities throughout the United States and has been active in plant-based remediation of hazardous waste sites since 1987.

Mr. Thomas has designed and installed phytoremediation systems to address a range of groundwater and soil contaminants including pesticides, volatile organics, and metals. Projects have been completed or are underway at CERCLA, RCRA, Brownfields, and voluntary cleanup sites. Mr. Thomas' focus is on the optimization and practical use of woody phreatophytes in remediation practice. Current research areas include the effects of hybrid poplars on soil microbial biomass and organochlorine pesticide degradation.

Publications:

Thomas, P.R., and Buck, J. B. 1999. "Agronomic Management for Phytoremediation" in *Phytoremediation and Innovative Strategies for Specialized Remedial Applications,* ed. Andrea Leeson and Bruce C. Alleman. Battelle Press, vol. 6, pp 115-120.

Thomas, P.R., and Krueger, J.J. 1999. "Salt Tolerance of Woody Phreatophytes for Phytoremediation Applications" in *Phytoremediation and Innovative Strategies for Specialized Remedial Applications,* ed. Andrea Leeson and Bruce C. Alleman. Battelle Press, vol. 6, pp 21-26.

Abstract

One important aspect of phytoremediation practice is the proper application of evapotranspiration monitoring techniques. The use of hybrid poplars (and other woody phreatophytes) as water-moving remediation tools is becoming more common with each growing season. Methods for measuring and predicting evapotranspiration at the stand level are well established, but recent advances in sensors and software make it possible to directly measure sap flow and its response to leaf area and climatic variables at specific sites where phytoremediation is in use. Xylem sap flow strongly correlates to variations in photosynthetically active solar radiation (PAR). Calibration of sap flow (per unit of leaf area) with PAR allows accurate scaling up of measured water consumption rates to the stand level. Accurate and precise measurement of PAR from all portions of the stand are possible. PAR sensors also allow season-long monitoring without the challenges associated with extended duration sap flow measurement.

A method is proposed to systematically characterize the volume of consumptive water use in stands of woody phreatophytes. The method involves monitoring weather variables (including PAR) throughout the local growing season as well as periodic measurements of sap flow and leaf area. It is intended to allow prediction of changes in consumptive rate as stands mature. Critical to the method is the inclusion of agronomic management methods that allow the effects of nutrient response, drought, and predation to be accounted for and, hopefully, controlled. These variables have the potential to significantly impact viable leaf area. Data from several sites are presented.

Sap Flow Methods to Measure Phytoremediation Water Removal

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Michael van Bavel graduated from Texas A&M University with a B.S. in electrical engineering in 1972. He served with Texas Instruments as design engineer, program manager, and engineering manager in the development and application of microprocessors, microcomputers, and digital signal processing. He was awarded two patents for the self-testing and control of microprocessor-based electronic systems in 1976. After 13 years with Texas Instruments, he founded Dynamax, Inc., in 1985 and began the development of portable electronic systems, portable sensors, and expanded the scope to include agricultural product development.

Michael van Bavel is currently the president and CEO of Dynamax, Inc. He is responsible for the engineering service contacts, R&D direction and the long-term strategy to support new emerging markets. He is responsible for the co-development of two new sap flow sensors and was awarded two U.S. patents in 1990 and in 1994. He has worked with the remote sensing and electronic technology transfer from agricultural and forest science to industry with the USDA, the National Forest Service, INRA - France, and Battelle National Laboratories. He manages further development and product introduction from patents licensed by Battelle and INRA that measure the growth and water use of trees. He has recently provided contract-engineering services for Lockheed Martin REAC on the EPA phytoremediation studies at Aberdeen Proving Grounds. The primary objective was to analyze three years of sap flow and tree growth data to provide long-term forecasts, and to assist in solving the hydrology models. Currently he is a member of the American Society of Agronomy, National Irrigation Association, American Society of Horticultural Science, Technical Association of the Pulp and Paper Industry, and the American Society of Enology and Viticulture. He was awarded three times for innovative sap flow measurement products by the Agricultural Engineering Society of America.

Abstract

To support the proof of efficacy of phytoremediation, two *in situ* measurement methods are employed that record sap flow, the transpiration rate, of plants and trees. The sap flow records support the hydrology models for long-term predictions, the real time removal rate of plants, and track the progress of plants' water uptake as they mature. The sap flow sensor data can assist the development of new and more cost efficient methods. A number of plants are measured over the active seasons and tracked from year to year. These data are essential to show the removal rates of trees planted in a contaminated zone, to support the observations by sampling of contaminates either being degraded, accumulated, volatilized, extracted, or stabilized. Furthermore, the sap flow data support the establishment of high water-using plants to prevent contaminants in the vadose zone or landfills from leaching into deeper layers, as well as providing a barrier to contaminated plume movements.

As environmental engineering companies and regulatory agencies take on the phytoremediation projects, a number of anecdotal and historically unproven water consumption rates are quoted in proposals for a variety of reasons. To provide a realistic estimate of the time involved and efficacy, the companies and agencies will need to gather factual data derived from plants on location. The sap flow data take into account not only the plant characteristics, but also the soil conditions, planting density, weather patterns, rooting depth, leaf area progression, and long-term growth rates.

Two sap flow measurement systems and related support tools are described in this presentation. The first, Dynagage™, is based on patented mass flow sensors that are wrapped around the stems or trunks, and measure the flow rates by the heat carried by sap flow convection and the temperature increase of the water moved. These energy balance sensors require no calibration, are portable, and have been used successfully in the crop and forest sciences since 1989. The Dynagage sensors range from 1/8 in diameter up to five-in. diameter. New Flow32 systems software and improved analysis methods are presented here.

The second measurement method for larger trees is based on the patented TDP - Sap Velocity Thermal Dissipation Probes (TDP). The TDP sensors are heated and needles inserted into the xylem of trees three inches in diameter or larger. The calibrations of the sensors

are widely accepted and convert the temperature differential of the heated needle to a sap velocity (cm/hr or mm/s). The sap wood thickness and xylem area are then determined to convert to a volume flow.

Both methods of monitoring sap flow have their advantages, and depending on the progress of the remediation plants, recommendations are made to help the selection. Recent system designs are also presented here that combined both sensors into the same logging instrument. A summary follows which describes the recommended practices that will yield accurate remediation rate data.

Transport of Methyl Tert-Butyl Ether (MTBE) through Alfalfa Plants

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Qizhi Zhang has a B.S. in environmental engineering from East China University of Chemical Technology, an M.S. in chemical engineering from Zhejiang University and a Ph.D. in chemical engineering from Kansas State University. She has 15 years of research and teaching combined experience in chemical engineering. Currently employed by the Biological & Agricultural Engineering Department at Kansas State University as a postdoctoral research associate, Dr. Zhang is working on the transport and control of pathogens from feedlot surface runoff and assessment of the effectiveness of vegetative filter strips on the removal of contaminants.

Lawrence C. Davis has his Ph.D. degree from Albert Einstein College of Medicine. He has broad research interests including nitrogen fixation mutants, structure-function relationships, associating macromolecules; environmental metabolic processes, plant-based bioremediation; and science education. He is a professor of Biochemistry and Chair of the Graduate Biochemistry Group at Kansas State University. Dr. Davis has more than 100 publications.

Larry E. Erickson has a B.S.Ch.E. and a Ph.D. in chemical engineering from Kansas State University. He has been a member of the chemical engineering faculty at Kansas State University since 1964. Dr. Erickson is presently professor of chemical engineering and director of the Great Plains/Rocky Mountain Hazardous Substance Research Center. He has been conducting research on the beneficial effects of vegetation in contaminated soil since 1991. He has been an author or co-author of more than 300 papers published as journal articles or reports. He is editor of the *Journal of Hazardous Substance Research*, an online journal published by Kansas State University at http://www.engg.ksu.edu/HSRC/.

Abstract

Concentrations measured in alfalfa plant stem segments indicated that plants grown in methyl tert-butyl ether (MTBE)-contaminated soil took up the chemical through their roots. Assuming a cylindrical shape for the plant stem, a mathematical model was developed to describe the transport of MTBE through the stems. Simulation results from uniform and non-uniform initial concentration distributions across the stem radius were compared with the experimental data. With known values of plant stem radius, water usage, water content and the distance over which the concentration decreased bv 50%, the diffusion coefficient of contaminant across the plant stem was calculated by using the modeling results. For the experimental conditions of this work, the diffusion coefficient for radial transport of MTBE through alfalfa stems was estimated to be in the range of 8.43 ~16.2 x 10^{-8}cm^2/sec, and for water it was 6.28 x 10^{-9}cm^2/sec. The model is applicable to other species including sunflowers and poplars, upon substitution of appropriate parameters.

Keywords: transport, MTBE, alfalfa, diffusion coecient

APPENDIX A

Agenda

EPA United States Environmental Protection Agency

Phytoremediation State of the Science Conference

Omni Parker House Hotel
Boston, MA
May 1–2, 2000

Agenda

MONDAY, MAY 1, 2000

Note: All sessions, except the opening plenary, consist of 25 minute presentations and a 10 minute panel Q&A session.

8:00AM **Registration** - Rooftop Ballroom Foyer

8:30AM **Session I: Introduction and Plenary** - Rooftop Ballroom

Welcome and Introductions
Norm Kulujian, U.S. Environmental Protection Agency (EPA)

EPA Policy Overview
Stephen Luftig, Office of Solid Waste & Emergency Response (OSWER), EPA

The Science and Practice of Phytoremediation
Steven McCutcheon, EPA

Interstate Technology Regulatory Cooperation (ITRC): Making It Easier for Regulators
Robert Mueller, New Jersey Department of Environmental Protection/ITRC

International Perspective on the Clean Up of Metals and Other Contaminants
Terry McIntyre, Environment Canada

Looking Forward on Phytotechnologies
Steven Rock, EPA

10:45AM BREAK

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11:00AM **Session II: Fundamental Processes of Plants and Soil** - Rooftop Ballroom
Co-Chairs: Steven McCutcheon, EPA and Lee Newman, University of Washington

Transport of Contaminants in Plant and Soil Systems
Larry Erickson, Lawrence Davis, Qizhi Zhang, and Muralidharan Narayanan, Kansas State University

Enzymatic Processes Used by Plants to Degrade Organic Compounds
Nelson Lee Wolfe, EPA

Sustained Rhizosphere Remediation of Recalcitrant Contaminants in Soil: Forensic Investigations with Laboratory Confirmation
John Fletcher, University of Oklahoma

Speaker Panel and Audience Discussion

12:30PM L U N C H (on own)

2:00PM **Concurrent Sessions**

Session IIIA: Brownfields Applications and Beneficial Use of Land - Rooftop Ballroom
Chair: Niall Kirkwood, Graduate School of Design, Harvard University

Integrating Remediation Into Landscape Design
Niall Kirkwood, Graduate School of Design, Harvard University

Goals for Brownfields Pilots - O'Sullivan Island
John Podgurski, EPA, Region 1

Hartford Brownfield Demonstration
Panel discussion

Speaker Panel and Audience Discussion

Session IIIB: Radionuclides - Press Room
Chair: Scott McMullin, Department of Energy (DOE)

Department of Energy Projects, Report on Recent Department of Energy Workshop
Scott McMullin, DOE

Capturing a "Mixed" Contaminant Plume:
Tritium Phytoevaporation at Argonne National Laboratory
M. Cristina Negri, Ray Hinchman, and James Wozniak, Argonne National Laboratory

Application of Phytoremediation to Remove Cs-137 at Argonne National Laboratory - West
Scott Lee, Argonne National Laboratory

Speaker Panel and Audience Discussion

3:25PM B R E A K

MONDAY, MAY 1, 2000 - CONTINUED

3:40PM **Concurrent Sessions**

Session IVA: The Fate of Chlorinated Solvents that Disappear from Planted Systems - Rooftop Ballroom
Chair: Gregory Harvey, U.S. Air Force

Phytoremediation of Solvents
Milton Gordon, University of Washington

The Case for Volatilization
William Doucette, Utah State University

Phyto-Transformation Pathways and Mass Balance for Chlorinated Alkanes and Alkenes
Valentine Nzengung, University of Georgia

Speaker Panel and Audience Discussion

Session IVB: Innovative Solutions for Metals Removal - Press Room
Chair: Mitch Lasat, EPA

Phytoextraction of Metals from Contaminated and Mineralized Soils Using Hyperaccumulator Plants
Rufus Chaney, U.S. Department of Agriculture

Phytoextraction: Commercial Considerations
Michael Blaylock, Edenspace

Zinc Hyperaccumulation in Plants: The Case of Zinc Hyperaccumulation in *Thlaspi caerulescens*
Mitch Lasat, EPA

Speaker Panel and Audience Discussion

5:00PM BREAK

6:00PM **Evening Poster Session and Reception** (cash bar) - Wheatley Terrace Room

9:00PM ADJOURN

TUESDAY, MAY 2, 2000

8:00AM **Session V: Plume Control: Simulations and Forecasts** - Rooftop Ballroom
Co-Chairs: Judy Canova, South Carolina Department of Environmental Protection and Steven Hirsh, EPA, Region 3

Chasing Subsurface Contaminants
Joel Burken, University of Missouri

Effect of Woody Plants on Ground-Water Hydrology and Contaminant Fate
James Landmeyer, U.S. Geological Survey

Session V: Plume Control: Simulations and Forecasts - Continued

Modeling Plume Capture at Argonne National Laboratory - East
John Quinn, Argonne National Laboratory

Phytoremediation Potential of a Chlorinated Solvents Plume in Central Florida
Stacy Lewis Hutchinson and James Weaver, EPA

Speaker Panel and Audience Discussion

9:50AM BREAK

10:05AM **Session VI: Plume Control: On the Ground Experience** - Rooftop Ballroom
Chair: Harry Compton, EPA

Phytoremediation at Aberdeen Proving Ground, Maryland:
Operation and Maintenance, Monitoring and Modeling
Steven Hirsh, EPA, Region 3 and Harry Compton, EPA

Phytoremediation Systems Designed to Control Contaminant Migration
Ari Ferro, Phytokinetics

Deep Planting
Edward Gatliff, Applied Natural Sciences

Transpiration: Measurements and Forecasts
James Vose, U.S. Forest Service

Speaker Panel and Audience Discussion

11:55AM LUNCH (on own)

1:00PM **Session VII: Vegetative Covers** - Rooftop Ballroom
Co-Chairs: Steven Rock, EPA and Donna McCartney, EPA, Region 3

Monitoring Alternative Covers
Craig Benson, University of Wisconsin

Growing a 1000 Year Landfill Cover
William Jody Waugh, Roy F. Weston

Tree Covers for Containment and Leachate Recirculation
Eric Aitchison, Ecolotree, Inc.

EPA Draft Guidance on Landfill Covers
Andrea McLaughlin and Ken Skahn, EPA

Speaker Panel and Audience Discussion

2:50PM BREAK

3:05PM **Session VIII: Degradation of Organic Compounds in Soils** - Rooftop Ballroom
Chair: Phil Sayre, EPA

Hydrocarbon Treatment Using Grasses
M. Katherine Banks, Purdue University

Phytoremediation of Explosives
Phillip Thompson, Seattle University

Case Study: Union Pacific Railroad
Felix Flechas, EPA, Region 8

Phytoremediation in Alaska and Korea
Charles (Mike) Reynolds, U.S. Army Corps of Engineers

Speaker Panel and Audience Discussion

4:55PM ADJOURN

APPENDIX B

Speaker List

United States Environmental Protection Agency

Phytoremediation State of the Science Conference

Omni Parker House Hotel Boston, MA
May 1-2, 2000

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Phytoremediation State of the Science Conference

Omni Parker House Hotel
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APPENDIX D

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Phytoremediation
State of the Science Conference

Omni Parker House Hotel
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