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Summary of the Phytoremediation State of the Science Conference

Boston, Massachusetts
May 1-2, 2000

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National Risk Management Research Laboratory
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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 (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten 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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Steven Rock, U.S. Environmental Protection Agency (U.S. EPA), National Risk Management Research Laboratory (NRMRL), Cincinnati. OH
Steven McCutcheon, U.S. EPA, National Exposure Research Laboratory (NERL), Athens, GA
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Jeff Heimerman, U.S. EPA, OSWER, Washington, DC
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The success of the conference and the preparation of this document are also due to the efforts of the many speakers and poster presenters.

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SUMMARY OF THE PHYTOREMEDIATION STATE OF THE SCIENCE CONFERENCE

Omni Parker House Hotel
Boston, Massachusetts
May 1–2, 2000

SESSION I: INTRODUCTION AND PLENARY

Welcome and Introductions
Norm Kulujian, EPA, Office of Science and Policy

On behalf of the U.S. Environmental Protection Agency (EPA), Norm Kulujian welcomed speakers (see Appendix B), poster presenters (see Appendix C), and meeting attendees (see Appendix D). Five years ago, he said, many people were unfamiliar with the concepts that underlie phytoremediation. Today, the field is burgeoning with interest, and many site owners are asking for permission to implement phytoremediation at their sites. Regulators, Kulujian said, are eager to obtain a better understanding of phytoremediation so that they will know where it is likely to be successful, when to dismiss it, and when to perform preliminary tests to determine whether it is appropriate for a particular site. Of the proposals that have been submitted, Kulujian said, most have focused on using phytoremediation as a containment technology. This does not mean that enough data have been collected to prove conclusively that phytoremediation is successful when applied this way, nor does it mean that phytoremediation has no potential to reduce contaminant concentrations. Phytoremediation's optimal application, said Kulujian, will differ across sites and will be determined by what contaminants, climatological conditions, and geological conditions are present. Thus, phytoremediation will be useful as a containment technology at some sites and as a destruction approach at others; at some sites, it will probably serve as part of a treatment train.

Kulujian said that sites in arid or semi-arid climates might be excellent candidates for phytoremediation, noting that plants might be able to extract enough moisture to prevent leachate from forming at these sites. In addition, he said, phytoremediation might be beneficial to use at sites that have widespread contamination and concentrations that are close to cleanup levels. Also, he said, sites that require ecosystem restoration might obtain significant benefits by applying phytoremediation.

EPA Policy Overview
Stephen Luftig, EPA, Office of Solid Waste and Environmental Response

Stephen Luftig provided an overview of the Superfund program and explained how it views phytoremediation technologies. He said that this year marks the 20th anniversary of the Superfund program, and that the program is operating well. Over the last few years, the program has (1) released guidance on future land uses, (2) established a national remedy board, and (3) revisited hundreds of Records of Decision that were written in the 1980s. The latter was done, he said, to determine whether sites would benefit from the use of innovative technologies that have been developed over the last 10 years. Luftig provided statistics to summarize the accomplishments of the Superfund program made since its inception. About 685 National Priorities List (NPL) sites have been completed, he said, noting that the number is expected to rise to 750 before the end of the fiscal year and to 900 before the end of 2001. Of the 43,000 Comprehensive Environmental Responsibility, Compensation, and Liability Act (CERCLA) sites that have been inventoried, he continued, about 40,000 have been addressed and 32,000 have been designated as no further action (NFA) sites. In addition, the Superfund program has completed about 6,000 removal actions. Luftig said that the Superfund program must remain viable for many years to come, because there are still several established sites that must be addressed and about 40 new sites are added to the NPL every year. In addition, he said, the federal Superfund program is important because it prompts site owners to participate in state voluntary cleanup programs, state Superfund programs, and the Brownfields program. Many site owners, he explained, clean up their sites through these programs as alternatives to being listed on the NPL.

Luftig said that the Superfund program is interested in phytoremediation, a technology that uses living plants to reduce the *in situ* risk of contaminated media through contaminant removal, degradation, or containment. EPA's Environmental Response Team (ERT) has already started working on nine different phytoremediation projects. (These sites are distributed throughout the country. Locations include New Hampshire, Rhode Island, Maryland, Colorado, Utah, Wyoming, and Oregon.) Luftig said that the program program is excited about phytoremediation technologies because they are less expensive than many technologies , effective, driven by solar power, aesthetically pleasing, and capable of restoring properties for future use. He said that phytoremediation might be a viable approach to use at a variety of Superfund, Resource Conservation and Recovery Act (RCRA), brownfields, and leaking underground storage tank sites. He envisioned it being particularly useful at sites that have shallow contaminants that are present at low levels. In addition, Luftig said phytoremediation could be useful to include in treatment trains.

Despite its impressive benefits, Luftig said, phytoremediation does have some limitations. For example, the technology may not be appropriate for all locations, because it is heavily influenced by seasonal, geographic, and climatological conditions. Also, phytoremediation may not be very useful at sites that have deep contaminants—roots might not be able to reach these—or at sites that must meet cleanup goals rapidly. In addition, phytoremediation (like almost all technologies) may only be effective for certain types of contaminants and at certain contaminant concentrations. Luftig said that some regulatory concerns have been expressed about phytoremediation. For example, will it introduce subsurface contaminants into the food chain? Restricting access to the site is an issue that must be done to protect the public. Potential damage (*e.g.*, fires, drought, or storms) may impact phytoremedial systems.

Luftig listed some of the things that should be taken into account if phytoremediation is being considered at a site. First, he said, site-specific testing should be conducted for site characterization purposes and for information to be used in the design phase. (He said that EPA's ERT could help with this.) In addition, he said, according to Executive Orders, native plants should be used if possible, and invasive alien species should be managed. If phytoremediation is going to be used at a federal Superfund site, Luftig said, the technology must comply with the National Contingency Plan and meet the nine criteria that drive remedy selection. He described two of the criteria: (1) protect human health and the environment, and (2) meet Applicable or Relevant and Appropriate Requirements (ARARs).

Luftig said that phytoremediation references are available at http://www.clu-in.org. He recommended reading *A Citizen's Guide to Phytoremediation* and the *Phytoremediation Resource Guide*. In the future, he said, EPA will release guidance on evapotranspiration covers. Also, the Interstate Technology Regulatory Cooperation (ITRC) Work Group will write a document that addresses regulatory impediments at the state level.

The Science and Practice of Phytoremediation

Steven McCutcheon, EPA, National Exposure Research Laboratory

Steve McCutcheon summarized what is currently known about phytoremediation. The term, he said, was introduced in 1991, in a proposal by Ilya Raskin which was submitted to the Superfund program. An article published in 1995 in *Environmental Science and Technology* recognized plants as agents that could degrade organic chemicals and expanded the definition of phytoremediation. This article's release stimulated a cascade of interest and research projects. Data collected from these efforts suggest that plants can be used to address a wide variety of contaminants, such as heavy metals (lead, nickel, zinc, and chromium); other inorganics (perchlorate, selenium, arsenic, and radionuclides); chlorinated aliphatics (*e.g.,* trichloroethylene [TCE] and tetrachloroethylene [PCE]); benzene, toluene, ethylbenzene, and xylene (BTEX); total petroleum hydrocarbons [TPH]; polycyclic aromatic hydrocarbons (PAHs); polychlorinated biphenyls (PCBs); phosphorus-based pesticides and nerve agents; munitions (2,4,6-trinitrotoluene [TNT], hexhydro-1,3,5-trinitrotoluene [RDX], and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine [HMX]); and other nitroaromatics. In addition, studies are being performed to evaluate whether plants can be used to remediate atrazine, cyanided compounds, DDT, methyl bromide, nitriles, phenols, and methyl tetra butyl ether (MTBE).

McCutcheon provided a brief overview of the limitations and the obstacles that phytoremediation faces. He said that the technology may only be practical at sites that have shallow contaminants that are present at low to moderate levels. Also, he said, the technology has mass transport limitations, and this slows down remedial processes. In addition, regulatory obstacles still remain. Efforts must be made to address the questions of regulators about phytoremediation and gather information that addresses bioaccumulation and product toxicity concerns.

McCutcheon said that there are six types of phytoremediation. He described these and summarized what is known about them:

Types of Phytoremediation/State of the Science/Proof of Concept
Phytotransformation or phytodegradation: Contaminants are metabolized or broken down within plants. State of the Science: • Researchers have isolated and are starting to forecast some of the plant enzymes that degrade organic contaminants. • Researchers have shown that some contaminants are completely degraded in plants. (This was shown in mass balance and pathway analyses.) • Researchers have used axenic tissues to show that some plant enzymatic processes are powerful remediation agents. • The following biotechnology tools are being used: (1) monoclonal antibodies, (2) ELISA field kits, and (3) immunofluorescence. Proof of Concept: • Field study at the Iowa Army Ammunition Plant (AAP) shows that plants metabolize TNT and RDX. • Feasibility study at Joliet AAP shows that natural attenuation by plants and microbes can be used to clean up munitions. • Georgia Tech laboratory study shows that plants clean up industrial waste waters that are contaminated with munitions. • Laboratory studies show that plants degrade chlorinated solvents. • Field studies performed at Hill Air Force Base (AFB), Carswell AFB, and the Cape Canaveral Air Station show that phytoremedial systems degrade chlorinated solvents. Studies performed by the University of Washington also support this finding.

Types of Phytoremediation/State of the Science/Proof of Concept
Rhizosphere bioremediation, phytostimulation, or plant-assisted bioremediation: Plants promote remediation by enhancing microbial activity in the rhizosphere. State of the Science: • Researchers have isolated microbes that degrade petroleum hydrocarbons and PAHs. • Investigators have identified advanced field management techniques for determining what plants to use and whether to fertilize and irrigate. • Precise and accurate analytical methods have been developed; these are used to evaluate treatment efficacy. Proof of Concept: • Field studies performed at Craney Island and the Texas Gulf Coast show that plant-based systems degrade petroleum hydrocarbons and PAHs. • Field study at Milan AAP shows that phytoremediation systems degrade TNT and RDX.
Phytostabilization: Uses plants to change soil conditions or to stabilize or hold contaminants in place. Proof of Concept: • Stabilization has been demonstrated at a Canadian mining site and at zinc smelter sites. • Lead, nickel, zinc, and cadmium have been stabilized at some industrial sites.
Phytovolatilization: Contaminants are taken up by plants and transpired to the atmosphere. State of the Science: • Researchers discovered that grasses and plants speciate and transpire selenium. • Transgenic *Arabidopsis* is immune to mercury (Hg) poisoning and transpires Hg(0). Proof of Concept: • Selenium uptake has been documented in the Central Valley of California. • Wetlands have been shown to remove selenium from oil refinery wastes.
Rhizofiltration: Plants extract contaminants from flowing water.
Phytoaccumulation, phytoextraction, or hyperaccumulation: Plants extract metals and organics from the subsurface for storage in plant leaves and shoots. State of the Science: • More than 400 species of hyperaccumulaters have been cataloged worldwide. • Field test kits have been developed to identify plants that are rich in metals. Proof of Concept: • Plants have removed lead at the NJ Magic Marker plots and at a site in Boston, Massachusetts. • Plants have removed heavy metals and radionuclides at Department of Energy (DOE) facilities. • Sunflowers have been evaluated to remove radionuclides from ponds at Chernobyl. • Plants have been evaluated to remove uranium from groundwater at Ashtabula.

In summary, McCutcheon said that phytoremediation has been shown to (1) control and accumulate lead and nickel, (2) treat water that is contaminated with munitions, (3) treat petroleum hydrocarbons and PAHs in contaminated soils, (4) control and treat shallow chlorinated solvent plumes, (5), control selenium in soils and wetlands, (6) control and treat radionuclides in soil, and (7) achieve water balance and leachate control at landfills. Engineers are investigating a broad variety of other applications.

Interstate Technical Regulatory Cooperation (ITRC): Making It Easier for Regulators

Robert Mueller, New Jersey Department of Environmental Protection

Robert Mueller said that ITRC, a state-led organization, promotes innovative technologies by reducing regulatory barriers, improving state permitting processes, and facilitating technology deployment. He said that ITRC is currently composed of representatives from 31 states, as well as members from industry, the

Western Governors Association, the Southern States Energy Board, EPA, DOE, the U.S. Department of Defense (DOD), and the Environmental Coalition of States. Working together, ITRC's members have delivered training courses, established information-sharing avenues, served as technology advocates, and have released case studies, regulatory and technical guidelines, and technology overviews. Mueller described the benefits that ITRC members receive by participating. State representatives, he said, learn about demonstrations that are conducted in other jurisdictions, obtain advance knowledge about innovative technologies, and are able to use ITRC as a sounding board for problems. Industry members gain insight into the regulatory process and this helps them understand regulatory requirements. Federal agencies have a forum in which to exchange ideas. DOD and DOE benefit because the ITRC addresses many of the contaminants that are of concern to them.

Mueller said that 12 work groups have formed within ITRC; each focuses on a particular technology or technical issue. One is focusing on phytoremediation, he said, noting that this group released a 40-page decision tree in December 1999 and that it planned to release a detailed regulatory and technical guidance document in July 2000. He said that ITRC's 11 other work groups have also generated a number of products, some of which might be of great interest to meeting attendees. Therefore, he summarized the products and success stories of each of ITRC's work groups:

Status and Activities of ITRC Work Groups	
Accelerated Site Characterization Work Group • Products: ♦ Two technology overviews ♦ Two guidelines on technical requirements: – Site characterization and analysis systems (SCAPS), laser induced fluorometry (LIF) – SCAPS-VOCs • Success stories: SCAPS-LIF document helped with decision to use LIF at an EPA Superfund creosote site.	**Enhanced *In Situ* Bioremediation Work Group** • Products: ♦ Technology overview ♦ Four guidelines, including *Natural Attenuation of Chlorinated Solvents in Groundwater—Principles and Practices* ♦ Case studies ♦ Natural attenuation courses (delivered in 1998) • Success stories: More than 900 regulators and 500 consultants attended the training courses.
Permeable Reactive Barriers (PRBs) Work Group • Products: ♦ Regulatory guidance for chlorinated solvents ♦ Regulatory guidance for inorganics and radionuclides ♦ Design guidance for chlorinated solvents ♦ Training course (delivered in 1999 and 2000) • Success stories: At a site in New Jersey, it took less than four months to design and install a PRB system. (Decreased permitting time by about four months.)	**Metals in Soil Work Group** • Products: ♦ Overviews of three emerging technologies: – Phytoremediation – Electrokinetics – *In situ* stabilization ♦ Soil Washing Guideline issued in 1997 and updated in 1999 • Success stories: Facilitated community acceptance of soil washing and phytoremediation at Fort Dix.
Low Temperature Thermal Desorption Work Group • Products: ♦ Three guidelines, addressing: – Petroleum/coal tar/gas plant wastes – Chlorinated organics – Mixed waste and/or mercury • Success stories: Contributed to $100/ton savings for treatment in New York.	**Verification Work Group** • Products: ♦ A matrix of data (provided by 16 states) on the elements that verification program should have • Success stories: Technology verification programs are incorporating states' verification needs into their programs. This makes it easier for states to approve technologies.

Status and Activities of ITRC Work Groups	
Plasma Technologies Work Group • Products: ♦ Technology overview	**Enhanced *In Situ* Biodentrification Work Group** • Planned Products: ♦ Technology overview
Dense Nonaqueous Phase Liquids (DNAPLs) Work Group • Planned Products: ♦ Overview of the technologies that can be used to characterize and treat DNAPLs.	**Radionuclides Work Group** • Planned Products: ♦ A catalog of state, federal, and international radionuclide organizations and their activities ♦ A glossary of radionuclide terms
Unexploded Ordnance (UXO) Work Group • Planned Products: ♦ Case studies examining how to remove barriers to using innovative UXO remediation technologies	**Phytoremediation Work Group** See text above this table.

In closing, Mueller encouraged attendees to visit http://www.itrcweb.org or to contact the ITRC's co-chairs (Brian Sogorka and Roger Kennett) or project manager (Rick Tomlinson) for additional information.

International Perspective on the Cleanup of Metals and Other Contaminants
Terry McIntyre, Environment Canada

Terry McIntyre said that phytoremediation, which has attracted interest internationally, is the most exciting area of research that he has worked on over the last 30 years. McIntyre's presentation summarized research efforts that are being performed in Canada as well as other countries outside the United States. He said that researchers around the world are working to improve their understanding of the interactions that occur between contaminants, plant exudates, microorganisms, and a variety of other abiotic and biotic processes. For example, he said, researchers in Canada are evaluating whether plant exudates can remediate inorganic and organic contaminants. They are also working diligently to elucidate the role that rhizosphere microbes play in plant-based remediation. Once more information is available, McIntyre said, researchers will have a better understanding of phytoremediation's true potential.

In Canada, McIntyre said, the majority of phytoremediation research has focused on using plants to address metals. The decision to focus on metals was made because: (1) many sites in Canada are contaminated with them; (2) regulators are becoming increasingly interested in cleaning up lead, mercury, and cadmium; and (3) available physical, chemical, and thermal remediation technologies have had limited success in cleaning up inorganics. McIntyre said that Canadian researchers are examining various plants to determine whether they can mobilize metals. For example, hemlock bark is being used to mobilize metals at a military site in British Columbia. Also, seaweeds are being evaluated to determine how well they accumulate a variety of substances (*e.g.*, arsenic, vanadium, iodine, and uranium). Researchers in Australia and New Zealand have also taken an active interest in plant-based systems that accumulate metals and they have launched efforts to understand the mechanisms that are involved.

McIntyre said that Environment Canada believes that it is important to generate a comprehensive list of plants that have remedial properties. Toward this end, two inventories—Phytorem and Phytopet—have been developed. McIntyre said that Phytorem lists about 810 plants that accumulate, tolerate, or hyperaccumulate metals. (This list was put together from the collective input of 39 countries.) The other database, Phytopet, lists about 110 grasses, 25 bacteria, and 35 fungi that are known to degrade petroleum hydrocarbons. McIntyre said that both databases are available on CD-ROM, and that they would be given to all meeting attendees at no charge. He said that some of the plants that are listed might raise regulatory concerns if they were chosen for a phytoremediation project in North America. This is because some are not native to the continent, some are poisonous, some are considered noxious weeds, some are commercial crop species, and others are on the rare or endangered species list. In addition, he said, some are not available commercially; thus, some regulators are concerned that the plants might be robbed from relatively pristine wild areas if approved for use in phytoremediation projects. McIntyre said that plant selection is not the only aspect of phytoremediation that has raised regulatory concerns. For example, he said, regulators want to know how contaminated plants will be disposed of. They are also wrestling with the following issues: (1) is it acceptable to leave contaminants in the ground if they are not bioavailable? and (2) is Environment Canada's regulatory oversight on the use and production of plant exudates adequate?

McIntyre summarized some of the other activities that are currently ongoing in Canada. Strides are being made to gain a better understanding of agronomics, silvaculture, and ecological factors that must be considered when choosing which plants to use in a phytoremediation system. McIntyre said that efforts are underway to identify the characteristics that make an ecosystem susceptible to plant invasion. Researchers in Canada are also performing work in the area of biotechnology; some believe that the remedial mechanisms of plants can be enhanced in the future.

Before closing, McIntyre reiterated his first point: phytoremediation has attracted international interest. He said demonstration projects will be initiated in China, Cuba, and the Ukraine before the end of the year. Also, representatives from Japan have expressed interest in learning more about plant-based technologies. In addition, phytoremediation conferences are being held around the world and attracting international audiences. In March 2000, Environment Canada, EPA, and the United Nations Environment Program (UNEP) met to discuss the possibility of implementing phytoremediation in developing countries. In June 2000, the North Atlantic Treaty Organization plannned to discuss phytoremediation at a meeting in Prague. In addition, a meeting was planned in Canada in June 2001. Lastly, Environment Canada, EPA, UNEP, and the United Nations Educational, Scientific, and Cultural Organization (UNESCO) hope to hold a phytoremediation workshop in Prague sometime over the next few years.

Looking Forward on Phytotechnologies
Steven Rock, EPA, National Risk Management Research Laboratory

Steven Rock expressed great interest in phytotechnologies, saying that plant-based systems have a bright future and are likely to grow in popularity. So far, he said, about 22 patents have been awarded, and research efforts have been initiated by a number of academic institutions and other organizations. Rock said that he envisions plants being used across a wide variety of applications and believes that interdisciplinary research efforts will lead to innovative uses. He described a number of scenarios in which plant-based systems could be of use. For example, they can be used to address contaminated soil and groundwater, he said, and have a promising future in the areas of waste-water treatment, erosion control, mine site reclamation, and landfill management. The latter application has already attracted significant attention; several site owners have expressed interest in installing evapotranspiration covers. At many sites, Rock said, phytotechnologies will probably be used as part of a treatment train. He described one site, which has shallow contaminated groundwater, where a plant-based system is being used in combination with other treatment systems. As part of the site's original remediation plan, Rock said, a barrier was installed and a pump-and-treat system was established. Not surprisingly, site owners found operating a pump-and-treat system to be very costly. In an effort to defray costs, a tree plantation has been installed at the site. Once fully established, the trees should serve as an adequate pump during the growing season. This will allow site managers to shut down their pump-and-treat system for three to five months of the year, which will result in tremendous cost savings.

(The costs incurred by implementing the plant-based system will be compensated during the first year for which site managers shut their pumps down.)

At some sites, Rock said, phytotechnologies can be used to address a number of environmental problems simultaneously. For example, at a Region III site, managers decided that installing a plant-based system would revegetate sterile land, get rid of wastes that are high in fertility, and prevent methane from forming. As part of this project, wastes from concentrated animal feeding operations were distributed over a sterile mining site that was covered with fly ash. Once the site was fertilized, plants were installed to clean it up. If aminal waste had remained confined, it would have become anaerobic and produced methane—a greenhouse gas.

Rock said that phytotechnologies must be designed on a site-specific basis, noting that researchers should obtain a thorough understanding of a site's contaminants, subsurface conditions, and climate before designing a plant-based system. Because phytotechnologies are so new, Rock said, researchers must incorporate a number of treatability and greenhouse studies in their predesign activities. These tests, which are costly, raise the overall price tag of phytoremedial approaches. In the future, Rock said, as a broader body of knowledge is accumulated, researchers may not have to run as many predesign tests. Instead, they might be able to choose a design by reviewing the results obtained at other sites that had similar conditions. Rock said that he is glad that developed countries are working toward expanding the knowledge base, noting that this information will benefit developing countries, which have limited research funds but a great need for phytotechnologies.

Before closing, Rock sent a special thanks to Tom Wilson, who was not able to attend the conference. He also recommended two books: *Natural Capitalism: Creating the Next Industrial Revolution,* by Paul Hawkens, Amory B. Lovins, and L. Hunter Lovins, and *The Lorax,* by Dr. Seuss.

Speaker Panel and Audience Discussion

Audience members asked questions or provided comments about the following topics:

- *Plant disposal.*One attendee asked if regulators are concerned about contaminants accumulating in plant shoots, leaves, and fruits. Rock said that the likelihood of contaminants accumulating will differ across sites, depending on the contaminants present and the plants used. For example, he said, accumulation is likely at sites that have radionuclides, but not at those that have organic contaminants. McCutcheon said that plants that accumulate metals are typically harvested and disposed of in hazardous waste landfills. It may be possible, however, to recover some of these metals. For example, McCutcheon said, the Bureau of Mines developed a method to recycle nickel and other metals from plants. McIntyre said that Environment Canada is: (1) evaluating disposal and recovery techniques, and (2) analyzing the impact that contaminated biomass has on herbivores and omnivores.

- *Gaining regulatory approval to use plants at sites that are contaminated with metals and radionuclides.* One meeting attendee asked whether U.S. regulators will allow site managers to use phytotechnologies at sites that have metal and radionuclide contamination. Rock said that demonstration projects have already been initiated at sites that fit this profile. Thus, approval has already been granted, at least to some degree. Rock said that proposals must adequately address media transfer issues if they are to be approved.

- *Stewards for the environment and phytotechnology.* A meeting participant asked the attendees to think about how they can act as stewards for the environment. Rock said that stewards come in many forms: not only regulators, consultants, academics, and activists, but also industry representatives. Many of the latter, he said, are sincerely interested in adopting better pollution prevention and cleanup practices.

SESSION II: FUNDAMENTAL PROCESSES OF PLANTS AND SOIL

Transport of Contaminants in Plant and Soil Systems

Larry Erickson, Kansas State University

Larry Erickson said that laboratory studies have been performed to determine how plants impact contaminant fate and transport. He described the laboratory setup that is used to track these processes. Planted systems are enclosed within a chamber, he said, and contaminated water is pumped into the bottom to establish a saturated zone and a vadose zone. Then, measurements are taken to determine how much water and contaminant moves into the plant, how much is converted to gas, and how much exits the chamber.

Erickson said that researchers from Kansas State University (KSU) evaluated the fate and transport of toluene and phenol in mass balance studies. Both of these contaminants virtually disappeared when exposed to plants, he said, and neither was detected in plant transpirate. Researchers used these findings to formulate the following hypothesis: toluene is drawn into the rhizosphere and degraded by aerobic microbes. Erickson said that phenol is probably degraded in a similar fashion, but that anaerobic degradation might also play a role in degrading it.

Erickson said that several research teams have performed experiments to evaluate TCE fate and transport. Some studies suggest that TCE diffuses through plant roots and is carried to aboveground plant tissues. In large bald cypress trees, he said, TCE has been detected in tree trunks. (Concentrations were highest near ground surface and decreased with trunk height.) Studies also show, Erickson said, that TCE diffuses out of tree walls. He cited TCE diffusivity values that have been measured in bald cyprus (3×10^{-6} square centimeters per second [cm^2/s]), poplars (1×10^{-6} cm^2/s to 3×10^{-6} cm^2/s), and willows (1.5×10^{-6} cm^2/s to 3×10^{-6} cm^2/s). These diffusivity values, he said, are just one order of magnitude lower than that measured for TCE in water (1×10^{-5} cm^2/s). Studies also suggest that plants release TCE to the atmosphere. Under confined conditions, concentrations in air may be fairly significant. However, when TCE and water evaporate together, there is a dramatic reduction in the concentration of TCE that is detected in the gas phase. Thus, in the field, the amount of TCE released to the atmosphere is rapidly dissipated. (More information on TCE fate and transport, said Erickson, can be found in an article that was recently released in *Environmental Progress*.)

Erickson said that KSU used a six-chamber study design to evaluate MTBE transport through alfalfa plants. (One chamber was unplanted, but the other five were planted. Some chambers were inoculated with microbes, but others were not. Some chambers were air sparged, but others were not.) From this study, Erickson said, investigators learned that MTBE behaves differently than TCE. MTBE does get taken up by plants, he said, but it does not diffuse out as readily as TCE does. Erickson said that KSU calculated diffusivity for MTBE under uniform and nonuniform boundary conditions. All of the values recorded were lower than those measured for TCE. (Diffusivity estimates for MTBE ranged from 5×10^{-8} cm^2/s to 1.11×10^{-7} cm^2/s under uniform boundary conditions and from 8.57×10^{-8} cm^2/s to 1.62×10^{-7} cm^2/s under nonuniform boundary conditions.) Erickson said that KSU's results indicate that plants transpire a significant amount of water, but a much smaller amount of MTBE. According to mass balance studies, Erickson said, only a fraction of the MTBE that is present in groundwater is taken up into alfalfa plants. Evidence suggests that some of the contaminant is biodegraded in the rhizosphere; KSU estimated biodegradation rates (under aerobic conditions) to be about 2 to 5 milligrams (mg) per kilogram (kg) of soil per day.

Erickson closed by providing references—he advised attendees to peruse *Hazardous Substance Research*, which is available online at http://www.engg.ksu.edu/HSRC—and expressing great enthusiasm for phytoremediation's future. He said that several universities are interested in this area of research, and noted that many sites have already started using phytoremediation.

Enzymatic Processes Used by Plants to Degrade Organic Compounds
Nelson Lee Wolfe, EPA, National Exposure Research Laboratory

Nelson Lee Wolfe said that efforts are underway to study the role that plant enzymes play in degrading recalcitrant contaminants. These enzymes do not necessarily mineralize contaminants, he said, but they do break them down into forms that are more susceptible to microbial degradation and hydrolysis. Wolfe said that many researchers are evaluating plant redox and hydrolysis reactions to determine whether these play a role in plant-mediated contaminant breakdown. Before summarizing some of the studies that have been performed, Wolfe described laboratory techniques that are used to isolate plant enzymes. First, he said, researchers make sure that plant samples are sterile. That way, they can be confident that the enzymes identified are not from microorganisms or fungi that have attached themselves to the plants. Wolfe said that surface sterilization, which involves washing and plating plants, is most commonly used, but that sterilization by gamma radiation is also used on occasion. Once researchers are certain that plants are sterile, he said, plants are ground up, an extraction solution is added, and enzymes are separated using chromatography and sequencing techniques. As an alternative to the process just described, Wolfe said, enzymes can be isolated from seedlings.

Wolfe said that he and others have studied plant nitroreductases, noting that researchers believe that these enzymes play an important role in the degradation of munitions and pesticides. Results collected to date support this idea. In one study, Wolfe said, researchers found that whole plants are able to degrade TNT and RDX by reducing nitro groups to amino groups. In another study, plants were placed in TNT-contaminated water and constituent concentrations were measured over time. The contaminant degraded rapidly, with a half-life of only 70 minutes. Wolfe said that the processes involved in TNT degradation are not completely known, but that they are complicated, involving the transfer of 18 electrons. Wolfe said that different plant organs appear to have more nitoreductase activity than others. Studies suggest that activity is highest in roots and lowest in stems. Efforts have been made to identify specific nitoreductase enzymes in several plants, such as spinach and *Elodea.* In the latter, Wolfe said, five enzymes from the nitroreductase class have already been detected; all of them have different molecular weights.

Wolfe said that several experiments have been performed to evaluate dehalogenase activities in plants. For example, he said, Dr. Valentine Nzengung found that spirogyra breaks down hexachloroethane (HCA) rapidly, forming some pentachloroethane, trichloroacetic acid, TCE, and PCE in the process. In another study, Wolfe said, TCE was shown to degrade quickly when exposed to spirogyra. The degradation rate, Wolfe said, was influenced by the condition of the spirogyra. When exposed to live spirogyra, TCE had a half-life of about 22 hours. Rates were much higher when the TCE was exposed to dead spirogyra. Wolfe said that studies have been performed to determine whether plant leaves have high dehalogenase activity. In one study, Dr. Peter Jeffries collected leaves from 29 different types of plants, placed them in separate containers, and spiked the surrounding air with methylene bromide. In all cases, the contaminant decreased, with disappearance rates proportional to leaf surface area. Wolfe said that Jeffries also experimented with chlorinated compounds, finding that HCA disappears in the presence of holly trees and that some PCE and chloroform form in the process. Wolfe said that studies have been performed to determine how fast TCE degrades in leaves. For this effort, he said, cottonwood leaves from Carswell AFB were ground up and spiked with TCE. Significant degradation was observed; the average half-life recorded was 14.1 hours.

Wolfe said that research has also been performed on plant phosphatases to determine whether they can degrade organophosphate pesticides. Researchers in Japan isolated an alkaline phosphatase from duckweed, he said, but it did not exhibit degradation activity towards organophosphate pesticides. Wolfe's group has isolated an acid phosphatase, that has been shown to break down three organophosphate pesticides that differ in structure.

Wolfe said that efforts have recently been initiated to evaluate plant peroxidases, enzymes that are considered fairly stable and therefore capable of persisting on the ground long enough to percolate into soil. To date, he said, several peroxidases have been isolated from grasses. In addition, Wolfe said, new efforts are just getting underway to evaluate laccases and nitrilases for phytoremediation.

Biosystem Treatment of Recalcitrant Soil Contaminants
John Fletcher, University of Oklahoma

John Fletcher said that the University of Oklahoma is optimistic that plant-based systems can be used to treat sites that are contaminated with PCBs and PAHs. He said that these recalcitrant contaminants are highly immobile. They have low water solubilities and high log K_{ow}. Within the last 150 years, Fletcher said, PAH contaminants have been disposed of at about 18,000 industrial installations. He could not estimate how many PCB-contaminated sites exist, but did say that some may have been contaminated as far back as 70 years ago. Fletcher said that he has turned to nature in an effort to find solutions to environmental problems, and that he is optimistic that contaminated sites can be remediated using biosystem treatments that incorporate evapotranspiration, rhizosphere degradation, and natural attenuation.

Fletcher said that plants produce polyaromatics (*e.g.*, tannins and flavanoids), that can break these compounds down. (Researchers know this because the amount of natural polyaromatics detected in soil is much less than the amount that has been produced by plants over extended time periods.) Fletcher said that these natural events serve as the underpinning for a hypothesis that he formulated about 10 years ago. The hypothesis is: roots of some plant species enhance the degradation of recalcitrant, organic soil contaminants (e.g., PCBs and PAHs) by releasing co-metabolites (e.g., flavanoids) and facilitating soil aeration as fine roots turn over. Fletcher said that research has been conducted to test this hypothesis and to gain a better understanding of the mechanistic basis for rhizosphere degradation. The results obtained support the hypothesis. For example, in studies performed on mulberry plants, Fletcher said, researchers learned that natural polyaromatics reside in fine roots (less than 5 millimeters in diameter). When roots die, these polyaromatics are released to the surrounding soil, where they promote the growth of rhizosphere microbes. Fletcher said that he suspects that these microbes, which proliferate in the presence of the natural polyaromatics, can also degrade compounds with similar structures, such as recalcitrant PCBs and PAHs. Assuming that this is true, he said, contaminants that are located near dying root hairs would be degraded. As each year passes, Fletcher continued, roots expand their network, contact more contaminants, facilitate oxygen diffusion, and sustain an active community of PAH-degrading microbes. Fletcher asked participants to take note of four points: (1) fine roots grow to contaminants over time, (2) roots turn over each year, (3) plants must be able to produce polyaromatics that are structurally similar to anthropogenic contaminants, and (4) plants must grow for several years before reductions in contaminant concentrations will be statistically significant. Fletcher stressed the latter point, noting that plant-based systems will be unfairly set up for failure if their efficacy is measured based on short-term studies that simply consider end results (*i.e.*, the disappearance of contaminants). During the first five years of a phytoremediation study, Fletcher said, it is more meaningful to study the mechanisms that are responsible for degradation, such as root growth, root depth, and the presence and activity of PAH- and PCB-degrading microbes. He said that the University of Oklahoma is working toward identifying useful tools for assessing these parameters.

With the help of Union Carbide, Fletcher said, the University of Oklahoma studied the impact that plants had at a former sludge lagoon. This site, Fletcher said, was invaded by plants in 1983, one year after the lagoon was drained. Since that time, he continued, mulberry trees and 50 other plant species have become firmly established at the site. Fletcher said that researchers collected about 60 cores from the lagoon, over three different depths, to determine whether the 17-year-old plant-based system had caused a reduction in PAH concentrations. It had. While total PAHs in the parent sludge were present at about 17,000 parts per million (ppm), concentrations were only 1,121 ppm in the site's first foot of soil, 2,654 ppm in the second foot, and 9,190 ppm at the bottom of the root zone. Fletcher said that the same pattern was observed with individual compounds. For example, the concentrations of benzo(a)pyrene (a water soluble contaminant) were 135 ppm in the parent sludge, 21 ppm in the first foot of soil, 34 ppm in the second foot, and 70 ppm at the bottom of the root zone. Fletcher said that researchers collected a number of soil samples from the site and isolated microorganisms. About 250 different isolates that have the ability to degrade PAHs were identified. In-depth studies were conducted on three of these microbes; all three were shown to grow on polyaromatics (*e.g.,* morusin and catechin) that are present in mulberry and oak systems.

Fletcher addressed some of the concerns that have been voiced about plant-based systems. First, he said, some people claim that it takes too long to determine whether plants are effectively remediating a site. Fletcher said that this view is based upon using contaminant concentrations as the only measure of success. If the mechanisms of degradation are monitored instead, Fletcher said, it will be possible to show, relatively quickly, whether a plant-based system is working. Another view is that phytoremediation does not work quickly enough, saying that it takes too long to achieve end results. Fletcher said that he did not think the time periods required were unreasonable, given that some sites have already been contaminated for many years. Lastly, Fletcher noted, some people say that it is better to use impermeable caps instead of plant-based systems, because using the former has already been demonstrated as a proven solution. Fletcher pointed out that the decision to use impermeable caps was made in the 1970s, long before information had been gathered on natural attenuation or phytoremediation. Also, he said encapsulating waste retains it for future generations.

In closing, Fletcher said that he is a proponent of biosystem treatment, a holistic approach that involves evapotranspiration, rhizosphere degradation, and natural attenuation. He advised establishing systems that perform long-term sustained cleanups which in his view, natural systems can accomplish.

Speaker Panel and Audience Discussion

Audience members asked questions or provided comments about the following topics:

- *Biodiversity.* McIntyre asked Fletcher to comment on biodiversity at the Union Carbide site. Fletcher said that there was much variety at this site, and said that more specific information will be presented in three upcoming papers. (One of the papers will be called "Ecological Recovery with Phytoremediation Overtones.") Fletcher said that it is not uncommon for contaminated sites to exhibit as much diversity as uncontaminated sites do. The types of plants that are represented at contaminated and uncontaminated sites, however, are not necessarily the same.

- *Biological* versus *physical processes*. McMillan asked Fletcher how he could be sure that biological processes were responsible for contaminant reductions at the Union Carbide site. Wasn't it possible, he asked, that the contaminants simply migrated downward over time? Fletcher said that he is confident that biological processes were responsible. He noted that sludge is still present below the site's root zone. If contaminants had simply migrated downward, he said, a contaminated hot zone would have been detected at the border between the root zone and the sludge. No such zone was detected. Also, he said, many of the contaminants at the site are immobile. Thus, it is unlikely that they would have migrated downward at any significant rate.

- *Perspectives on the length of time it takes for plant-based systems to achieve end results*. An attendee noted that plant-based systems may require as long as 20 years to reduce chemical concentrations to acceptable levels. She asked whether regulators are willing to wait that long for results. McIntyre said that regulators from Environment Canada would probably not regard this as an unreasonable time frame. Rock said that he did not think it would be a huge stumbling block among EPA regulators either, noting that many conventional treatments (*e.g.*, pump-and-treat) require at least that much time to achieve their goals. Harry Compton agreed, noting that regulators are often flexible with the amount of time it takes to clean up sites, as along as the site poses no immediate threat to human health or the environment. Judy Canova said that the same holds true at the state level, at least in South Carolina. EPA representatives, said that regulators might not be willing to wait for 20 years unless they could have some assurances along the way that the system was working. Responding to this last statement, Fletcher said that he hopes to find ways to give these assurances. He reiterated a point he made earlier: it is time to start monitoring the processes that cause degradation rather than just focusing on contaminant concentrations. If researchers can prove that the appropriate degradation mechanisms are operating at a site, Fletcher said, that should serve as sufficient proof that plant-based systems are working. He said that much research remains to be done to identify ways to monitor the mechanisms, but said that this research really must be done. Fletcher said that it is time that phytoremediation gets the funding and the prominence it deserves. Meeting attendees responded in a chorus of agreement.

- *Life cycle studies*. One meeting attendee said that he was glad to hear Fletcher and Wolfe address the role of plant life cycles.

SESSION IIIA: BROWNFIELDS APPLICATIONS AND BENEFICIAL USE OF LAND

Goals for Brownfields Pilots

John Podgurski, EPA, Region 1

John Podgurski opened his presentation by providing general information about brownfields sites, noting that some estimates suggest that there are 500,000 located across the country. He defined these sites as vacant or underutilized industrial/commercial properties where redevelopment is complicated by real or perceived contamination. Brownfields are located, he said, in small communities as well as large urban centers. In the latter areas, most of the sites are relatively small and have structures on top of them. Podgurski presented data collected from Lawrence, Massachusetts, to demonstrate his point. In this city, 60% of brownfields sites are less than 1.5 acres in size, 60% have one building, and 10% have two or more buildings.

Podgurski described the steps that developers take and the issues they encounter when deciding whether to redevelop brownfields sites. They must assess the local property value of the site, he said, along with existing infrastructure (*e.g.*, utilities and roadways), security, and safety. Also, developers must address several technical issues. For example, if the extent of site contamination is not known, developers must invest in assessment activities. Also, if a developer finds out that a remediation effort will be required, he or she will consider the following when choosing a cleanup technology: cost, time frame, efficacy, regulatory acceptance, space constraints, and the potential that community concerns will delay remedial efforts.

Podgurski said that phytoremediation has the potential to be useful at many, but not all, urban brownfields sites. Poor candidates include sites located on very small parcels of land, sites whose surfaces are largely covered by structures or pavement, and sites that have difficult growing conditions. (Podgurski said that growing conditions may be less than ideal at brownfields sites, especially if they are shaded by tall buildings or if their soils are littered with debris.) In addition, Podgurski said, phytoremediation is not appropriate for sites that require quick clean up. At privately controlled sites, he said, it is likely that developers have already made reuse plans. If so, they typically require cleanup quicker than phytoremediation can offer. Other issues that must be addressed when determining whether phytotechnologies are appropriate include security, vandalism, equipment access, and the public's willingness to have an innovative remediation technology used for an area that many people have access to.

Despite the obstacles listed above, Podgurski said, he does believe that there is great potential for phytoremediation at a large number of urban brownfields sites, particularly those that are publicly controlled. The time frame for remediation may not be an important issue at these sites. If this is the case, city managers might use phytoremediation as a cleanup strategy, because it is a more cost-effective way to remediate and stabilize sites in preparation for future redevelopment. In addition, he said, city managers will be attracted to phytoremediation because it could reduce contaminant exposures to the public and improve an area's aesthetics,. Podgurski said that city managers might find the startup costs of phytoremediation to be high, but said that equipment and other startup costs could be spread out if managers decided to use phytoremediation at several sites. Podgurski said that Operation and Maintenance (O&M) costs would probably not be very significant particularly if they can be maintained by the local government itself.

Hartford Brownfields Site: Site Description and Summary of Phytoremediation Project
Jeanne Webb, City of Hartford

Jeannie Webb provided a description of the Chestnut and Edwards Street site, a brownfields site in Hartford, Connecticut, and explained how phytoremediation is being used to remediate it. The site is about 1.7 acres in size and is located in a transitional neighborhood. A soup kitchen is located next door, Webb said, and many people use the site as a pathway to and from the kitchen. Webb said that there are also shelters, residential buildings, and a furniture store in close proximity.

A few years ago, Webb said, neighborhood representatives asked whether the site could be used as a recreational area and community garden. She said that this idea stimulated significant interest, and a team of organizations banded together to determine whether this wish could become reality. Some of the major players on the team included the City of Hartford, Trinity College, a local middle school, House of Bread, neighborhood revitalization committees, and the University of Connecticut Master Gardeners Program.

Webb said that a Phase II site investigation was performed at the site to determine whether it could be used as a community garden. The results indicated that lead was scattered throughout the site's surface soil at concentrations as high as 2,800 ppm in some areas. Thus, it was clear that remedial action had to be taken, and several different approaches were assessed. For example, soil removal was considered, but city managers decided that they did not have enough funds for this. Also, Webb said, some consideration was given to covering the soil with mulch and creating raised-bed gardens. In the end, the decision was made to fence off the most contaminated portion of the site and establish a phytoremediation project on it. Field activities for this effort were initiated in the summer of 1999. Trinity College, which proposed using phytoremediation in the first place, worked with Edenspace Systems Corporation to establish crops of mustard, sudan grass, and sunflowers. Webb said that the crop was planted twice. During the first planting, it was difficult for seeds to penetrate the ground, because the site was littered with so many bricks and other kinds of litter. Before the second planting effort was initiated, the site was rototilled, and the plants grew much better. Webb said that the city recently identified additional funds that can be used for the site. As a result, plans were made to install a plant-based system at another portion of the site during summer 2000.

Webb said that communication has played a key role in propelling this phytoremediation project, noting that substantial efforts have been made to educate community members and municipal workers. The latter, she said, will perform O&M at the site. Webb said that all of the interested parties sat down together to discuss options for the site. As a result, people felt that their opinions and concerns had been heard. In the end, the community became very excited about the prospect of phytoremediation.

Hartford Brownfields Site: Public Health Perspective
Jennifer Kertanis, Connecticut Department of Public Health

Jennifer Kertanis, an epidemiologist and public health official, said that she was also involved with the Chestnut and Edwards Street site. (This site was described in the previous presentation.) Kertanis said that her department performed a thorough exposure pathway assessment for the site. This involved evaluating the source and type of contamination, the media impacted, potential exposure routes (*i.e.,* ingestion, dermal contact, or inhalation), and property usage patterns. Several public health concerns were identified during the assessment process. For example, Kertanis said, there was concern that people could be contacting the site's contaminated soil directly or inhaling airborne soil particles, because there was unrestricted access to the site, passive recreational usage, and limited ground cover over contaminated soils. Thus, she said, before voicing approval for a remedial approach, she had to be assured that the technology chosen would address existing public health hazards without creating brand new ones.

Kertanis said that community members and public health officials both thought it was important to evaluate phytoremediation to make sure it would not create new exposure routes. Some concerns were identified, she said, but solutions were found to address each of them. For example, there was some concern that rototilling could create airborne dust, but soils were wetted beforehand to reduce the chance of this happening. Also, she said, concern was expressed about soils becoming airborne in the winter, when plants die and soils are bare. She said that these concerns can be addressed by placing ground mats on top of the soils or adding mulch to the site. Also, Kertanis said, public health officials were concerned that professors and students, who were involved with plant installation, could be exposed to contaminants. Thus, these populations were given instructions on how to reduce the potential for contact. Kertanis said that community members expressed concern about people having access to the project's crops. By listening to the community, public health officials learned that members of certain local ethnic groups eat a lot of mustard, one of the crops used in the phytoremedial system. To prevent people from eating the crops, Kertanis said, a fence was installed and information was distributed advising community members to stay away from the plants.

Kertanis stressed the importance of including local public health departments in decision-making processes. She said that public health officials can do the following to assist phytoremediation projects: (1) assess and address community concerns, (2) sort out real *versus* perceived health risks, (3) highlight issues that are not covered by EPA or local departments of environmental protection, (4) provide input and support, and (5) communicate effectively with the public. Kertanis said that she believes that the most successful projects are those in which all involved parties—site owners, community members, environmental agencies, public health organizations, and a variety of other stakeholders—sit down together to discuss issues and solutions. When collaborative efforts are fostered, it becomes clear that economic development, site reuse, public health issues, environmental issues, and innovative technologies do not have to be competing interests.

Integrating Remediation into Landscape Design
Niall Kirkwood, Harvard University, Graduate School of Design

Niall Kirkwood said that landscape architects are interested in applying phytoremediation and hope that additional research will be performed to support the use of such technologies. He said that landscape architects and phytoremediation designers have much in common: both have extensive knowledge about plants, and both are interested in using plants to improve quality of life. Furthermore, they use similar processes to address sites. He described the steps that landscape designers go through: (1) site analysis, (2) conceptual design, (3) schematic design, (4) documentation and bidding, (5) implementation, and (6) maintenance and post-occupancy evaluation. Kirkwood said that there is potential for great synergy between the two disciplines, and he is optimistic that objectives will merge in the future. If so, plant-based systems could provide multiple benefits simultaneously. For example, he said, systems could be designed so that they simultaneously provide remedial benefits, aesthetics and visual screening, microclimate control, spatial enclosure and form, and a "green" buffer that attracts wildlife.

Kirkwood showed slides of a variety of plant-based projects. At one site along the Colorado River, he said, about 30,000 cottonwoods have been planted in an effort to stabilize soil. Outside of London, he said, a landscape design project has been initiated to implement infrastructure. He noted that fuel oil is present in the groundwater under this site, and wondered whether the design could have been set up to address this and implement infrastructure at the same time. At another site, located in Germany, landscape design was used to convert a former steel smelting site into a public park with beautiful fields and gardens. Kirkwood said that trees are being used to take up groundwater. Thus, the site is also serving a remedial purpose, although it is not advertised as a phytoremediation project.

Kirkwood said that he envisions several areas where phytoremediation could have potential: (1) regional parks, city parks, and community recreational open spaces; (2) commercial/industrial parks and biotechnology centers; (3) assisted and private housing areas; (4) locations that require "green" infrastructure, such as roads and rail corridors; (5) landfills that are being converted into golf courses; and (6) areas that are being developed as urban arboretums or environmental education centers. He expressed much enthusiasm for the latter, noting that consideration is currently being given to creating an arboretum/botanical garden at a former zinc smelting site in Mexico.

Kirkwood spent the remainder of his presentation talking about brownfields sites and how phytoremediation could be used to address them. Within the brownfields community, he said, four issues must be addressed: (1) sustainable economics, (2) social issues, (3) environmental educational opportunities, and (4) innovations in assessment and remediation technologies. He said that phytoremediation could be beneficial at many brownfields sites, but said that some misconceptions must be corrected before it is seriously considered as a viable approach. For example, he said, it must be made clear that phytoremediation has applications at the urban scale, not only at the agricultural scale. To determine whether phytoremediation is appropriate for a specific brownfields site, he said, the following issues must be assessed: urban context, existing site conditions, other engineering activities, plant growth concerns, adjacent community concerns, proposed reuse program, implementation controls, disposal methods, and time lines. Kirkwood said that he believes that phytoremediation will be able to address a wide variety of issues that arise at brownfields sites, including environmental protection, public health, economic development, and municipal planning for development. If phytoremediation is adopted as a popular approach at brownfields sites, he said, it will allow researchers to explore how the technology works across a variety of scales and contaminant profiles. It will also allow researchers to test a variety of plant species all over the country.

In closing, Kirkwood encouraged attendees to think of ways in which phytoremediation could offer multiple benefits at brownfields sites. For example, he said, it could be used to create sustainable open space or be combined with biomass fuel projects or "Brightsfield" solar projects. Also, he said, phytoremediation could be used to improve aesthetics and public perception, promote smart growth, and restore habitats.

Speaker Panel and Audience Discussion

Audience members asked questions or provided comments about the following topics:

- *Accumulation of contaminants and plant disposal issues*. A question was asked whether lead was detected in the Chestnut and Edwards Street site mustard plants, and at what concentrations. Webb and Kertanis did not know. Another meeting attendee asked how the mustard plants were disposed of. Webb said that they were harvested, burned at the Trinity College biology laboratory, and then disposed of as contaminated materials. One meeting attendee asked Kirkwood a question about the landscape design project that was performed in Germany: are tree leaves harvested and disposed of off site? Kirkwood said that they are raked up during normal maintenance activities and burned in the open air.

- *Brownfields site near Boston, Massachusetts*. It was suggested by an attendee, that the Boston Public Health Commission might initiate a phytoremediation project at a site near Boston.

- *Treatment trains*. Erickson said that some researchers use phytoremediation to reduce lead concentrations, and then use stabilization techniques to convert the remainder to lead pyromorphite, a benign compound. He asked whether a similar approach will be used at the Chestnut and Edwards Street site. Kertanis said this will probably not be necessary. She is optimistic that phytoremedial efforts will reduce lead concentrations below 500 ppm, the Connecticut residential cleanup standard. If this is achieved, she said, no more remedial activities will be required, and the site will be considered safe for community gardening.

- *Weighing public health risks*. One meeting attendee asked Kertanis to explain how assessors determine when the public health hazards posed by phytoremediation are so significant that a project cannot be allowed to proceed. Kertanis said that the decision is site-specific. From a public health perspective, she said, it would have been easier to excavate and remove soils from the Chestnut and Edwards Street site, because doing so would have eliminated the potential for any exposure. However, she said, at this site, the community was educated about phytoremediation and very excited about the demonstration. Thus, the decision was made to use phytoremediation, and to identify solutions to the potential risks that the technology could pose.

SESSION IIIB: RADIONUCLIDES

Summary of DOE Projects and Recommendations Offered at a Recent DOE Workshop
Scott McMullin, DOE

Scott McMullin said that several DOE sites are contaminated with heavy metals and radionuclides. In the past, DOE officials thought that excavation and removal would be used to address the vast majority of this contamination. More recently, however, it has become clear that *in situ* technologies will play a large role in the remediation of these inorganic wastes; in fact, one DOE official has predicted that as much as three-quarters of the wastes will be addressed *in situ*. Thus, DOE has started evaluating stabilization, containment, and a variety of biologically driven technologies, such as phytoremediation and natural attenuation. McMullin said that DOE's science program has already issued 17 grants for projects that involve phytoremediation or biological processes. For example, he said, plant-based systems are being used as cleanup technologies for tritium-contaminated groundwater at Savannah River and Argonne National Laboratory–East. In addition, at a site in Poland, phytoremediation is being used to extract heavy metals from surficial soils.

In November 1999, McMullin said, DOE hosted a workshop to discuss what is currently known about using plant-based systems to address inorganics. About 75 people attended; representatives from consulting companies, federal agencies, state agencies, and a number of international groups were present. Four breakout groups formed, each of which discussed a specific phytoremedial application. The following table lists the groups, along with the key issues and suggestions that each identified during the meeting.

Focus Group	Key Issues and Recommendations
Using plants to address groundwater	• More information is needed on rhizosphere activities. • More demonstration sites are needed. • A plant database is needed.
Phytoextraction	• More demonstration sites are needed. • Cost data need to be generated and a life-cycle accounting system should be developed. • Basic research on plant physiology should be conducted. • Ecological risks must be addressed.
Phytostabilization	• Efforts should be made to improve the understanding of: – Long-term bioavailability. – Rhizosphere biochemistry. – Toxicity relative to the food chain. – Predictive models. – The physiological processes involved with sequestration.
Using plants as a monitoring tool	• Field tests should be conducted. • Plant characterization tools should be developed. • Monitoring elements should be defined. • A monitoring framework should be defined.

McMullin said that DOE is evaluating the recommendations that each breakout group offered. In 2001, another workshop will be held to match up some of these recommendations with programmatic directives. McMullin was optimistic that phytoremediation will continue to grow under DOE.

Capturing a "Mixed" Contaminant Plume: Tritium Phytoevaporation at Argonne National Laboratory–East
M. Cristina Negri, Argonne National Laboratory

Cristina Negri said that a phytoremediation project has been initiated at the 317/319 area at Argonne National Laboratory–East (ANL-E). This area received wastes between 1940 and 1960, Negri said, noting that solvents were poured down a french drain and a variety of wastes were disposed of in a landfill. As a result of these practices, soils are contaminated with volatile organic compounds (VOCs) and groundwater is contaminated with VOCs and tritium. (Tritium is a low-energy beta emitter that has a half-life of 12.6 years; decays to helium-3; shares hydrogen's chemical and physical properties; can pose human health hazards when absorbed, ingested, or inhaled; and has an average biological half-life of 7.5 to 9.5 days within the human body.) Negri said that the site's glacial subsurface is very complex and heterogenous, consisting of boulders, gravel, sand lenses, clay lenses, and silts. Water-bearing intervals are interconnected sand and gravel zones.

Negri said that groundwater at the site is about 20 to 30 feet deep and is migrating toward property boundary lines. Extraction wells have been installed to capture some of the plume; the water collected is forwarded to Argonne's treatment plant before being released. Although the extraction wells do capture a portion of the plume, Negri said, site managers agreed that more had to be done to address the site. They decided not to use DOE's "baseline" technology, which would have involved installing an asphalt cap and adding additional extraction wells, because the site's complicated subsurface makes it too difficult to predict where to drill wells so that they have a significant zone of influence. Instead, site managers decided to install plants, because they have the ability to grow and extend roots towards water. Negri said that using phytoremediation made sense, since the following had already been shown or hypothesized: (1) tritium can be directly incorporated into water and biological tissues; (2) plants transpire tritiated water vapor; (3) tritium can accumulate in plant tissues, but the contaminant mean residence time is only about 4 to 37 days; and (4) contaminated groundwater can be controlled using engineered plant-based systems.

To gain regulatory approval for the phytoremediation project, Negri said, site managers had to prove that the plants would not release hazardous quantities of airborne tritium. They did so using EPA's CAP-88PC exposure equations to calculate tritium emissions. When putting parameters into the equation, she said, site managers assumed worst-case scenarios. That is, they identified the highest tritium concentrations that had ever been detected in the groundwater, assumed that plants would be exposed to that level at all times, and assumed that all of the tritium would be transpired. Emission levels were then calculated for an entire mature plantation, based on the assumption that transpiration rates would range from 2 to 50 gallons per day per tree, depending on the season. The results, said Negri, indicated that emission rates would be several orders of magnitude lower than what is allowed under National Emission Standards For Hazardous Air Pollutants.

In 1999, Negri said, a phytoremediation project was initiated at ANL-E. It has the following components: (1) a herbaceous cover that is designed to minimize water infiltration and soil erosion; (2) deep-planted unlined TreeMediation® hybrid willows, which have been installed to address VOC source areas; and (3) deep-planted TreeWell® hybrid poplars, which are expected to achieve hydraulic groundwater control. The latter were planted in lined caissons that extended to depths of 30 feet and were backfilled with materials that promote root development. Thus, the TreeWell® roots are cut off from all shallow sources of water and have been forced to grow downward in search of groundwater. Negri said that plume velocity and winter dormancy were considered when the number of trees to include in the phytoremediation design was determined. She said that the phytoremediation system is currently being monitored by two entities:

Argonne National Laboratory and the EPA Superfund Innovative Technologies Evaluation (SITE) program. Site managers hope that results will show that: (1) hydraulic control can be obtained within four years, (2) tritium can be transpired without causing significant hazardous emissions, and (3) existing extraction wells can be shut off.

Negri closed her presentation by citing the potential benefits that could be realized using phytoremediation instead of DOE's "baseline" technology for this site. First, she said, installation costs associated with phytoremediation were about 33% less and O&M costs are projected to provide a cost savings of more than 30%. Also, she said, using *in situ* technologies: (1) minimizes the amount of contact that remediation workers have with contaminants and (2) eliminates the need to transport hazardous materials off site. In addition, Negri said, phytoremediation has the potential to accelerate the cleanup time of VOCs, restore the site's rhizosphere, prepare the site for native prairie species, and provide protection against unknown source areas that might be located within the site.

Phytoremediation Application for Radionuclide Removal at Argonne National Laboratory–West
Scott Lee, Argonne National Laboratory

Scott Lee said that a phytoremediation project has been initiated at Argonne National Laboratory–West (ANL-W). The laboratory, located in Idaho, was listed on the NPL in 1991. Several contaminated sites have been identified within the property's boundaries, many of which are contaminated with heavy metals and radionuclides. Cesium-137 (Cs-137), a radionuclide with a half-life of 30 years, is present at concentrations that could pose potential human health hazards. Lee described efforts that are being made to address Cs-137 contamination at ANL-W's industrial waste pond, interceptor canal, and interceptor canal mound. Cs-137 is detected at elevated levels in all three of these areas, but the site's groundwater, which is about 650 feet deep, has not been contaminated. Lee said that ANL-W evaluated a number of technologies (*e.g.*, excavation and capping) before deciding to use phytoremediation. Before gaining approval for this technology, he said, ANL-W representatives had to address the following concerns:

- *Ecological risks*. There is a wide variety of wildlife at ANL-W. For example, burrowing animals, owls, antelope, and rabbits frequent the site and use the industrial waste pond as a watering hole. Community members were concerned that Cs-137 could be introduced to the food chain if plants were used to extract the constituent from the ground. Lee said that this concern did not pose an obstacle to the phytoremediation project, because Cs-137 was not identified as an major ecological risk at the site. (Chromium^{+3}, mercury, selenium, silver, and zinc have been identified as ecological risk drivers.)

- *Public concerns*. Lee said that radionuclides generate great fear among the public. ANL-W representatives addressed public health concerns.

- *Leaching of contaminants*. Lee said that irrigation is included in ANL-W's phytoremediation design; the water frees up the Cs-137 so that it can be taken up by plant roots. Lee said that some people were concerned that Cs-137 would leach downward. To assure community members that this would not occur, soil moisture reflectometers were installed. These are stacked on top of each other, he said; the one on top is connected to the irrigation system and signals it to turn off when soil moisture is high. The one on the bottom is used to determine whether moisture is migrating downward.

- *Noxious weeds*. ANL-W proposed using Russian thistle, but the state would not allow it because that plant was considered a noxious weed. ANL-W then proposed using kochia weed. This choice was approved after ANL-W agreed to control growth by harvesting plants before they flower, establish a clear zone around the site, and apply seeds with a paper mulch so that the seeds would not be dispersed by the wind.

Lee said that the phytoremediation project was initiated in 1999. ANL-W did the following before planting: (1) installed irrigation lines, pressure regulators, risers, heads and moisture probes; (2) added organic matter to the site; (3) prepared the soil using a plow, ripper, and rototiller; and (4) collected real-time gamma emissions using a global positioning radiometric scanner (GPRS). Then, kochia weed was hydroseeded—seeds were distributed about 4 inches apart from each other—and allowed to grow. The weed was harvested after about 110 days, Lee said, using potato harvesting farming equipment. He said that this equipment was used because it harvests roots as well as aboveground portions of plants. After the plants were harvested, a separator was used to remove attached soils, and the plants were baled and taken to an incinerator. Once the site was cleared, gamma emissions were measured again using the GPRS. Lee said that problems were encountered using the detectors. Thus, it was difficult to determine whether Cs-137 levels had decreased over the course of the first growing season. Over the next several years, Lee said, several additional plants will be seeded and harvested at the site. He believes that it will take about five growing seasons to meet cleanup goals.

Lee closed his presentation by listing some of the upcoming activities that are planned for this site. First, he said, the efficacy of three amaranth species will be compared against that of the kochia weed to determine which plants are best to use for Cs-137 cleanup. Second, he said, ANL-W will perform studies to determine whether efficacy rates differ between stressed and unstressed plants. Lastly, he said, ISSOX, a directional sodium germanium detector, will be used prior to planting, harvesting, raking, and bailing.

Speaker Panel and Audience Discussion

Audience members asked questions or provided comments about the following topics:

- *Bioaccumulation of radionuclides*. One attendee asked whether Cs-137 bioaccumulates in kochia weeds. Lee said that the bioaccumulation ratio is low; for example, at soil concentrations of 30 picocuries per gram (pCi/g), only about 1 pCi/g is accumulated in plants. The attendee said that higher bioaccumulation rates have been reported by researchers who have experimented with other plants.

- *Cs-137 accumulation in roots* versus *shoots*. One attendee asked whether roots and shoots accumulate different amounts of Cs-137. Lee said that they do. As shown in a greenhouse study, he said, Cs-137 accumulation rates in kochia weed roots and shoots are about 10 to 1.

- *Ways to optimize treatment*. One attendee asked whether soil amendments could be applied to increase Cs-137 uptake by plants. Negri said that a number of treatability studies were performed on ANL-W's soils to determine whether removal rates could be improved by adding ammonium salts, potassium salts, EDTA, or citric acid. No significant improvements were detected. McIntyre asked whether any efforts are being made to enhance the remedial capabilities of plants: have efforts been made to identify the kochia weed's mode of action and to incorporate it into plants that produce more biomass? McIntyre also asked whether other plants have been studied to evaluate their potential to uptake Cs-137. Lee said that *Amaranthus retroflexus*, *A. bicolor*, and *A. paniculatum* will be evaluated for their potential to uptake Cs-137. Negri said that it might be possible to identify plants that uptake Cs-137 more vigorously than kochia weed, but said that she thinks it is more useful to evaluate soil amendments at the ANL-W site.

- *Costs*. One attendee asked Lee how much farming equipment cost. Lee said that $10,000 of equipment was purchased for the ANL-W site. Another attendee said that O&M procedures at ANL-W are intensive. He asked whether site managers had considered designing a system that required less labor and irrigation. Lee said that lower-maintenance approaches will be considered for ANL-W after cleanup goals are met.

- *Using soil moisture reflectometers to determine whether leaching is occurring*. Glendon Gee noted that soil moisture reflectometers measure water content, but not downward water flux. He said that information on subsurface hydraulic properties must be combined with reflectometer data to make meaningful conclusions about leaching potentials.

SESSION IVA: THE FATE OF CHLORINATED SOLVENTS THAT DISAPPEAR FROM PLANTED SYSTEMS

Phytoremediation of Solvents

Milton Gordon, University of Washington

Milton Gordon described studies that the University of Washington has performed to elucidate the role that poplars play in remediating chlorinated solvents. He said that poplars were chosen for study because the University had already collected about 20 years of data on poplar breeding and metabolism. Gordon launched his discussion by describing laboratory studies that have been performed to determine whether poplars can remediate TCE. In one study, Gordon said, poplar tumor cells were shown to break down TCE. Trichloroethanol, trichloroacetic acid, and dichloroacetic acid, all oxidative metabolites of TCE, were detected, as well as carbon dioxide. Gordon said that mass balance studies have also been conducted on a number of chlorinated solvents to determine how poplar cuttings impact these contaminants. Gordon described the experimental apparatus that the University of Washington used to perform mass balance studies, noting that efforts were made to replicate outdoor conditions. For example, a steady flow of air was passed through the test chamber and intense light was shined on the plants. Even using the strongest light available, however, researchers were only able to provide about one-fifth of the intensity of normal sunlight. In the laboratory studies, Gordon said, a large proportion of the contaminants that were introduced simply transpired through the plant. For example, he said, about 70% of the TCE was detected as a gas in the upper portions of the study chamber. Gordon said that good mass recovery was observed when the polar cuttings were grown hydroponically, but that rates were only about 60% to 70% when the plants were grown in soil.

Gordon also described experiments that the University of Washington has performed in the field. Working with Occidental Chemical Corporation and the Department of Ecology, Gordon said, the University set up a field study. In this study, a series of crypts were designed, each of which had poplar cuttings planted on top of them. The crypts were irrigated with TCE-contaminated water and all liquid effluent leaving the system was captured by an extraction well. (Safety mechanisms were in place to make sure that the site did not become contaminated during the study.) Over a three-year period, Gordon said, hundreds of analyses were performed to compare TCE concentrations in the irrigation stream and in the extraction well. Only about 1% to 2% of the TCE that was added over this period was detected in the extraction well. Gordon said that breakthrough only occurred at the end of growing seasons, coinciding with the time that leaves fell from trees. As each year passed, and the trees matured, TCE concentrations in the extraction well decreased. Gordon said that investigators wanted to know what was causing the TCE to disappear in the field. Wood from the poplars was analyzed, but only small quantities of TCE were detected in the samples. To determine whether TCE was being transpired, leaves were enclosed in Teflon bags; air was pulled through them at a rate of 1 to 2 liters per minute; gases were collected, sent through a carbon filter, and heated; and TCE was measured. Gordon said that TCE was detected in the gas, but results indicated that only about 5% of the TCE that was added over the three-year study was transpiring through the trees. (This quantity is less than investigators expected based on the results of the mass balance laboratory study.) After additional investigations, it became clear that many TCE degradation products were present in the rhizosphere. During soil sampling, large quantities of chloride were detected near root systems. Investigators concluded that TCE is degraded in poplar roots and excess chloride is excreted into surrounding soils. To confirm that rhizobial microbes were not responsible for the degradation, at least at this particular field site, investigators irrigated the site with more water than the tree roots could absorb. When they did this, they found that TCE levels in the extraction well increased. Thus, it appears that TCE-contaminated water must enter poplar roots for degradation to occur.

Gordon said that a variety of other studies were performed at the field site as well. For example, a student at Clemson University evaluated the toxicity of poplar detritus by feeding it to pill bugs. The insects did not suffer adverse effects. In addition, Gordon said, the site was used to study the effect that poplars have on carbon tetrachloride. The study showed that this chemical is also remediated by poplar trees, but that the mechanisms involved differ somewhat from those observed for TCE. That is, none of the carbon tetrachloride was released from the leaves as a gas. In general, Gordon said, these studies (as well as others that have been performed on chlorinated solvents) suggest the following: poplars are able to uptake contaminants, metabolize chlorinated solvents in plant tissues, and break down the solvents into chloride and carbon dioxide.

Before closing, Gordon brought up a controversial subject: using transgenic plants to remediate contaminants. In mammalian systems, he said, the cytochrome P450 enzyme plays a key role in TCE degradation. In one study, he said, researchers incorporated a mammalian P450 enzyme into the genome of a tobacco plant. They found that the oxidation rate of TCE was increased about 600 times when this modification was made. Gordon said that this raises the question of whether it would be wise to tailor-make plants that have an increased activity against chlorinated solvents. He said that phytoremediation might travel down this path in the future, but acknowledged that using such an approach could raise some controversial issues.

The Case for Phytovolatilization
William Doucette, Utah State University

William Doucette noted that a variety of mechanisms (*e.g.*, enhanced rhizosphere microbial degradation, sorption, plant uptake, plant metabolism, and phytovolatilization) are proposed to play a role in plant-mediated remediation. He said that he would discuss the role that uptake and phytovolatilization (also called transpiration) play in remediating TCE. Doucette said that there are three major pathways for organics to enter plants: (1) root uptake, (2) atmospheric deposition, and (3) diffusive transport through air spaces into roots and shoots. He said that his presentation would address the first route, in which TCE is dissolved in subsurface waters or vapors and then passively diffuses through root membranes. He said that he would also examine how readily TCE translocates from roots to shoots, and whether, once TCE reaches the aboveground portions of a plant, it is released to the atmosphere through transpiration. Before proceeding, he defined a term: transpiration stream concentration factor (TSCF), which defines how readily compounds move from roots to shoots. In 1982, he said, some researchers suggested that a contaminant's log K_{ow} determined its TSCF value, and that contaminants with a log K_{ow} of 2.0 had the highest TSCF values. After collecting more data, however, scientists learned that compounds with the same log K_{ow} do not always have the same TSCF values. Thus, the relationship is more complicated than originally proposed.

Doucette provided a brief literature review, summarizing the major conclusions that have been made over the last six years about plant uptake and phytovolatilization of TCE. Regarding uptake, he said, Schnoor *et al.* reported little root uptake and Schnabel *et al.* detected low (1% to 2%) uptake in shoots. As for phytovolatilization, Doucette continued, several researchers have detected TCE in plant transpirate, but reported values differ across the studies. For example, Newman *et al.* reported transpiration as "measurable" in one study and about 5% in another one, but a 1998 study by Burken and Schnoor cited values of 21%. Doucette said that many researchers have measured TSCF values for TCE as well, and that reported values range between 0.02 to 0.75. Doucette acknowledged that the data presented in the literature are quite scattered. He described some of the reasons why this might be. First, he said, some of the data were generated in the laboratory and some were generated in the field. Also, he said, experimenters did not all use the same TCE concentrations, exposure durations, plant species, or growing conditions. For example, some plants were grown in soil and some were grown hydroponically. Also, the age of the plants differed between experiments. In addition, Doucette said, a variety of different experimental approaches have been used, and this might contribute to the variation in results that is observed across studies. While some laboratory experiments were performed in static chambers, he said, others were conducted in flow-through chambers. Also, some researchers established a barrier between plant root zones and foliar portions, but others did not. Doucette said that there are a variety of factors that must be considered when performing laboratory experiments, including (1) humidity and temperature build-up, (2) unnatural plant conditions, (3) foliar deposition *versus* root uptake, (4) leaks and low recovery, and (5) trapping mechanisms. The extent to which researchers address these, he said, affects results. In the field, Doucette continued, researchers have used a wide variety of approaches to measure phytovolatilization, including using (1) open bags, (2) sealed bags, (3) flow-through bags or chambers, and (4) open path Fourier Transform Infrared (FTIR).

Doucette described laboratory studies that Utah State University (USU) has performed to quantify phytovolatilization. He described the experimental design used in these studies, noting that a dual-chamber flow-through system was used for all of the investigations and that researchers made great efforts to mimic outdoor environments. Mass recovery in three of the studies was greater than 92%, he said, and the studies revealed that: (1) TCE and the resulting oxidative metabolite (*e.g.,* trichloroacetic acid and dichloroacetic acid) concentrations were highest in roots, lower in leaves, and lowest in stems, (2) little to no phytovolatilization occurred, (3) TSCF values ranged between 0.02 and 0.21, and (4) TSCF values were not influenced by exposure concentrations (a range of 1 ppm to 70 ppm was tested) or exposure duration (12 to 26 days). Doucette described another study, which used a slightly modified experimental apparatus and was performed over a 43-day period; in that study, mass recovery was about 97%, and results indicated that about 70% to 75% of the TCE was present in plant roots, 10% to 13% was stored in leaves, 5% to 6% was stored in stems, and about 4% to 7% had been volatilized out of the plant. He noted a point of interest: in short-term studies, TCE concentrations in the stems were greater than those in the leaves, but the opposite was true in longer-term studies.

Doucette said that USU has also evaluated the fate of chlorinated solvents at two different field sites. At both sites, he said, mature trees had established themselves naturally in contaminated areas. Doucette described the sites and the evaluations performed:

- *Cape Canaveral Air Station (CCAS), Site 1381.* Doucette said that plants have been growing for 10 to 20 years at this site, and that TCE (1 to 10 milligrams per liter, or mg/L) has been detected in an aquifer that is located 2 to 4 feet below ground surface (bgs). Doucette said that USU took measurements from three different tree species, as well as from the media that surrounded them. Results indicated that (1) TCE was present in groundwater and soil samples but its metabolites were not typically found; (2) no TCE was transpired through the plant; (2) TCE and its metabolites were present in plant roots, shoots, and leaves; (3) TCE and dichloroethene (DCE) were present in soil gas, but there was no measurable surface emission flux; and (4) 75% of the roots were located in the top 2 feet of soil.

- *Hill AFB*. Doucette said that this site had many things in common with the CCAS site. For example, TCE concentrations were similar, and plants had established roots in contaminated areas many years before USU initiated field studies. Doucette said that plant tissues were analyzed and that PCE, TCE, and resulting metabolites were detected in stems and leaves. The ratio of PCE to TCE in the plants, he said, was similar to that found in the site's groundwater. He also said that the TCE concentrations detected in plant tissues were several orders of magnitude greater than those detected in the CCAS plants. In addition, he said, contaminants were detected in plant transpirate at fairly high concentrations; these reached 0.04 mg/L for PCE and 0.8 mg/L for TCE. Doucette did wonder, however, whether the transpiration rates were a bit skewed, noting that investigators had problems controlling humidity in the measurement chambers that were installed around leaves.

Doucette noted that the results obtained at CCAS and Hill AFB differed quite a bit. More TCE accumulated in plant tissues and transpired at the latter. He said that differences in precipitation rates may be responsible for the different results. (Average annual rainfalls are 50 inches and 15 inches at CCAS and Hill AFB, respectively.) Plants in areas with a lot of precipitation may not grow as deep, or tap into groundwater sources as efficiently, as plants that are growing in areas where water is scarce.

Phytotransformation Pathways and Mass Balance for Chlorinated Alkanes and Alkenes
Valentine Nzengung, University of Georgia

Valentine Nzengung described studies that have been performed to determine how willows and cottonwoods impact chlorinated alkenes and alkanes. The following table summarizes the studies and the results:

Laboratory and Greenhouse Studies

- Willows were dosed with 60 ppm of TCE. Over 50 days, TCE concentrations in solution decreased to less than 10 ppm.
- Willows were dosed with PCE. At the end of the study, significant amounts of PCE were still detected in the rhizosphere. PCE was also detected in aboveground portions of the plant, but concentrations decreased with plant height. The following oxidative metabolites were detected during the study: trichloroethanol, trichloroacetic acid, and dichloroacetic acid.
- Cottonwoods were dosed with PCE. TCE concentrations increased as PCE concentrations decreased. Nzengung said that this result was observed after researchers made some adjustments to experimental reactors. He said that he would like to know if other researchers could duplicate these results. He acknowledged that the results could surprise some people, because they suggest that reductive dechlorination processes are involved in plant degradation.
- Cottonwoods and willows were exposed to PCE. The following were detected in the rhizosphere head space: PCE, TCE, trans 1,2-DCE, ethene, ethane, and methane.
- Mass balance studies were performed. Total mass recovery was poor (about 45% for TCE and 74% for PCE), but investigators hope to improve these rates by modifying test reactors. The following was learned: (1) a significant portion of contaminant was volatilized, (2) carbon dioxide was recovered in traps when plants were exposed to TCE, and (3) carbon dioxide was mostly in the solution phase when plants were exposed to PCE.
- Aquatic plants were dosed with radiolabeled carbon tetrachloride. The results showed that: (1) 10% to 12% of the contaminant was transformed to chloroform, (2) 80% to 85% was bound residue, and (3) 45% of the bound fraction was assimilated.
- Aquatic plants were dosed with HCA. A portion of the sequestered HCA became irreversibly bound residue. Several contaminant breakdown products were detected, including PCE, TCE, pentachloroethane, trichloroacetic acid, and dichloroacetic acid.

Studies Conducted on the Leaves and Roots of Cottonwoods That Are Growing at the Carswell AFB Site

Nzengung said that cottonwoods were planted at the Carswell site in April 1996 in an effort to clean up groundwater that is contaminated with PCE. Some of the trees were planted as whips and others as "5-gallon bucket" size cuttings. Researchers collected leaf and root samples from the cottonwoods in 1998 (after the second growing season) and in 1999 (after the third growing season. Results (expressed in mg/kg) indicated the following:

	September 1998 Results			January 1999 Results		
	Trichloroethanol	Trichloroacetic Acid	TCE	Trichloroethanol	Trichloroacetic Acid	TCE
Whip, leaf	0.161 ± 0.016	2.54 ± 0.003	ND	1.566 ± 0.056	ND	ND
Whip, root	0.640 ± 0.057	ND	Trace	0.623 ± 0.025	28.44	ND
5-gallon, leaf	1.059 ± 0.127	1.30 ± 0.066	ND	0.257 ± 0.125	>30	ND
5-gallon, root	0.211 ± 0.024	ND	Trace	0.252 ± 0.074	31.34 ± 0.72	ND

Nzengung noted that values differed between the whips and the cuttings. He said that this probably reflects the fact that one reached groundwater before the other. After evaluating the results, researchers returned to Carswell AFB to collect leaves from mature cottonwoods that had been established at the site before the phytoremediation demonstration project was started. The results indicated that no detectable TCE or trichloroethanol was measured in the leaf extract, but that trichloroacetic acid and dichloroacetic acid concentrations were very high. Nzengung hypothesized that the age of a plant influences phytotransformation pathways.

Basing his findings on these and other studies, Nzengung proposed the following as a possible conclusion: there are three phyto-processes that play a primary role in remediating volatile chlorinated aliphatics. These are phytovolatilization, rhizodegradation, and phytodegradation. (Nzengung defined the latter as including only those processes that occur in the aboveground portions of plants.) He also concluded that: (1) sequestration and assimilation are important processes for some plants, especially aquatic plants; (2) phytotransformation of volatile chlorinated aliphatics involves multiple pathways; (3) reductive dechlorination and mineralization of TCE and PCE occurs mainly in the rhizosphere of woody plants; and (4) oxidation and reductive transformation occurs in the tissues of aquatic and terrestrial plants. Nzengung also said that data collected suggest that woody plants volatilize a significant portion of TCE and PCE under greenhouse conditions.

Speaker Panel and Audience Discussion

Audience members asked questions or provided comments about the following topics:

- *Will phytovolatilization cause significant air contamination*? Rock asked panelists whether trees should be considered significant sources of air contamination. Gordon said that phytovolatilization was minimal in the studies he performed, but did say that rates might vary across sites. Thus, he said, tests should be performed to measure phytovolatilization at every site that is proposed for phytoremediation. Doucette agreed that phytovolatilization rates are site-specific, noting that this was confirmed in the studies performed at CCAS and Hill AFB. Also, he said, it may be premature to make definitive conclusions about the significance of phytovolatilization, since few efforts have been made to determine how much contaminant will be transpired over an entire canopy. Nzengung said that he still thinks that volatilization rates could prove to be significant in some cases, especially if a plant system has a significant amount of reductive dechlorination (where parent compounds are converted to highly volatile products, such as DCE) occurring in the rhizosphere. One participant said that he did not think more than 10 to 15 pounds of contaminant would be released per acre over the course of a growing season, but said that he could not predict whether this type of release would cause concern among regulators. One attendee said that this amount is negligible compared to the total amount of organic compounds that trees release naturally each year. Building on this point, Doucette said that many naturally occurring hydrocarbons are released from trees, and that emissions could be as much as 2,000 times greater than the rates of TCE release measured in phytovolatilization studies. Before closing on this topic, Harry Compton advised field investigators to monitor air at all phytoremediation sites. Regardless of what is found in the laboratory, he said, regulators will be satisfied that no dangerous air emissions pathways have been created if field data back up this conclusion.

- *Tips on how to perform laboratory experiments*. Gordon said that investigators could be led to believe that reductive dechlorination reactions are taking place in the rhizosphere if anaerobic conditions are inadvertently established in the laboratory. In early studies performed by the University of Washington, Gordon said, dissolved TCE and ethanol were pumped in to study chambers, driving out oxygen. As a result, cis 1,2-DCE, a product of reductive dehalogenation, formed. When investigators started injecting TCE and water rather than TCE and ethanol, he said, dissolved oxygen rates increased and cis 1,2-DCE concentrations decreased. Gordon also advised investigators to check the purity of TCE that is provided by chemical supply houses before using it in laboratory studies. He also said that air should be filtered before it flows through a laboratory chamber. Doucette agreed, noting that he has found TCE in "clean" bottled air.

SESSION IVB: INNOVATIVE SOLUTIONS FOR METALS REMOVAL

Phytoextraction of Metals from Contaminated and Mineralized Soils Using Hyperaccumulator Plants

Rufus Chaney, U.S. Department of Agriculture

Rufus Chaney said that phytostabilization and phytoextraction can be used to address soils that are contaminated with metals. The former converts metals into less toxic or less bioavailable forms *in situ*. The latter, Chaney continued, extracts metals from the root zone and accumulates the contaminants within plant shoots. In many cases, Chaney said, metal-contaminated sites have very low pH and are deficient in nutrients. As a result, these sites are often barren and unable to support plant growth. To achieve phytostabilization of such toxic soils, Chaney said, researchers must act as agronomists, improving soil conditions and converting metals to non-bioavailable forms. Chaney said that much exciting research has been conducted to determine ways to improve soil conditions so that plants can grow in highly toxic soil. In recent years, investigators have starting mixing fertilizers with byproducts, such as biosolids, paper wastes, and composts, and applying these to poor soils. This approach has achieved the desired phytostabilization results in many cases. Thus, a beneficial use is being identified for byproducts that are not always considered desirable. Chaney provided some specific examples of metal-contaminated sites that were barren before having their soils amended, including the Bunker Hill site; Aberdeen Proving Ground; a zinc-smelting site in Palmerton, Pennsylvania; a nickel-smelting site in Canada; and a smelter slag waste site in Poland.

Chaney described the concepts that underlie phytoextraction, a technology that removes metals that are present in the rhizosphere at low costs. Most plants, he said, cannot withstand high metal concentrations. Most die when exposed to zinc concentrations of 500 ppm, cadmium concentrations of 10 to 20 ppm, copper concentrations greater than 25 ppm, or nickel concentration greater than 100 ppm. There are some plants, however, that exhibit great tolerance for metals, and actually accumulate them in very large quantities within their tissues. Chaney said that the ability to accumulate metals may have originally evolved as a defense against plant-eating insects. Today, these plants, called hyperaccumulators, are recognized to have great remedial potential. Species that naturally hyperaccumulate selenium, zinc, copper, cadmium, and nickel have been identified, but none have yet been found that will hyperaccumulate lead or chromium.

Chaney said that the U.S. Department of Agriculture (USDA) has patented a phytoextraction procedure. The patent involves planting hyperaccumulators on contaminated sites, harvesting the plants, incinerating them, recycling extracted metals from ash, and then selling the recycled metals for profit. He described two plants that have been identified as hyperaccumulators. *Alyssum murale* can be used to hyperaccumulate nickel and cobalt, which both have fairly high market value in the United States. *Thlaspi caerulescens,* Chaney said, can be used to remove cadmium and zinc. He said that neither of these metals are worth much in the United States; thus, site managers who have cadmium and zinc contamination may not jump at the chance to use phytoextraction unless they are mandated to perform a cleanup. *T. caerulescens* might prove to be an extraordinarily important remedial tool, however, in developing countries, where mines and smelters have contaminated rice paddies and consumption of the rice has caused cadmium poisoning in subsistence farming families. Peasant farmers in these countries could probably make a profit on recycled metals, Chaney said, while simultaneously reducing the potential for human cadmium toxicity.

Chaney described the process that USDA uses to promote the development of hyperaccumulators. First, he said, researchers identify species that are worth investing in. Once this is accomplished, germplasm is collected and genetic diversity is evaluated. The genotypes are tested under uniform conditions using contaminated soil, and efforts are made to identify the agronomic needs of the plant. Also, researchers evaluate the fertility needs of hyperaccumulators and learn how to breed the plants. In addition, researchers evaluate the economic benefits that the plants offer, address concerns about ecological risks, and test the plants in the field.

In closing, Chaney said that hyperaccumulators have great potential. If developed and applied properly, he said, they can provide economic benefits and address difficult environmental problems simultaneously.

Phytoextraction: Commercial Considerations
Michael Blaylock, Edenspace Systems Corporation

Michael Blaylock said that Edenspace Systems Corporation (Edenspace) promotes the use of phytoextraction, a technology that can be used to remediate metal-contaminated sites. He did note, however, that there are some obstacles that must be hurdled before phytoextraction will be used on a wide-scale commercial basis. The first of these is inertia, Blaylock said: many site managers have no motivation to remediate sites until a government agency forces them to do so. Another issue that must be addressed, he said, is determining a way to measure the success of a technology. Also, he said, efforts must be made to answer the following questions:

- *Can phytorextraction serve any benefit if contaminants are located deeper than 2 or 3 feet?* Blaylock said that efforts are underway to determine whether phytoextraction and electrokinetic transport can be used in combination. Also, he said, at some sites, deep soils are being excavated, spread out in *ex situ* treatment cells, and planted with species that extract metals.

- *Will phytoextraction cause ecological toxicity?* Blaylock said that some studies are underway to evaluate this concern. For example, at the Aberdeen Proving Grounds, researchers are evaluating whether plants that have been used to remediate uranium could pose a risk to the surrounding ecosystem.

- *Will phytoextraction increase the solubility of some contaminants and cause leaching?* Blaylock said that lysimeters can be used to address these concerns. Also, if the issue is of great concern at a particular site, phytoextraction could be used *ex situ* rather than *in situ.*

- *Will phytoextraction serve any benefit at sites that have insoluble contaminants?* Blaylock said that researchers are experimenting with soil amendments to determine whether metals can be made more soluble and absorbed through plant roots.

Blaylock said that it is often best to integrate conventional remediation techniques with innovative ones. When combinations are used, the strengths of multiple technologies can be used to overcome site-specific challenges. Blaylock said that soil washing, particle size separation, excavation, electrokinetics, and stabilization can all be used with phytoextraction. In fact, phytoextraction and phytostabilization approaches are both being used at the Simsbury, Connecticut, site, a site that Edenspace is currently remediating. Before initiating remedial activities at this site, Edenspace measured total lead concentrations in surficial soils at concentrations as high as 6,000 ppm. Average SPLP leachable lead values were 0.85 mg/L. Blaylock said that phytoextraction—using *Brassica juncea*—will be used for two years in an effort to remediate total lead. After that time, the site will be reassessed, and phytostabilization will be used to address any remaining problems. Blaylock said that the *B. juncea* has already been harvested once, and that average concentrations from all the crops exceeded 1,000 ppm. Also, he said, soils have been sampled to track progress to date. Already, total lead concentrations have decreased dramatically and SPLP leachable lead values have decreased to 0.08 mg/L.

Blaylock said that Edenspace has completed phytoextraction projects at several sites. For example, he said, the technology was applied at a DaimlerChrysler site that had lead contaminants below root zones and required cleanup activities to be completed over a one-year period. Edenspace identified a creative remedial strategy to use at this site. First, subsurface soils were excavated; spread out over a lined, unused, paved area; and mapped. Then, contaminant hot spots were identified and excavated for disposal. The remaining soil, which was spread over about 2 acres, was planted with *B. juncea* in April and replanted with sunflowers in June. (Blaylock said that the sunflowers do not extract lead as readily as *B. juncea*, but they do produce more biomass and extend roots deeper.) After harvesting and removing all the plants, Blaylock said, Edenspace sampled soils to identify whether lead was still present above regulatory standards. Only about 2 cubic yards of soil still had too much lead; this soil was properly disposed of off site. Blaylock said that the site owner was very happy with the results, and estimated that $1 million was saved by using phytoextraction instead of a conventional approach. Blaylock said that Edenspace received an award for this project.

Blaylock said that there are several exciting research efforts ongoing in the area of phytoextraction. For example, the University of Florida is working with a fern that might be capable of hyperaccumulating arsenic. Also, he said, Edenspace has started evaluating turf grasses, a low-maintenance crop, to determine whether they can be induced to uptake lead. Initial laboratory results are promising, he said, noting that this low-maintenance crop might have the potential to serve as a long-term sustainable approach for addressing roadside lead contamination.

Zinc Hyperaccumulation in Plants: The Case of Zinc Hyperaccumulation in *T. Caerulescens*
Mitch Lasat, EPA

Mitch Lasat explained why there is great need to develop phytoextraction, a cost-effective technology that removes metals from the soil. First, he said, there are a number of sites that would benefit from using it, noting that elevated metal concentrations have been detected at many NPL sites and brownfields sites. Second, phytoextraction is an environment-friendly approach that appeals to the public. Most importantly, Lasat said, the technology is able to succeed where others have failed: it extracts metals from large surface areas in a cost-effective fashion.

Lasat said that some metals are considered essential plant micronutrients. Plants have developed mechanisms to extract these metals from the soil, absorb the metals into their roots, and translocate the metals to aboveground plant tissues. While most plants accumulate only small quantities of metals, hyperaccumulators have the ability to accumulate enormous quantities. For example, Lasat said, while a regular plant accumulates about 50 ppm of nickel or zinc in its shoots, a hyperaccumulator can store more than 20,000 ppm. Lasat said that much interest has been generated in using hyperaccumulators as remedial agents, but that scientists have identified one problem: the hyperaccumulators are typically small, with a low potential for biomass production. This problem could be ameliorated, Lasat said, if researchers identify, clone, and transfer the genes that cause hyperaccumulation into plants that yield higher biomass.

Lasat said the remainder of his presentation would describe what scientists have learned about the mechanisms that underlie zinc hyperaccumulation in *T. caerulescens.* He said that this plant was chosen for study because it is an excellent hyperaccumulator. Some studies indicate that the plant suffers no toxic effects even when more than 3% of its shoot weight consists of metals. To gain an understanding of what causes hyperaccumulation, Lasat said, the physiological and molecular processes of *T. caerulescens* were compared against those of *T. arvense*. The latter is closely related to *T. caerulescens*, but cannot survive in heavily contaminated soils or hyperaccumulate metals. Lasat said that radiotracer flux studies were performed to determine the physiology of zinc transport in the two species. The studies showed that *T. caerulescens* uptakes zinc into its roots more readily than *T. arvense*. (In a three-hour study, the root concentration of zinc was about two times higher in *T. caerulescens*.) Over longer periods, however, zinc concentrations were higher in the *T. arvense* roots; compartmentalization studies indicated that zinc concentrations in the root cell wall and cytoplasm were similar between the two species, but that vacuolar zinc concentrations were significantly higher in *T. arvense*. In the shoots and leaves, zinc concentrations in

* Views expressed are those of the participants, not necessarily EPA.

T. arvense were significantly lower than those measured in *T. caerulescens*. Based on this information, the following hypothesis was generated: zinc is sequestered in *T. arvense* root vacuoles and made unavailable for translocation to shoots, but this mechanism is disabled in *T. caerulescens*. Lasat said that information about the mechanisms of zinc transport in the aboveground portions of *T. caerulescens* was also revealed during the radiotracer studies. For example, investigators found that zinc tends to associate with vascular tissues, but that it diffuses into intervenous spaces when concentrations are very high.

After obtaining information on the mechanisms that underlie zinc transport in *T. caerulescens*, Lasat said, efforts were made to identify and clone the responsible genes. To do so, he said, the following steps were taken: (1) a *T. caerulescens* cDNA library was constructed in a yeast expression vector pFL61; (2) *zhy3*, a yeast mutant defective in zinc uptake, was complemented with *T. caerulescens* genes from the library; and (3) the library was screened for clones that are capable of growing on restrictive zinc levels. Lasat said that seven colonies were identified, five of which were discovered to represent the *ZNT1* gene. He said that a Northern analysis was performed to evaluate *ZNT1* expression in *T. caerulescens* and *T. arvense* shoots and roots. These analyses showed that *T. arvense* stimulates the expression of *ZNT1* under zinc-deficient conditions. In *T. caerulescens*, however, the gene is expressed strongly even when there is plenty of zinc available in growth media. This suggests that the *T. caerulescens* does not downregulate zinc uptake once it has accumulated enough zinc to meet its metabolic needs.

Lasat said that some investigators are confident that they have identified the gene that is responsible for zinc hyperaccumulation in *T. caerulescens*. As a next step, he said, they will need to identify the gene that allows this plant to tolerate highly toxic metal concentrations. Once this is determined, he said, researchers might be able to bioengineer a hyperaccumulator that yields high biomass, tolerates toxic metal concentrations, and extracts them from the subsurface at high rates.

Speaker Panel and Audience Discussion

Audience members asked questions or provided comments about the following topics:

- *Harvesting plant roots*. An attendee asked whether roots should be harvested along with aboveground plant materials. Specifically, she asked whether investigators were concerned about animals that could contact contaminated roots. Blaylock said that Edenspace has evaluated metal concentrations in the roots and shoots of many plants. In general, he said, concentrations in shoots are about 5 to 10 times greater than in roots. He said that an ecotoxicity study, performed at the Aberdeen Proving Ground, suggests that earthworms and soil-dwelling insects do not experience adverse effects when exposed to uranium-contaminated roots. Chaney said that some of the hyperaccumulators are perennials and that it would not be economical to harvest their roots each season.

- *Costs*. One participant asked for information on how much it costs to apply phytoextraction technologies. Blaylock said that cost varies from site to site, but that $50,000 an acre is a rough average. At the DaimlerChrysler site, he said, it cost between about $100,000 to $200,000 to clean up a 3-acre area. Chaney reminded participants that the costs of application can be defrayed if site managers choose to recycle the metals that they extract. It may even be possible to profit from the activity.

- *The use of the term "hyperaccumulator."* Chaney said that he defines hyperaccumulators as plants that have evolved, through natural processes, to uptake large quantities of metals. Some plants can be induced to act as hyperaccumulators if EDTA is applied, he said, but these are not "true" hyperaccumulators. (Chaney said that *B. juncea* and sunflower are not hyperaccumulators.)

- *Incineration and methods used to extract metals.* A participant asked whether metals could be released to the air when plant materials are burned at incinerators. Chaney said that this was unlikely, as long as the materials were sent to a permitted incinerator that was up to date on emission control technologies. Blaylock said that several researchers are evaluating whether there are other ways to handle harvested biomass. For example, a group in the Soviet Union has developed a technology that extracts metals from biomass without requiring them to be incinerated first.

- *Using local plants in phytostabilization projects.* One participant asked whether efforts are being made to use local plants in phytostabilization projects. Chaney said that this is the end goal, but other species often have to be planted first to improve the quality of soils. At many sites, sterile plants are used with mixtures of byproducts to hold the amendments on the soil and improve conditions before establishing native crops that can proliferate.

- *Using aquatic plants to extract metals.* One participant asked whether plants can be used to extract metals from contaminated water. Blaylock said that Rutgers University has experimented with rhizofiltration, which involves exposing contaminated water to plant roots. Chaney said that work has also been performed using constructed wetlands.

SESSION V: SIMULATIONS AND FORECASTS

Chasing Subsurface Contaminants

Joel G. Burken, University of Missouri

Joel Burken summarized mechanisms that are involved with the phytoremediation of organic compounds. He said that subsurface contaminants can be either bound to soils, mineralized, or taken up by plants. Once inside plants, contaminants can be metabolized, bound in plant materials, or released through phytovolatilization. Burken said that these mechanisms have been documented, but the importance of each is still being debated.

Burken described laboratory studies in which he has been involved, noting that the study results offer interesting insights, but cannot necessarily be extrapolated directly to the field. In the early 1990s, he said, researchers evaluated whether poplars can clean up atrazine. Several interesting findings were recorded. First, investigators learned that poplars do not increase mineralization rates in the subsurface, but they do reduce contaminant concentrations. Also, poplars were shown to take up the atrazine. Once the contaminant was inside the plant, some of it degraded (about eight breakdown products were detected), some became bound, and some transpired. In addition, researchers learned that subsurface soil conditions have a large impact on transpiration rates. Uptake is not as vigorous when components of the subsurface sorb or compete with contaminants. (When poplars were planted in silica sand, all of the atrazine was taken up by plants over a 10-day period. Only 30% was taken up over an 80-day period when a silt-loam soil was used.)

In recent years, Burken said, the University of Missouri has performed several studies to evaluate how poplar cuttings impact a variety of VOCs. In all of the studies, he said, a steady flow of air was injected into a reactor, aerial and subsurface regions were compartmentalized, and significant efforts were made to mimic outdoor conditions. Plants were grown hydroponically in some of the studies, but were rooted in soil in others. When soils were used, investigators were able to create two subsurface zones: a saturated layer (where contaminated water was injected) and a vadose zone. Burken described what was learned when benzene was exposed to poplar cuttings:

- *Subsurface benzene concentrations were reduced.* Benzene was injected into unplanted and planted reactors, and investigators measured the effluent that came out of each. After six days passed, benzene was no longer detected in the planted reactor effluent. It persisted in the unplanted reactor effluent, however, for the entire course of the experiment.

- *Subsurface mineralization processes were enhanced.* Carbon dioxide was measured in the rhizosphere headspace of unplanted and planted reactors. Very little was detected in the former; significant quantities were found in the latter.

- *Very little benzene was stored in plants.* Negligible benzene concentrations were detected in plant tissues.

- *Benzene was transpired, but the amounts recorded differed across experiments.* Significant amounts of benzene were transpired by hydroponically grown plants, but those that were grown in soil released much less benzene. This proves that differences in experimental design have profound impacts on results.

- *Subsurface contaminant migration, water table height, and subsurface oxygen levels were impacted.* Very little benzene migrated to the upper soil layers in unplanted reactors because soil pore spaces were mostly filled with water. In the planted reactors, contaminants moved more freely throughout the subsurface. (Roots removed water, and this opened up pore spaces.) The studies also showed that poplars have a profound effect on rhizosphere oxygen levels. The rhizosphere in planted reactors was aerobic, but soils in the unplanted reactors proved to be oxygen deprived. Aerobic environments attract microbes that help to degrade organics. Thus, it is clear that plants exert a combination of beneficial effects concurrently.

Burken identified areas that require additional research. Efforts should be made to understand plants better, he said, noting that researchers should assess the phytoremedial properties of a wide variety of plants. In addition, he said, researchers should ask: can plant systems be altered to improve their phytoremedial properties? Burken said that some scientists propose using genetically enhanced plants or genetically engineered microbes (GEM) in the rhizosphere. He described some work that has been performed on the latter. Toluene *o* monooxygenase has been incorporated into three different rhizosphere microbes, Burken said, and experiments have been performed to (1) evaluate how well GEM compete in wheat, bean, barley, and poplar rhizospheres; (2) determine the degradation properties of GEM; and (3) determine whether GEM increase TCE reduction rates when they are used in a poplar rhizosphere. The results of the latter, Burken said, suggest that adding GEM to plant systems increase degradation rates dramatically.

Effect of Woody Plants on Groundwater Hydrology and Contaminant Fate
James Landmeyer, U.S. Geological Survey

James Landmeyer said that a study is being performed at a site in Charleston, South Carolina, to evaluate the impact that poplars have on groundwater hydrology. The site is located in an urbanized setting, near a residential area and an aquarium. Groundwater at the site, which is about 2 to 4 feet bgs, is polluted with PAH and BTEX. It is also impacted by a coastal water body; thus portions of the site have saline groundwater and are influenced by the tides. In December 1998, Landmeyer said, 2-foot-tall poplar whips were planted in an effort to address the site's groundwater contamination. Many of the trees prospered even though the site experienced a harsh drought shortly after planting. By September 1999, several of the trees had reached about 14 feet in height. Landmeyer said that excavations were performed to evaluate root profiles. From this activity, investigators learned that the poplar roots are growing vertically, into the capillary fringe of the shallow water table. Landmeyer said that researchers were relieved to find this, because tree roots typically grow horizontally, rather than vertically, in this part of the country.

Landmeyer said that the Penman equation was used to estimate how much water the poplars extract from the site's groundwater and surrounding soil. A weather station was installed to collect several of the parameters (*e.g.*, wind speed and direction, air temperature, precipitation, solar radiation, relative humidity, barometric pressure) that are required for the equation. In addition, Landmeyer said, information on leaf temperature and wetness was also collected and entered into the equation. The equation's output indicated that the potential evapotranspiration (PET) is about 0.5 inches per day. Extrapolating this over the entire plantation, Landmeyer said, researchers concluded that 2,000 gallons of soil moisture and groundwater would be removed from the site each day. He said that this value exceeds the amount of water (1,500 gallons) that is thought to enter the study area each day. Thus, according to the modeled data, the poplar plantation should cause a depression in the water table. Landmeyer said that extensive groundwater-level sampling would have to be conducted to determine whether depressions are actually resulting.

Landmeyer said that some efforts have been made to measure groundwater fluctuation at the site. He presented a series of graphs, which showed how groundwater levels changed during three different study periods (August 6–11, 1999; August 24–September 2, 1999; and April 5–9, 2000) and at three different locations across the site (in the center of the site, 1,000 feet from the tidal body, and 2,000 feet from the tidal body). These data showed that: (1) rainfall causes the groundwater table to rise, (2) there is no evidence of hydraulic capture yet, (3) fluctuation is more significant in locations that are closer to the tidal body, and (4) groundwater levels dip slightly around noon—the time when evapotranspiration rates are expected to be highest. Using the data obtained, Landmeyer said, investigators determined that each one-year-old poplar at the site is taking up about 0.08 gallons of groundwater and soil moisture each day. This translates to an uptake rate of about 0.0002 gallons per minute. After more data are collected, Landmeyer said, he will use a modeling program to estimate how the trees will perform as they get older.

Landmeyer said that some efforts have been made to determine whether the poplars are impacting subsurface geochemistry. For example, a dissolved oxygen probe has been installed in one well to determine whether poplars have caused dissolved oxygen levels to increase in groundwater. To date, he said, fluctuations in this parameter seem only to correlate with rainfall occurrences. He said that some preliminary efforts have been made to determine the fate of the groundwater PAH and BTEX. These contaminants have been detected in tree leaves, but it is unclear whether these chemicals originated in the groundwater or came from some other source.

Before closing, Landmeyer presented information on another site, located in Beaufort, South Carolina, which has a BTEX and MTBE plume emanating from an underground storage tank. He said that oak trees established themselves at the site about 40 years ago. In 1997, researchers initiated evaluations to determine whether these oaks were effecting groundwater contaminants. They concluded that hydraulic capture has not been achieved because groundwater flow rates are too fast and portions of the plume are too deep. However, they did find strong evidence that contaminants are being taken up into the oak trees. Landmeyer said that the trees were cored and evaluated using gas chromatography/mass spectrometry, and that BTEX, MTBE and trimethylbenzene isomers were detected in those trees that had extended roots into the groundwater table. Landmeyer said that the oaks might be transpiring a significant amount of MTBE, which could cause some people to express concern about cross-media contamination. He said that it may be more effective to decrease MTBE concentrations by using plants that release MTBE to the air (where it has a half-life on the order of hours or days) than to allow MTBE to be transported in anaerobic aquifer systems (where its half-life is on the order of years).

Modeling Plume Capture at Argonne National Laboratory-East (ANL-E)
John Quinn, Argonne National Laboratory

John Quinn described some of the modeling activities that were performed for the phytoremediation project at ANL-E's 317/319 area. He noted that this site was described earlier in the conference, but offered the following information as a brief summary: (1) the groundwater is contaminated with VOCs and tritium, (2) 13 extraction wells were installed as an interim measure to control groundwater, (3) the contaminated groundwater plume is about 25 to 30 feet deep, (4) the site's subsurface stratigraphy is extremely complex, (5) the aquifer is fairly thin—about 5 feet thick—but varies widely in texture and permeability, (6) groundwater flows towards the Waterfall Glen Forest Preserve and a recreational path, (7) contaminants have appeared in downgradient seeps, (8) an engineered phytoremediation system has been installed to control site contamination, and (9) fences have been installed to prevent deer from contacting the planted system.

Quinn described the phytoremediation system that has been installed at the site. He said that a herbaceous cover has been installed to minimize water infiltration and soil erosion. In addition, trees have been installed near the site's french drain in an effort to enhance the remediation of subsurface VOCs. (Quinn said that the downward migration of tree roots should not be hindered by subsurface heterogeneities, because the area around the french drain was homogenized by deep soil mixing a couple of years earlier.) Also, Quinn said, TreeWells® have been installed in an effort to achieve hydraulic control. He said that these trees were planted in 30-foot-deep, lined, large-diameter boreholes. Thus, roots are cut off from any shallow water sources and forced to grow vertically in search of deeper groundwater sources.

Quinn described modeling efforts that have been conducted on the aquifer that lies 25 to 30 feet below the site. He said that MODFLOW was used to model transient groundwater flow under pre- and post-phytoremediation conditions. For the latter, he said, TreeWell® evapotranspiration estimates were provided by Ray Hinchman and Edward Gatliff. Quinn showed computer simulations for the pre- and post-conditions, and told attendees that these could be viewed more leisurely by visiting http://web.ead.anl.gov/phyto. In both simulations, Quinn pointed out, water levels pulsate, with the highest levels predicted in spring, during snow melt events, and the lowest levels predicted during late summer and early fall. Quinn said that he also performed particle tracing studies to evaluate groundwater flow throughout the plantation. Summarizing the results of his studies and simulations, Quinn made the following conclusions about the ANL-E site: (1) mature plantations will achieve groundwater containment, even during the dormant winter months; (2) the site's 13 extraction wells can be phased out in the future; (3) groundwater that is pulled into microbially active rhizosphere areas will have a residence time of 5 to 17 months; and (4) de-watering of the perched aquifer could occur.

In closing, Quinn listed some of the activities that are ongoing or planned at the ANL-E site. These include collecting groundwater samples, making water-level measurements, collecting weather data, sampling tree tissues, evaluating transpirate, analyzing subsurface soils, and installing viewing tubes so that miniature cameras can be used to view root development.

Phytoremediation Potential of a Chlorinated Solvents Plume in Central Florida
Stacy Lewis Hutchinson, EPA, National Exposure Research Laboratory

Stacy Lewis Hutchinson said that models can be used to predict whether a plant-based system will be able to control groundwater at a site. She said that water balance can be determined by evaluating groundwater flow patterns and the amount of water that plants withdraw from aquifers. She presented the water balance equation—a calculation that is incorporated into predictive models—and listed parameters included in it: hydraulic conductivity, aquifer thickness, hydraulic head, sources and sinks of water, precipitation, irrigation, surface runoff, and evapotranspiration. The latter two, she said, are often estimated, and therefore tend to have more error associated with them.

Hutchinson talked briefly about the evapotranspiration parameter, noting that plants that exhibit high values may be able to reduce average net recharge to subsurface aquifers, prevent plume diving, and create an upward flux of groundwater. A plantation's capability of achieving these results, she said, is influenced by geography and climate. For example, she said, evidence suggests that plants are more likely to achieve hydraulic control in the Southwest than in the Southeast. (Both areas are hot and exhibit fairly equivalent evaporation energies, but precipitation rates differ between the two. In the wet Southeast, plant roots are more likely to use precipitation as a water source. In the dry Southwest, roots are forced to search for deeper groundwater aquifers.) Hutchinson described the methods that are used to determine evapotranspiration values. She said that many researchers use the Penman-Montieth equation to generate estimates, but cautioned that this equation may provide overinflated evapotranspiration values. Recently, Hutchinson said, researchers have started using sap flow collars and probes to obtain a more direct measurement of evapotranspiration.

Hutchinson described modeling efforts that were conducted at a site in Orlando, Florida. This site's groundwater, which is contaminated with PCE and TCE, flows under a paved area, to a ditch, a grassy area, and then a more densely vegetated area before discharging to a lake. Groundwater analyses, she said, reveal that there is plume diving at the site. Thus, groundwater is too deep for existing trees to tap into. In an effort to fix the plume diving problem, Hutchinson said, investigators used models to determine (1) why the plume diving is occurring and (2) how the problem could be fixed. She said that a one-dimensional analytical recharge model was used to evaluate the local patterns of aquifer recharge. Using this, researchers were able to mimic the pattern of plume diving that was observed at the site. (The model was not perfect, she said, noting that it did not precisely predict how deep the plume would dive.) Once researchers had a better understanding of recharge, a numerical model was developed for the site, using the MODFLOW code and a U.S. Geological Survey (USGS) regional calibration of the same model. Two layers of differing conductivity were incorporated into the model, and fine scale layering was incorporated to define lake bathymetry. Hutchinson said that addressing vertical discretization is important for evaluating three-dimensional flow features. She said that the model was run using three different evapotranspiration estimates: 50 cm/year (a value cited in a USGS report), 80 cm/year (a value cited in a report about the actual site), and 130 cm/year (a value cited by the Florida Agricultural Extension Service). All of these values, she noted, are less than 140 cm/year—the average annual precipitation estimate.

After the model was used to simulate existing conditions, Hutchinson said, it was used to predict the impact that different engineering solutions might have. For example, she said, simulations were performed to determine whether plume diving could be reversed by (1) diverting runoff from the ditch, and (2) planting some trees in the paved area. She noted that the latter area has no recharge, because water cannot infiltrate pavement. Thus, by dispersing some trees in this area, site managers could be assured of causing a net loss of groundwater over this area. The modeling results indicated that combining the two approaches would reverse much of the diving that is currently observed at the site. Assuming that recharge in the paved area is zero and evapotranspiration rates are 80 cm/year, she said, vegetation would be able to capture about 77% of the plume. The percentage is even higher (88%), she said, when evapotranspiration rates are assumed to be 130 cm/year. In closing, Hutchinson stressed two important points: (1) vertical characterization is required to delineate plumes, and (2) the localized recharge distribution should be carefully assessed.

Speaker Panel and Audience Discussion

Audience members asked questions or provided comments about the following topics:

- *The role models play in obtaining regulatory approval.* Hirsh said that regulators will want to review modeling and forecasting data when trying to determine whether to approve a phytoremediation project. Having these data available, he said, will help build convincing arguments in support of phytoremediation.

- *Using evergreens.* A participant asked whether evapotranspiration rates at the ANL-E site could have been enhanced by including evergreens in the phytoremediation design. Quinn said that this was a good question, but that he did not have an answer. Quinn said that evergreens do transpire water for a longer portion of the year, but pointed out that their evapotranspiration rates are lower than those exhibited by poplars and willows. McMillan acknowledged that the rates are lower, but thought it might be beneficial to include evergreens in a tree mix, since they actively transpire during early spring and late fall—two critical recharge periods that occur when poplars and willows are not transpiring optimally.

- *Public perception on genetic enhancements.* One meeting attendee said that the public might express concern about genetically enhanced plants and GEM. She asked Burken if he had any recommendations on how to handle this. He suggested hiring someone with public relations experience to address the public's concerns. He said that the public would need to be educated on these topics. For example, he said, it is important for the public to understand that the GEM that are being created have suicide implantations.
- *GEM.* Phil Sayre advised researchers who are creating GEM to be careful if they are working with the *Burkholderia cepacia* complex, which has been reported to cause death in people with cystic fibrosis. Sayre also advised investigators to evaluate GEM for resistance to antibiotics.

SESSION VI: PLUME CONTROL—ON-THE-GROUND EXPERIENCE

Phytoremediation at Aberdeen Proving Ground, Maryland: O&M, Monitoring, and Modeling
Steven Hirsh, EPA Region 3

Steven Hirsh described a phytoremediation project that has been initiated at the Aberdeen Proving Ground, a site that has conducted chemical warfare research since 1917. Prior to the 1960s, Hirsh said, munitions, laboratory wastes, and solvents were dumped at the site's burn pits and ignited. A contaminated groundwater plume has formed below the pits, and is discharging to a fresh-water marsh and the Chesapeake Bay. Hirsh said that contaminant concentrations are very high. For example, 1,1,2,2,-tetrachloroethane has been detected in groundwater at 390,000 ppm and TCE is present at 93,000 ppm. Hirsh said that the surficial aquifer is about 30 to 40 feet thick, has a thick confining unit, consists mostly of silty sands, and has a conductivity of about 1 foot per day.

Hirsh said that two objectives were identified for managing the plume—reducing VOC mass and achieving hydraulic control—and that a variety of remedial technologies were evaluated as potential solutions, including hydrogen release compounds (HRC™), *in situ* chemical reactions, monitored natural attenuation, recirculating wells, and phytoremediation. Significant interest was generated in the latter; therefore, about 200 hybrid poplars have been planted in a horseshoe shape at the site. Before the trees were planted, Hirsh said, an agronomic assessment was performed, a drainage system was installed to divert rainwater off of the burn pits, and monitoring wells were installed. The trees were installed by Applied Natural Sciences, Inc., he said, using techniques that promote vertical root growth. Boreholes were augered, plastic sleeves were installed, two-year-old trees were planted, and boreholes were backfilled. Hirsh said that excavation activities were performed last year to evaluate root growth. For the most part, very little horizontal growth was observed, and the roots appeared to be bound within the borehole. Hirsh said that the trees are growing well at the site, noting that they were about 30 feet tall in 1999. The site was hit by a hurricane in the fall of 1999 and this caused about 30% of the trees to lean over, Hirsh said, but site managers have straightened them.

Hirsh said that groundwater samples are being collected, but that it is too early to determine whether the trees are reducing contaminant concentrations at this site. He said that a number of other parameters are also being monitored to determine how much groundwater the tree plantation is removing from the plume. For example, data are being collected on leaf area, tree diameter, land area, sap flow rates, and a variety of climatological parameters, such as temperature, relative humidity, solar radiation, and wind speed. These data are then used, Hirsh said, to calculate PET and crop coefficients. Based on the calculated values, researchers estimate that each tree is currently taking up about 8 gallons of water per day, and that this value will grow to 12 gallons per day once the canopy closes. Extrapolating, Hirsh said, this suggests that the mature plantation will pump about 2,000 gallons per day. He said that this is only about one-fifth of the pumping rate that is needed to achieve hydraulic control at this particular site.

Hirsh said that transpiration gas is being measured at the site, and that 1,1,2,2-tetrachloroethane and TCE have been detected as offgassing products in at least a couple of trees. (Gases were measured by placing bags over leaves and sealing them. Cold traps were added to some of the bags, but investigators found that these devices had minimal impact on gas measurements.) Hirsh said that flux chambers have also been established to determine whether contaminants are offgassing from soils. Some TCE has been detected in the chambers. Fourier transform infrared (FTIR), another air sampling technique, is also being used to determine whether the plantation, as a whole, is emitting VOCs to the environment at dangerous levels. Results collected to date indicate that this is not the case.

Hirsh said that site managers at the Aberdeen Proving Ground know that phytoremediation systems do raise some ecological concerns. Therefore, soap has been hung on the poplars to deter herbivores from feeding on them. In addition, efforts are being made to determine whether soil functioning is adversely impacted when contaminated leaves degrade on the ground. For example, Hirsh said, nematode populations are being evaluated. Honeybee hives are also being monitored to determine if volatiles are accumulating within them.

Hirsh closed his presentation by talking about modeling efforts that have been performed for the site. He said that these were run under the assumption that phytoremediation, recirculating wells, and natural attenuation would all be working in concert. According to MODFLOW, he said, phytoremediation should have a significant effect on the top portions of the aquifer, but the impact will decrease in deeper layers. He said that three-dimensional modeling was performed so that researchers could estimate how much contaminant would be removed by each technology. Results indicated that 400 pounds would be degraded through phytoremediation, 1,500 pounds by microbial degradation, and 1,950 pounds removed by recirculating wells.

Phytoremediation Systems Designed to Control Contaminant Migration
Ari Ferro, Phytokinetics

Ari Ferro said that researchers believe that tree plantations can be used to prevent subsurface contaminants from migrating. In fact, he said, this theory is currently being tested at a site in Ogden, Utah. The site, Chevron's Light Petroleum Products Terminal, has a dissolved-phase TPH plume located about 6 to 8 feet bgs. (Concentrations have been detected between about 5,000 parts per billion [ppb] and 10,000 ppb.) In April of 1996, Ferro said, a dense stand of hybrid poplar trees was planted perpendicular to groundwater flow. (The design has three rows of poplars. There are about 6.5 feet between rows and about 7.5 feet between trees.) Ferro described the planting method that was used at the site: 8-foot deep boreholes were drilled, long poplar cuttings were placed into the holes, and the holes were backfilled with sand and peat. Ferro said that the trees were planted directly into the saturated zone; thus, from the start, the trees used subsurface groundwater as their water source rather than relying on surface irrigation. Growth has been robust, he said, and the trees are approaching canopy closure. Ferro said that the root structure for one tree was analyzed at the end of the third growing season. A dense proliferation of roots, many extending into the saturated zone, was observed in and around the borehole. Interestingly, the deepest roots did not come from the tree's original pole, which was dead; instead, the deepest roots originated from highly branched roots that were located nearer to the surface.

Ferro said that researchers have generated estimates on the amount of groundwater that is being used by the tree plantation. He said that each tree pumped about 0.25 gallons per day during the second growing season, that this value rose to 11.9 by the fourth growing season, and that it is expected to increase to 17.7 by the end of the fifth season. Ferro said that these values represent the volumetric water used by trees (V_t) minus the amount of precipitation that falls during a growing season. Both parameters have been measured directly at the site; precipitation is measured at an onsite weather station, and V_t is quantified using thermal dissipation probes that measure sap flow. V_t values can also be determined indirectly, Ferro said, using calculations that have the following inputs: PET, crop coefficient, leaf area index, and tree stand area. Ferro said that investigators did use calculations to estimate V_t, and that the results obtained were similar to those identified through direct measurements.

Ferro said that five piezometers have been installed at the Ogden, Utah, site. Some are located upgradient of the trees, some are in the middle of the plantation, and others are downgradient. These were sampled several times between May 1998 and August 1999, and TPH, BTEX, and water levels were measured. The results indicate that contaminant concentrations decrease as groundwater moves through the tree stand. As for water-level measurements, Ferro said, groundwater was not shown to dip during the growing season and this surprised site investigators. (Based on their calculations, researchers expected to find that the trees transpired a volume of water equivalent to an 11-foot thickness of the saturated zone. Using estimated V_t, crop coefficient, and leaf area index values for the fourth growing season, researchers determined that the tree stand would transpire about 480 gallons of groundwater per day. To determine whether transpirational water use by the trees would be significant relative to the total flow of groundwater, researchers used Darcy's Law to calculate the approximate volume of water that flows beneath a vertical cross-section of the site. The rate of groundwater flux through a 1-foot thick vertical cross-section was calculated to be about 44 gallons per day.) Ferro said that he is not sure why water-level measurements failed to show a dip; efforts are underway to identify plausible explanations.

Before closing, Ferro described a phytoremediation project that has been proposed for the Bofors-Nobel Superfund site in Muskegon, Michigan. This site, placed on the NPL in 1989, produced industrial chemicals between the 1960s and 1980s and disposed of waste sludge into 10 lagoons. The lagoons have been drained, Ferro said, but the sludge that remains is highly contaminated with 1,2,4-trichlorobenzene, 3,3,-dichlorobenzidine, 2-chloroanaline, and a variety of other contaminants. Ferro said that site managers want to plant deep-rooted trees in the lagoons in an effort to reduce leachate formation, stabilize contaminants, and promote rhizosphere degradation. The proposal also recommends planting trees and native grasses in the areas between the lagoons in an attempt to minimize rain-water infiltration. In addition, a poplar stand is proposed in another portion of the site to intercept groundwater flow, and revegetation has been proposed for a 9-acre segment of the site. Ferro said that predesign studies are being performed, noting that a small field study was initiated in 1999 to evaluate which planting methods would be best to use and which plants are most tolerant of the site's toxic sludges. He said that a greenhouse study will be initiated in the near future.

Deep Planting

Edward Gatliff, Applied Natural Sciences, Inc.

At most sites, Edward Gatliff said, 80% to 90% of tree roots develop within the first 3 feet of soil. If enough precipitation falls upon a site, he said, roots will not have an incentive to grow much deeper. Thus, Applied Natural Sciences, Inc., has developed "deep planting" techniques to coax plant roots to grow deeper and to tap into aquifers or horizon soils that lie deeper than 3 feet. By using this approach, Gatliff said, site managers can be assured that roots will come into contact with targeted subsurface areas. Gatliff said that Applied Natural Sciences, Inc., developed its first "deep planting" technique in 1990, while working on a site in New Jersey, which had a contaminated aquifer that was located about 16 to 20 feet bgs. Investigators considered using alfalfa to tackle the deep contamination at this site, but soon realized that the site's soil had too much clay for alfalfa roots to penetrate. So, they started experimenting with trees. Since that time, Gatliff said, Applied Natural Sciences, Inc., has identified several types of "deep planting" techniques that can be used. Some of these have been patented.

Gatliff described the process involved with "deep planting." If the top 5 to 10 feet of subsurface are targeted in a phytoremediation project, he said, trees can be installed using a trenching technique. For deeper depths, however, boreholes are drilled, trees are placed inside, and the boreholes are backfilled. Gatliff said that the borehole diameter and depth dictates the type of drill rig that must be used. For example, a three-point auger or a tractor can be used to install boreholes to depths less than 5 feet, but a skid steer with an auger extension is needed to install boreholes up to 10 feet deep. For holes that are drilled between 10 and 20 feet deep, a medium-sized drill rig with an 8-foot stroke can be used, but anything deeper requires a caisson rig. Gatliff said that casings are usually installed in the boreholes, noting that these help to limit preferential shallow root development and surface-water short-circuiting. He said that Applied Natural Sciences, Inc., has experimented with three different kinds—ADS and metal casings, sonotubes, and plastic casings—and found that each has pros and cons. In general, Gatliff prefers plastic casings, because these are cheap and easy to use. He said that casings do not have to be installed in the boreholes, but said that roots have been shown to develop in surficial areas when casings were not included. He said that this does not hold true for all sites, noting that roots grow deep in uncased boreholes that are drilled in areas that have high clay content. Gatliff said that Applied Natural Sciences, Inc., has not yet determined the optimal diameter for boreholes, but believes that they should be greater than 16 inches. At many sites, good results have been obtained with 18-inch boreholes. Gatliff said that trees planted in boreholes can be planted with the rootballs either near the surface or deeper in the subsurface. If the latter approach is used, roots reach targeted depths more quickly and trees are less likely to require irrigation, because their roots tap into groundwater almost immediately.

Gatliff said that trees that have been installed with "deep planting" techniques have been shown to remediate contaminants. For example, at a site in Finley, Ohio, TCE concentrations decreased significantly after a plantation was installed. Trees at this site are clearly tapping into groundwater sources, he said, noting that the trees were unaffected by a serious drought that recently impacted the region.

Gatliff said that he does not know what the depth limitations are for "deep planting" techniques. At some sites, trees have been installed in boreholes that reach 35 feet deep. At the ANL-E site's 317/319 area, he said, Treewells® have been planted in 30-foot-deep boreholes. The Treewell® design, Gatliff said, uses elongated roots, which are pregrown and attached to rootballs. At ANL-E, rootballs were placed about 5 to 10 feet bgs and elongated roots were suspended another 2 to 8 feet. Gatliff said that it may be possible to design systems that penetrate even deeper. For example, he said, acacia trees have been known to extend roots as deep as 100 feet bgs. Roots that grow in sewers have been reported to reach lengths greater than 200 feet.

Gatliff provided rough estimates of the costs that are associated with "deep planting" techniques:

System Description	Costs Per Tree	Costs Per Acre
Target depth of ≤ 10 feet	\$100 to \$300	\$20,000 to \$60,000
Target depth of 10 to 20 feet	\$250 to \$500	\$50,000 to \$100,000
Target depth of > 20 feet	\$500 to \$1,500	\$100,000 to \$300,000

He said that costs can be controlled by using the right methodologies and equipment for a particular site.

Transpiration: Measurements and Forecasts
James Vose, U.S. Forest Service

James Vose opened his presentation by clarifying the definitions of "transpiration" and "evapotranspiration," two terms, he said, that are often used interchangeably. Vose said that transpiration represents the amount of water that trees take up and release to the atmosphere. Evapotranspiration represents transpiration plus evaporation (*i.e.,* the free water in soils and on the surface that undergoes a phase transformation to water vapor). Vose said that the evaporation component is small compared to the transpiration component. Therefore, he focused on transpiration. He described the controlling factors. Climate plays a large role: temperature, solar radiation, vapor pressure, wind speed, and precipitation affect how much water a plant transpires. Also, he said, plant physiology, including stomatal conductance, xylem anatomy, rooting depth, sap wood quantities, and sap wood flow rates, dictate how much water is used. To demonstrate his point, Vose presented a graph that showed that transpiration rates generally increase with increasing sap wood quantities. He asked attendees to note, however, that plant species that have the same quantities of sap wood do not all have the same transpiration rates. This is due, in part, to the fact that plants have different anatomies, which affects how water flows through their sapwood. Vose said that leaf area index and leaf distribution also exert great influence on transpiration rates. In addition, site characteristics play an important role, Vose said, noting that a plant's capability to draw water into its roots is influenced by the accessibility of groundwater sources, the site rooting volume, and the soil water holding capacity.

Vose described the methods that can be used to estimate transpiration rates. At the tree level, he said, transpiration can be measured using weighing lysimeters, leaf-level measurements, and sap flow probes or collars. Once transpiration rates are established for an individual plant, Vose said, these rates are used to extrapolate rates for entire tree stands. He warned, however, that several assumptions must be made to perform the extrapolations, and said that this could compromise the accuracy of predictions. Vose said that there are ways to measure tree stand transpiration rates directly, such as the eddy flux or gauged water shed methods, but said that these techniques do have limitations. For example, both techniques measure whole-system response; thus, it is difficult to determine how much transpiration is coming from trees *versus* herbaceous cover. Vose said that a variety of models, ranging from simple empirical models to complex mechanistic ones, are also available to help investigators predict transpiration rates.

Vose described one site, located in Fort Worth, Texas, that initiated a phytoremediation project in 1996. Whips and one-year-old eastern cottonwoods were planted at this site in an effort to intercept a TCE plume. Starting in 1997, Vose said, data have been collected for a variety of parameters, such as leaf water potential, stomatal conductance, soil moisture release, and climatic conditions. In addition, collars and probes were installed to collect monthly sap flow measurements from about 16 cottonwoods. (More than one probe was used on each tree.) Vose said that the data collected were used to calculate transpiration, and he presented what has been learned over the last few years. He said that transpiration rates in the one-year-old trees were higher than those measured in the whips during the first year of growth, because the former were larger. However, he said, when investigators standardized for tree size, they found that the whips actually had higher sap flow rates. By the end of the second year, Vose said, transpiration rates in the one-year-old trees and the whips were about 6 gallons/day/tree and 1.6 gallons/day/tree, respectively. Vose said that investigators also used PROSPER, a model that has been in existence for about 25 years, to estimate transpiration rates at the site. Initially, he said, the model appeared to do a good job of simulating transpiration; modeled data were in good agreement with measured data. By the second year, however, correlations were not as strong, and modeled estimates diverged significantly from measured values during the driest months of the year. Over the next year, Vose said, he hopes to improve the PROSPER model.

Vose said that extrapolations were made on the measured and modeled data to predict how much water might be transpired across the Fort Worth, Texas, site in future years. Predictions ranged from 500,000 to 2,000,000 gallons/hectare/year. The lower bound, he said, represents what PROSPER estimated as the transpiration rate at a 15-year-old plantation. The upper bound, he said, represents projected transpiration rates in a mature open forest. The rates would be closer to about 1,000,000 gallons/hectare/year, Vose said, if investigators accounted for the shading that will result in a closed canopy situation. Vose said that it is useful to make predictions using a wide variety of methods, because it helps investigators determine the outer boundaries for possible transpiration rates. He is hopeful that models will be improved significantly in the future so that more accurate predictions can be made.

Speaker Panel and Audience Discussion

Audience members asked questions or provided comments about the following topics:

- *Red cedar juniper trees.* Fletcher noted that red cedar junipers, which are evergreens, are growing at the Fort Worth, Texas, site. He said that he thinks these trees might be desirable to use in phytoremediation designs, and asked Vose whether he plans to model performance of these trees. Vose said that he had not planned to do that for this site, but did agree that sites in the Southwest might benefit from having a mixture of conifers and hardwood in their remedial designs.

- *The suitability of using poplars and willows over wide geographical ranges*. J.G. Isebrand, who serves on the International Willow and Poplar Commission, said that it is his job to ensure that willow and polar cultures are exchanged responsibly. He said that he was delighted to learn about the different ways in which these trees are being used in phytoremediation projects. He did caution, however, that trees can fail if they are planted in inhospitable soils or in regions where the trees are prone to disease. He asked meeting attendees to keep this in mind, noting that all efforts should be made to avoid failures—even just a little negative publicity could set back the acceptance of phytoremediation.

- *Biochemical parameters that impact transpiration rates*. McMillan noted that Vose's presentation focused on physical parameters that control transpiration rates. He asked whether biochemical parameters, which have been discussed in the European literature, might also have an influence. Vose said that this could be, but that he was not aware of any that played a significant role. In general, he said, water uptake processes are really dominated by physical processes (*e.g.*, resistances and differences in potentials), as well as anatomical features (*e.g.*, number of stomata, distribution of stomata, amount of sap wood). He said that biophysical processes do control how water is pumped at the cellular level, but speculated that the influence on overall water usage is only minimal.

- *Poplar tree costs*. One meeting attendee asked how much poplar trees cost. Gatliff said that trees cost about $10 to $20, but that whips can be obtained for about $1 to $3.

SESSION VII: VEGETATIVE COVERS

Monitoring Alternative Covers
Craig Benson, University of Wisconsin

Craig Benson said that many people have expressed interest in using vegetated covers as an alternative to prescriptive RCRA-style landfill covers. He said that this is because the latter, which do not always perform well, typically cost a great deal of money. For example, compacted clay caps, which are listed under RCRA Subtitle D, cost about $125,000 per acre and are prone to desiccation cracking, frost damage, settlement, and root intrusion. Other prescribed covers, such as composite-type caps, do perform well, but these cost between $175,000 to $200,000 per acre. Benson said that investigators are confident that effective vegetative covers can be designed for far less money. He said that vegetative covers, like any landfill cover, must (1) prevent physical contact with underlying waste, (2) prevent harmful gas production, and (3) keep water from percolating downward toward groundwater tables. The latter objective, he said, is of paramount importance; he described how vegetative covers achieve it. The covers act like sponges: they have thick soil layers that hold water during dormant seasons, and are sucked dry during the growing season, when plant roots extract stored water. If a vegetative cover is designed so that soil storage capacity is never exceeded, Benson said, water will not leak into underlying wastes. There are two basic types of vegetative covers: monolithic barriers and capillary barriers. While a cap of the former type simply consists of a thick layer of dirt with vegetation on top of it, Benson said, a cap of the latter type has fine textured soils laid over coarser materials. The contrast in texture in the latter design buoys water up in the top layers, making the water more accessible to plant roots.

Benson said that several test covers have been installed under the Alternative Cover Assessment Program (ACAP). One of the main goals of ACAP is to determine whether vegetative covers perform as well as prescriptive designs. This must be determined, Benson said, because RCRA Subtitle D states that percolation from an alternative cover must be less than or equal to percolation from prescriptive covers. At many sites, Benson said, ACAP has installed vegetative and prescriptive covers side by side, believing that this is truly the best way to compare the percolation rates of the two. At some sites, it was not possible to set up side-by-side comparisons, and ACAP was forced to use default equivalency values to determine whether vegetative caps are equivalent to prescribed covers. For composite caps, he said, these values have been defined as 30 millimeters of percolation per year in humid environments and 10 millimeters per year in arid areas. With composite covers, he said, percolation default values are 3 millimeters per year in both humid and arid environments. (Regulatory documents do not list the amount of percolation that is allowed for prescriptive covers. Thus, ACAP had to define these default values.)

Benson said that ACAP is using an elaborate monitoring system at the demonstration sites. Test sections have been set up with lysimeters so that any drainage that leaks through a cover can be measured directly. The lysimeters are like big pans; each sits on a compacted base that is about 10 meters by 20 meters in size. The bottom layer of each lysimeter consists of an impervious geomembrane that is made of a low-density polyethylene. A geocomposite drainage layer lies over the geomembrane and carries any infiltrating water to a collection sump, which in turn shuttles the water to tipping buckets and siphons so that drainage can be measured. An interim soil cover is placed over the drainage layer, Benson said, and a root barrier is placed on top of that. (The barrier has an herbicide; roots that come in contact are redirected, but not killed.) The test cover sits on top of the root barrier. Benson said that careful quality control is performed when lysimeters are installed; for example, geomembrane seams are examined and test systems are filled with water to determine whether leaks are present. Aside from the lysimeters, Benson said, a variety of other monitoring systems are established at ACAP sites. For example, weather stations are set up to collect meteorological data, and a variety of water content reflectometers, thermocouples, and heat dissipation probes are installed. All of the monitoring systems, he said, are wired to solar-powered data loggers, which transmit data to the Desert Research Institute in a near-real-time fashion. These data are collected, organized, and made available to ACAP members *via* the Internet. Users can select specific parameters that interest them, Benson said, and graph the parameters over specified time periods. He said that access to the data is currently limited to those who have passwords, but the data will eventually be made public in published reports.

Growing a Thousand-Year Landfill Cover
William Jody Waugh, MacTec-ERS

Jody Waugh said that the U.S. Department of Energy (DOE) wants to design covers that perform adequately for 1,000 years or more. These kinds of covers are needed to isolate radioactive wastes (*e.g.*, uranium mill tailings and fission products). About 20 years ago, Waugh said, DOE started capping sites under the Uranium Mill Tailings Radiation Control Act (UMTRCA) project. As part of this effort, many sites were covered with compacted soil layers, a fine sand layer, and rock rip-rap. (Caps like this were installed in Tuba City, Arizona; Rifle, Colorado; Mexican Hat, Utah; and Lowman, Idaho.) Some vegetative caps were also installed, Waugh said. Vegetative caps of various kinds were installed at sites in Pennsylvania, Utah, and Colorado. Waugh said that DOE is assessing the lessons that have been learned on the UMTRCA covers, and will take these into account when designing the next generation of DOE covers, which are to be installed at DOE weapon sites. Waugh said that DOE will compile what it has learned in a guidance document on how to design covers for long-term performance. This document will help end users, he said, and will hopefully be embraced by the regulatory community.

Waugh said that all covers are subjected to dynamic ecosystems, and that a site's ecology changes over the long term. Thus, it is not realistic to use data from a short field study to predict cover performance in future centuries. More accurate predictions can be made, he said, if monitoring efforts, modeling efforts, and analog studies are combined to make these estimates. The latter involves evaluating natural or archaeological settings. By looking at analogs, Waugh said, researchers reconstruct the past and collect clues that can be used to predict what will happen in the future. He said that researchers can use analogs to gain an understanding of how pedogenesis (*i.e.,* soil development), ecological change, and climatic change could impact covers. With this information in hand, DOE might be able to design covers that endure changing conditions over the centuries. If so, this may save DOE billions of dollars in stewardship costs.

Waugh said that pedogenesis could affect the physical and hydraulic properties of a cover over time. He said that designers can obtain an idea of how their engineered caps might develop if they evaluate natural or archeological settings that have soil profiles similar to the engineered soils. For example, he said, researchers were able to predict how soil would develop in a cover that was installed in Monticello, Utah, by analyzing how soils developed in Anasazi pit houses that were abandoned about 800 to 1,000 years ago. Also, he said, by evaluating a natural capillary barrier that formed in the state of Washington, researchers learned about the water-holding capacity of a certain soil that was used at the Hanford DOE site. This natural barrier, which has a soil profile that is about 13,000 years old, has fine materials deposited over a coarse layer. Waugh said that carbonates, which serve as tracers for water movement, were found on the coarse materials. This means that the thin layer of fine soil was not thick enough to prevent downward percolation. Thus, if this material were used in a vegetative cover design, the layer would have to be made thicker.

Waugh said that ecological changes, such as plant succession and biological intrusion, can have dramatic impacts on a cover's evapotranspiration rate. He said that analogs were used to predict the impact of preferential flow on a cover that was installed in Pennsylvania. This cover has a clay layer that is overlain by a layer of sand and a layer of rock. Plants have penetrated the top two layers and have started establishing in the clay layer. *In situ* saturated hydraulic conductivity was measured in areas that had plants, as well as areas that had not been invaded. Values were about 10^{-7} cm/sec in the plant-free areas, but were two orders of magnitude higher near Japanese knotweed plants. Waugh said that the values detected near the plants were close to what was measured at an analog site that also had plants established. He also said studying natural environments has helped researchers at the Hanford site determine what potential vegetation patterns could emerge if area soils were incorporated into cover design. In addition, studies have been performed at an UMTRCA site near Lakeview, Oregon, to determine how leaf area index values change when plants invade an area.

Waugh said that climatic changes also occur over the long term, and that changes in meteorological parameters could have dramatic impacts on cover performance. Thus, when designing a cover to perform over the long term, researchers should evaluate natural paleoclimate analogs to obtain reasonable estimates of how climate could change in a certain area in the future. That way, the range of climate changes in the past can be entered as bounds in design models. Waugh described how climatic conditions in the Four Corners area were reconstructed. He said that pollen cores, packrat middens, and other proxy climate data were used to reconstruct past plant populations, and this helped to determine what past climates were like.

Tree Covers for Containment and Leachate Recirculation
Eric Aitchison, Ecolotree, Inc.

Eric Aitchison described the Ecolotree® Cap, a patented containment system designed to achieve hydraulic control. This cap, which consists of densely planted hybrid poplars and a grass understory, acts like a sponge, holding moisture during dormant seasons and then drying out during the growing season. Aitchison said that poplars are used in the Ecolotree® Cap because these trees grow fast, tolerate a variety of environmental and chemical stressors, develop deep and dense root systems, are relatively easy to plant and maintain, can be grown from cut stumps, and can be used as a cash crop. Aitchison said that Ecolotree® Caps have been installed at several sites across the county. He described six of them:

Ecolotree® Cap Projects
Lakeside Reclamation Landfill in Beaverton, Oregon: The first Ecolotree® Cap, designed to cover a 3-acre area with 11,000 hybrid poplars, was installed at this site in 1990. About 90% of the trees survived, and trees grow about 5 to 8 feet each year. Tree roots have grown through a 4-foot-thick soil layer and have penetrated the site's wastes. No contaminants have been detected in monitoring wells since the cap was installed. The site owner is happy with the system, and recently received approval to extend the cap over the entire site. The Ecolotree® Cap has also improved aesthetics and has attracted wildlife. The site owner has brought sheep in to graze among the trees.
The Bluestem Landfill in Cedar Rapids, Iowa: At this site, an Ecolotree® Cap was compared to a prescriptive cover that the Iowa Department of Natural Resources approved. Soil moisture was measured with reflectometers between November 1995 and October 1996. At all times, soil moisture was lower in the Ecolotree® Cap than in the prescribed cover. (Soils did not exceed the water-holding capacity in either cap.) In addition to achieving environmental objectives, the Ecolotree® Cap served a secondary purpose: the trees trapped and prevented litter from blowing off site.
PAH-contaminated site in Tennessee: Before planting, compost was spread over this site to improve soil fertility and water-holding capacity. The Ecolotree® Cap is expected to serve three purposes at this site: (1) achieve hydraulic control, (2) stabilize soil, and (3) enhance rhizosphere degradation.
Landfill in Seattle, Washington: The Ecolotree® Cap will not be able to achieve complete hydraulic control at this site because it receives too much winter rain. Modeling has been performed; the results suggest that the cap could reduce leachate production by 50%. For this site, regulators decided that this partial reduction is sufficient. So, the cap was installed over 13 acres in April 2000. The project cost about $600,000. Site owners believe that a geomembrane would have cost about $3,000,000 to install at this site.
Military base in Georgia: A side-by-side comparison is being performed between the Ecolotree® Cap and a prescribed cover. This work is being performed under ACAP.
Landfill in Michigan: Site owners told Ecolotree, Inc., representatives that the site's soils were suitable for plant growth. Thus, an Ecolotree® Cap was installed over a chemical waste landfill. When only 30% of the trees survived, a more detailed soil and groundwater sampling effort was conducted. Results showed that the site has high salinity and pH values. Greenhouse studies were performed to determine whether amendments could make the soils fertile. Results are promising, but site owners have not yet decided how to move forward

Aitchison also described the Ecolotree® Buffer, which was patented in summer 2000. In this system, he said, plants are exposed to contaminated water in a flow-through fashion. For example, waste water or leachate is used as irrigation for Ecolotree® Buffers. Aitchison described three sites where Ecolotree® Buffers have been used:

Ecolotree® Buffer Projects
Riverbend Landfill, McMinnville, Oregon: About 35,000 hybrid poplar trees were planted over 17 acres in 1992 and 1993. Ammonium-rich leachate is shuttled from a collection pond to the tree plantation and used as irrigation water. In the fourth growing season, about 860,000 gallons of leachate were applied to each acre of the plantation, and about 460 pounds of nitrogen was added per acre. By the end of the growing season, only about 30 pounds of nitrogen were found in the soils. (Investigators know that the nitrogen is not simply being flushed out of the system because Time Domain Reflectometry probes have been installed to determine whether water is moving downward.) Roots were shown to extend about 7 feet bgs, and leaf matter was also detected at this depth. It is believed that worms are dragging the organic material down, and that this will improve soil fertility and water-holding capacity. Ecolotree, Inc., and CH_2M Hill received an award for this project.
City of Woodburn Wastewater Treatment Plant: About 17,000 hybrid poplars were planted over 10 acres in 1995. In 1999, the project was extended over a 90-acre area. The goal was to remove thermal energy and ammonium from treated wastewater. Wastewater was used to irrigate the site during the summer months. Ecolotree, Inc., and CH_2M Hill received an award for this project.
GRRWA Landfill, Fort Madison, Iowa: About 6,800 hybrid poplar trees were planted over 6 acres in 1997 and 1998. Site managers installed the system in an effort to treat leachate in a cost-effective manner. Before installing the Ecolotree® Buffer, the managers paid about $150,000 annually to dispose of 7,000,000 gallons of leachate. After installing the plantation, site owners only had to dispose of 50,000 gallons. The trees transpired or absorbed the remainder. Leachate was sprayed right onto tree leaves. This burned the leaves, so site managers started irrigating at night so that materials would not get baked onto the leaves. Stanley Consultants and Ecolotree, Inc., received an award for this project.

EPA Draft Guidance on Landfill Covers

Andrea McLaughlin and Ken Skahn, EPA, Office of Emergency and Remedial Response

Andrea McLaughlin described regulatory frameworks, and explained what site managers must do to obtain approval to use alternative covers. Under the EPA Liquids Management Strategy, she said, landfill owners are expected to detect, collect, and remove any leachate that is generated in their landfills. In addition, owners are expected to prevent leachate generation by preventing liquids from percolating through waste materials.

McLaughlin described what is expected of landfills that are closed under RCRA Subtitle D. First, she said, permeability of bottom layers must be greater than or equal to those of top layers. Also, permeability rates may not be greater than 1×10^{-5} cm/sec. McLaughlin said that federal regulations explicitly indicate that state officials can approve alternative covers as long as the cap is able to achieve equivalent reductions in infiltration (*i.e.*, permeability must not exceed a rate of 1×10^{-5} cm/sec). McLaughlin said that some states may have even stricter performance standards. For example, in Illinois, covers must be designed so that they do not exceed infiltration rates of 1×10^{-7}cm/sec. McLaughlin said that covers that are selected for CERCLA-mandated landfills are expected to meet ARARs—standards or requirements that are specified under federal laws or promulgated under state environmental laws. According to federal regulations, she said, alternative covers may be used at CERCLA sites in states that already have provisions for alternative covers written into state law. If no such provision exists, alternative covers can still be considered as a potential remedial approach if ARAR waivers are obtained. These waivers can be obtained, she said, if an alternative cover is shown to perform at least as well as prescribed covers. To prove this, site owners must show that the alternative cover infiltration rate does not exceed the minimum permeability rate that is defined under RCRA Subtitle D. McLaughlin stressed that alternative covers must be able to meet the minimum permeability standards at all times, rather than over an averaged period. If an ARAR waiver is obtained, and an alternative cover meets the nine criteria of the National Contingency Plan, then the cover will be considered a viable remedial approach.

McLaughlin said that two EPA guidance documents are being developed under the EPA Liquid Management Strategy. One will address the use of alternative covers at CERCLA municipal landfills, and the other will provide comprehensive technical guidance on RCRA/CERCLA final covers. Ken Skahn is leading the effort to develop the latter, McLaughlin said. She turned the remainder of the presentation over to him.

Skahn said that EPA's technical guidance on RCRA/CERCLA final covers will be released in about 18 months. It will serve as an update to a previous guidance document that was written in 1991. He said that an update is needed because existing RCRA guidance documents do not discuss landfill gas managment, performance monitoring, or long-term maintenance. In addition, existing documents do not discuss alternative covers or list cover materials (*e.g.*, geocomposite clay liners and new drainage materials) that have become available over the last decade. Skahn said that it is important to discuss new materials because some state regulatory agencies are reluctant to use new materials until the materials are officially acknowledged by EPA. Skahn said that the revised guidance document will cover the following topics: regulatory requirements, design considerations, alternative designs, water balance models, geotechnical analysis and design, lessons learned, and long-term maintenance. He said that the document will explain that alternative covers can be used if the covers demonstrate equivalency, and that this can be proven either with predictive models or side-by-side demonstrations. Skahn said that the document will explain that covers can be designed to last for long periods if designers select appropriate materials and address slope stability, erosion, long-term maintenance, and flow capacities for internal drainage systems. In addition, the document will encourage designers to take the following steps: (1) determine if gas collection is necessary, (2) identify critical infiltration events, (3) calculate minimum storage capacity, (4) characterize soil properties, (5) identify appropriate cover thickness, (6) consider amending surface soils and installing vegetation, and (7) use predictive modeling to establish the adequacy of proposed designs.

Activities at an EPA Region 3 Site
Donna McCartney, EPA, Region 3

Donna McCartney described a site that received wastes from a chlorine manufacturer, a PCB manufacturer, and a neighboring facility for more than a decade. These wastes were disposed in two disposal impoundments. In February 2000, she said, approval was granted to test a vegetative cover as a potential containment measure for this site. Site managers are hopeful that the cover will reduce infiltration, mitigate erosion, eliminate direct contact with wastes, and promote contaminant degradation. The cover will be analyzed over a three-year period; if proven effective, the cover may be considered as a viable remedial approach during final remedy selection.

Speaker Panel and Audience Discussion

Audience members asked questions or provided comments about the following topics:

- *Measuring performance.* One attendee called attention to one of the comments that McLaughlin made during her presentation: alternative covers are expected to meet RCRA Subtitle D permeability standards at all times. He thought this was excessively strict, and asked whether the regulations would permit momentary lapses following extreme weather events, such as a 500-year rain. McLaughlin said that the regulations imply that no exceedences are acceptable. She recommended designing covers so that they are able to perform effectively during extreme events.

- *Percolation rates* versus *amounts*. Rock said that the regulations list percolation rates that cannot be exceeded, but that these rates are not translated into actual amounts. He said that it is difficult to measure rates in the field. Thus, many investigators are measuring drainage amounts instead, and performing side-by-side comparisons to determine whether vegetative caps are equivalent to prescribed covers.

- *Guidance documents for alternative covers*. Erickson asked whether guidance documents have been produced on vegetative cover designs. Waugh said that DOE created a guidance document that describes how to design UMTRCA covers. In addition, he said, DOE plans to release another guidance document in about three or four years. Rock said that ACAP has not developed guidance documents yet. Both he and Benson stressed that vegetative cover designs are very site-specific; one design cannot be applied to all sites. Aitchison agreed that vegetative cover designs are site-specific, but said that it might be possible to make some general design recommendations at this point. For example, he said, it might be realistic to say that the top layers of a vegetative cover should never be less than 18 inches thick. If thinner layers are used, he said, plants might be killed by high methane levels.

SESSION VIII: DEGRADATION OF ORGANIC COMPOUNDS IN SOILS

Remediation of Petroleum Contaminants Using Plants

M. Katherine Banks, Purdue University

Kathy Banks said that grasses can be used to remediate petroleum contaminants by enhancing microbial activity in the rhizosphere. She described studies that have been performed at three different field sites: Craney Island, Virginia; Port Hueneme, California; and Bedford, Indiana.

Banks said that sediments at the Craney Island site, a large 16-acre landfarming facility, are contaminated with diesel fuels. A portion of the site was used in a phytoremediation demonstration project, she said, and four treatments were evaluated: tall fescue, Bermuda grass with annual rye, white clover, and nonvegetated controls. Banks said that six replicates were included in the study design and that all plots were fertilized and irrigated as needed. Over a two-year period, aboveground biomass quantities were assessed, plant tissue samples were analyzed, and soil samples were analyzed. These analyses revealed that: (1) all of the plants were able to grow in the site's contaminated soils, (2) contaminants did not accumulate within plant tissues, and (3) plants did induce statistically significant contaminant reductions—the clover remediated more TPH than the other plants. Banks said microbial analyses were performed on soil samples using a variety of techniques. For example, researchers evaluated total plate counts to determine whether plants stimulated enhanced microbial activities, performed BIOLOG analyses to assess the functional diversity of microbial communities, and used most probable number (MPN) procedures to evaluate the proliferation of petroleum degraders. The results showed that planted treatments exhibited a higher degree of functional diversity and that MPN values were highest in clover treatments.

Banks said that a demonstration project was also performed at the Port Hueneme site, which had heavily weathered soils that were contaminated with fuel oil. Three treatments were tested: (1) fescue and legume, (2) California roadside mix, and (3) nonvegetated controls. Banks said that four replicates were included in the study design, all plots were fertilized and irrigated as needed, and samples were collected over a 30-month period. Most of the analyses described for the Craney Island site were also performed at Port Hueneme. In addition, efforts were made to assess ecological toxicity. Researchers found that: (1) plants were able to grow in the site's contaminated soils; (2) plants did induce statistically significant contaminant reductions (the fescue remediated PAHs more efficiently than the California roadside mix); (3) microbial activity was enhanced in the planted treatments; (4) the vegetated plots had a higher number of pseudomonads; (5) soils, which were slightly toxic at the beginning of the project, were considered nontoxic after treatment; and (6) the different treatments exhibited no difference in lettuce germination rates, which are used to measure toxicity, over the long term.

Banks said that a field study was recently initiated at a former manufactured gas plant in Bedford, Indiana. PAH concentrations are very high at this site, she said, and the contamination is about 3 to 6 feet bgs. Phytoremediation is being tested at this site, along with three other types of remedial systems: natural attenuation, land farming, and composting. Banks said that poplars and a grass understory, which are being irrigated and fertilized as needed, are being used in the phytoremediation plots. Researchers will determine how effective the planted treatments are by comparing these treatments to the natural attenuation plots. Banks said that the water table is high at this site, and that researchers hope the poplars will lower the water table so that more of the subsurface can be oxygenated and treated *via* natural aerobic degradation. Banks said that soils will be collected over a three-year period and analyzed for contaminants, microbial characteristics, and toxicity. Some preliminary data do suggest that the soils in the planted plots are becoming less toxic.

Banks said that phytoremediation sites must be managed, noting that contaminant reduction rates leveled off when investigators stopped fertilizing, irrigating, and removing invading species at the Craney Island site. In the greenhouse, Banks said, Stacy Lewis Hutchinson has shown that there is strong correlation between contaminant degradation rates, fertilization rates, and irrigation. In one of Hutchinson's studies, four types of irrigation—surface, continuous, cycling, and subsurface—were evaluated to determine whether using different application methods impacts degradation rates. Hutchinson found that degradation rates were highest when the subsurface irrigation was applied. Banks said that these are just preliminary results, and said that she hopes Hutchinson will perform additional experiments to back up her findings.

In closing, Banks summarized some of the research that Purdue University will perform over the next five years. Significant efforts will be made to evaluate microbial communities and identify the rhizosphere conditions that foster degradation. Banks said that she plans to evaluate microbial diversity, and suspects that researchers may be able to use this as an indicator to measure the remedial potential of a plant. In addition, the University will evaluate: (1) how plants affect soil toxicity, (2) the fate of PAH in the rhizosphere, (3) depth limitations for phytoremediation, and (4) using phytoremediation as a polishing tool.

Phytoremediation of Explosives
Phillip L. Thompson, Seattle University

Phillip Thompson said that several experiments have been performed to determine whether plants can be used to remediate explosives. For example, in the early 1980s, researchers evaluated the capability of yellow nutsedge to take up TNT. Uptake of this contaminant, as well as RDX, was also investigated in the late 1980s, in studies that the Pacific Northwest Laboratory performed using bush bean, maize, and wheat. Also, the University of Nebraska has evaluated the uptake of explosives in tall fescue and switchgrass. In recent years, Thompson said, the University of Iowa and Iowa AAP worked together to determine whether poplars can be used to remediate low concentrations of TNT and RDX.

Thompson provided brief chemical profiles for TNT and RDX. The former, which is a mutagen, has a Log K_{ow} of 1.9, a solubility of 100 mg/L at 25° C, and an electron-deficient ring. Aerobic degradation pathways have been identified for TNT and are documented in bioremediation and microbial remediation literature.

RDX, which has been shown to cause central nervous system disorders, has a Log K_{ow} of 0.9, a solubility of 40 mg/L at 25° C, and a saturated ring. Unlike TNT, RDX does not degrade readily under aerobic conditions.

Thompson said that treatability studies have been performed to determine how TNT and RDX impact poplar growth. In the laboratory, RDX was shown to be nontoxic, but trees experienced adverse effects when exposed to 5 mg/L of TNT. When the same experiment was performed in the greenhouse, with larger trees and under more natural sunlight conditions, the poplars were able to withstand higher TNT concentrations.

Thompson said that mass balance studies have been performed to determine how poplars affect the fate and transport of TNT. Excellent mass recovery rates (about 95%) were exhibited in these experiments. Results indicated that 70% of TNT accumulates in plant roots, and that much smaller amounts accumulate in shoots and leaves. Transformation products were measured, Thompson said, noting that about 50% were bound residue and could not be extracted. Of the other 50%, he said, only about 10% could be identified. Many of the products identified in the roots were those that form under aerobic degradation. Most of the products in the leaves were unknown polar compounds. These might represent novel oxidative products, Thompson said; if so, this suggests that plants create transformation products other than those identified in aerobic microbial-mediated degradation pathways.

Thompson said that mass balance studies were also performed using RDX, but that recovery rates were only about 80%. This may have been because the RDX used in the study was not pure and/or because some of the RDX was phytodegraded and transformed into formic acid within the leaves. Thompson was not sure whether the latter is occurring, but said this has been suggested as a potential fate for RDX in preliminary studies by other researchers. Thompson said that the fate of RDX differs markedly from that of TNT. About 65% to 70% of the RDX that was used in mass balance studies accumulated in plant leaves. Thompson said that this finding could raise some regulatory concern about high RDX concentrations. He did stress, however, that results that are obtained in the laboratory do not necessarily indicate what will be observed in the field. To demonstrate his point, he noted that poplars have been established as part of a phytoremediation effort at the Iowa Army Ammunition Plant. So far, he said, RDX has not been detected in tree leaves at the site. He said that this may be because RDX concentrations in the soil are very low, or because RDX in the leaves is being transformed to formic acid.

Thompson said that he has used models to predict how TNT and RDX would degrade if one contaminated acre was treated with about 600 to 700 poplar trees. He said that the following parameters were used to estimate uptake: TSCF, transpiration rates, and porewater concentration. (Thompson stressed the importance of accounting for the latter, noting that this parameter is often overlooked.) Also, he said, the following assumptions were made: contaminants are located in the top 3 feet of soil, bulk density is 1,500 kg/m^3, porosity is 0.3, contamination is homogeneous across the site, there is instantaneous desorption of contaminants, 10 to 20 gallons of water is transpired per day by each tree, and microbial influences are negligible. The results of this modeling effort, he said, suggest that TNT and RDX would have half-lives of 20 years and 5 years, respectively.

In closing, Thompson listed some issues that require further investigation. First, he said, researchers should evaluate how natural conditions affect RDX concentrations in leaves. It would also be wise, he said, to evaluate the toxicity of plant tissues by feeding leaves to snails and worms. In addition, he said, efforts should be initiated to determine how microbial/mycorrhizal associations affect phytoremedial systems. Thompson also recommended performing studies to determine how effective phytoremediation is at sites that are contaminated with a variety of different contaminants. Lastly, he said, researchers must gain a better understanding of the true time frames that are associated with phytoremedial systems.

Case Study: Union Pacific Railroad
Felix Flechas, EPA, Region 8

Felix Flechas opened his presentation by summarizing regulatory issues that must be considered when deciding whether phytoremediation is appropriate to use at a particular site. First, he said, the technology should be evaluated against the nine criteria of the National Contingency Plan. Flechas described the nine criteria, splitting them into two categories: selection criteria and balancing criteria. The former, he said, are the most important. They state that selected remedies must: (1) protect human health and the environment, (2) comply with applicable rules and regulations, (3) control sources of release, and (4) attain cleanup standards. Flechas said that it is not always possible to identify a remedy that can meet the latter criteria. For example, he said, if a site has NAPL concentrations or a karst formation, available technologies may not be capable of cleaning the site to meet applicable standards. In these cases, he said, Technical Impracticability Waivers can be obtained. Flechas also listed the five balancing criteria: (1) long-term effectiveness and permanence; (2) reduction of toxicity, mobility, or volume with a preference towards treatment; (3) short-term effectiveness; (4) implementability; and (5) cost.

Flechas said that phytoremediation can be used as a treatment technology, an immobilization technology, or a containment technology. Before presenting a proposed remedy to a regulator, he said, site managers should make sure to clearly define the functionality of the remedy. In addition, he said, site managers should identify an approach that can be used to track progress. He acknowledged that it may take several years for plant-based systems to achieve cleanup goals, but said that regulators will probably want periodic assurances that the remedy is working. At CERCLA and RCRA sites, he said, remedies will be evaluated every five years. In order to show that statistically significant contaminant reductions are occurring, site managers will need to collect extensive baseline data and fully characterize heterogeneities at the site. Before initiating field studies, Flechas said, site managers should create detailed sampling and analytical plans. If they do not, they have little hope of demonstrating statistically significant results. Flechas said that site managers must also be prepared to address ecological concerns. He said that EPA has created a guidance document for baseline ecological assessments; this document can be used to determine whether installing a phytoremediation system will create new ecological hazards. Flechas said that site managers should also make sure that they understand the needs of the community. If eager for green spaces to be created, the public may be very accepting of phytoremediation. However, if community members are hoping to redevelop a site for commercial use, they may want more aggressive technologies used so cleanup goals can be achieved quickly.

Flechas described a phytoremediation demonstration project that has been proposed for the Union Pacific Railroad site. This site, located in Laramie, Wyoming, was used as a railroad tie treatment plant for about 100 years. About 10 million gallons of creosote have been released over a 90-acre area, he said, and high polynuclear aromatic hydrocarbon and pentachlorophenol concentrations have been detected at this site. Flechas said that phytoremediation is just one of several technologies that are being used to clean up the site. For example, about 2 miles of slurry wall have been installed around the site to achieve hydraulic isolation. Also, a dual drain line system was installed to recover about 3.5 million gallons of creosote. Amendments have also been used in an effort to remediate drained surface impoundment areas.

Flechas said that unsaturated soils at the Union Pacific Railroad site are highly contaminated. Some of these areas, he said, are located near a proposed bike path area. Also, the soils occasionally travel to a nearby river *via* overland flow. Thus, there is strong incentive to clean up the site soils. Risk analyses have been performed on the soils. Results indicate that areas near the river posed cancer risks in the 10^{-6} or 10^{-7} range, but other areas pose risks in the 10^{-4} range. Both areas will be addressed through phytoremediation, he said, but the latter will be covered with 18 inches of clean soil first. Flechas said that four different treatments will be applied to the site: (1) cottonwood and willow trees, (2) hackberry bushes, (3) alfalfa, and (4) dryland grass mixture. The demonstration project will be performed over 20 years and evaluated every 5 years. Site managers have agreed to measure the following through the course of the demonstration project: plant survival and growth, vegetative cover, groundwater extraction rates, soil oxygen levels, rooting depths and density, soil organic matter, and contaminant concentrations. In addition, he said, site managers have agreed to think about restoration goals and beneficial site reuse.

Phytoremediation in Alaska and Korea
Charles (Mike) Reynolds, U.S. Army Corps of Engineers

Mike Reynolds said that the Cold Regions Research and Engineering Laboratory has established several phytoremediation demonstrations on former military sites that are located in cold regions. Many of these sites are contaminated with petroleum hydrocarbons, he said; remediating these cold-weather sites has been a challenge, because the sites are located in remote areas and often have limited infrastructure. In recent years, he said, researchers have started experimenting with phytoremediation at these sites. This is viewed as a reasonable solution because the approach is cheap, relatively easy to install and maintain, and can be installed over permafrost. It is not yet clear how these phytotechnologies will perform at these sites, however. Reynolds said that it will likely take several years to achieve cleanup goals, especially since the growing season at these extreme northern sites is short.

Reynolds presented contaminant degradation curves that are observed in phytoremediation projects. These curves typically exhibit an initial lag, he said, in which no contaminant concentration reductions are detected. (He said that researchers are interested in finding ways to minimize the lag time.) Then, contaminant concentrations decrease steadily for a while before reaching an asymptotic plateau. In some cases, Reynolds said, this asymptotic level falls above site cleanup standard. If this is the case, some regulators might regard phytoremediation to be a failure at a particular site. Reynolds questioned the legitimacy of such a conclusion, noting that he is not sure that contaminant concentrations are the most appropriate endpoints for measuring success. He said that some researchers believe that ecological endpoints should be used to define success instead. For example, he said, it might be more meaningful to use microbial diversity as a measure of success. He advised looking at the health of the overall community when trying to determine whether phytoremediation has been a success.

Reynolds said that a phytoremediation project has been installed at the Farmers Loop site in Fairbanks, Alaska. Soil samples have been collected from the site and microbes have been analyzed using different methods. All of the results point to the same conclusion: there is more microbial diversity in planted treatments than there are in unplanted treatments. Reynolds said that researchers believe that this diversity indicates that the system is becoming "healthier," either from reduced contaminant-caused stress, reduced bioavailability of the contaminant carbon, or both.

Reynolds said that efforts are underway to determine whether microbial diversity can be correlated with reductions in contaminant concentration. He said that phytoremediation projects have been initiated at five sites (three in Alaska and two in Korea), and that chemical and microbial data are being collected from these sites. At all of the sites, he said, four treatments are being evaluated: unplanted/fertilized, unplanted/unfertilized, vegetated/fertilized, and vegetated/unfertilized. Reynolds said that three of the sites are being evaluated in conjunction with the Remediation Technologies Development Forum's (RTDF's) TPH in Soil Subgroup, and chemical analyses are being performed in accordance with the Subgroup's protocol. He said that the percent of TPH degradation at these sites will be measured using a recalcitrant biomarker (*i.e.*, hopane) to normalize data. Using this approach helps investigators obtain meaningful results at sites that exhibit much variability. Reynolds summarized some of the data that have been collected from the sites in Alaska. At one site, he said, no contaminant concentration reductions were detected after the first year of plant growth, but researchers did find that microbial degraders are more abundant in unplanted/fertilized and planted/fertilized treatments. At two sites in Korea, Reynolds said, he observed no plant or fertilization effects on hopane-normalized TPH depletion relative to the controls, but using Gas Chromatography/Mass Spectography data, a clear vegetative effect was observed on the heavier PAH fraction compounds at both sites. These data agree with observations seen in laboratory studies using field soils, where degradation of heavy-end PAH was most robust in the planted/fertilized treatment. In general, Reynolds said, he has found that phytoremediation exerts the greatest benefits on heavy, more recalcitrant compounds, and that benefits are somewhat less pronounced for the lighter compounds that are relatively easy to degrade.

Reynolds reiterated a point that Banks made during her presentation: fertilization may have profound impacts on the efficacy of phytoremediation systems. At the sites that he has worked on so far, he said, fertilization has been applied to meet agronomic needs, but little thought has been given to managing fertilizer in an attempt to optimize degradation rates. He said that he plans to give this issue more attention in the near future.

Speaker Panel and Audience Discussion

Audience members asked questions or provided comments about the following topics:

- *Focusing on microbial diversity*. Fletcher commended Banks and Reynolds for their interest in learning more about microbial diversity in the rhizosphere. He reiterated that changes in microbial communities may serve as good indicators that phytoremediation is working.

- *Identifying microbes that are associated with specific plants*. Erickson asked Banks whether she proposes identifying the individual microbes that are associated with different plants. Banks said that she thought this would be too research-intensive. She thinks it might be more useful to focus on whole microbial communities. That is, she proposes determining which plants are able to create microbial communities that promote degradation.

- *Plant selection for cold-weather regions*. One meeting attendee noted that some of the sites that Reynolds is working on are located above the Arctic Circle. He asked how Reynolds selected species for his phytoremediation projects, and whether it was difficult to find plants that perform well under Arctic conditions. Reynolds said that the Alaskan sites are being evaluated under the RTDF TPH in Soil Subgroup; thus, plants were chosen to fit in with the Subgroup's protocol. McIntyre said that he recently found a Ph.D. thesis that lists about 150 plants that grow well in the eastern, central, and western Arctic. He said that he would share this paper with Reynolds.

- *Guidance documents for plant selection*. Erickson asked whether guidance documents have been produced on plant selection. Banks said that she did not know of any, and that she thought it was too early to create such a document. Reynolds said that it might be a good idea to start keeping a list of the plants that do not work. McIntyre reminded meeting attendees that plants are currently cataloged on two databases: Phytopet and Phytorem.

- *Remedy selection.* Burken asked Flechas whether regulators consider the aesthetic and restorative benefits of phytoremediation when choosing a remedial technology for a site. Specifically, he asked whether these two benefits could sway a regulator to accept phytoremediation over a faster-acting approach. Flechas said that these factors might be considered, but said that the weight they would be given would differ from site to site.

CLOSING REMARKS

Joan Colson thanked everyone for attending the meeting, and gave special thanks to all of the speakers, poster presenters, organizers, and everyone who helped plan the meeting.

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