EMERGING TECHNOLOGIES FOR THE REMEDIATION OF METALS IN SOILS

PHYTOREMEDIATION

-FINAL-

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Prepared by
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Metals in Soils Work Team
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ABOUT ITRC

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DISCLAIMER

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EXECUTIVE SUMMARY

Phytoremediation is the treatment of contaminated soils, sediments, and groundwater by plants. Phytoremediation is applicable for the treatment and / or removal of organic or inorganic contaminants in soil or groundwater. This document focuses on issues related to the remediation of metals in soils. The document outlines the technology and its applicability to sites and contaminants. It also explores several approaches to phytoremediation, as well as areas where future research is needed. The document presents regulatory and stakeholder concerns, and details preliminary cost figures from a variety of sources.

Membership on this work team was open to all ITRC members. Participants with expertise or interest in metals treatment technologies in their states elected to join the team and contributed consistently to the development of this work product. Members of the RTDF (Remediation Technologies Development Forum) IINERT technology team (In-Place Inactivation and Natural Ecological Restoration Technologies) also participated in this team and helped to provide an industry perspective. A representative from the U.S. Army Corps of Engineers and the Department of Energy actively participated on the team. Support was also provided by the United States Environmental Protection Agency and the Department of Defense. Input regarding public and community concerns for these technologies was provided by ITRC public stakeholder representatives.

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PHYTOREMEDIATION

1.0 INTRODUCTION

Soils, aqueous waste streams and groundwater contaminated with metals pose an environmental and human health hazard. Bioremediation, the use of living organisms to treat contaminants, is increasingly favored by both the public and private sectors as an alternative method for waste treatment due to its low costs and minimal secondary environmental impact. *Phyto-(or green plant based) remediation* technology is being developed to improve upon traditional remedial efforts.

1.1 Background

Phytoremediation is the treatment of contaminated soils, sediments, and groundwater by plants. The technology involves a variety of biological mechanisms including direct uptake, release of exudates and metabolites, and stimulation of the root-soil environment (rhizosphere) to enhance bacterial and fungal degradative processes. Phytoremediation applies to all biological, chemical, and physical processes that are influenced by plants and that aid in the cleanup of contaminated substances. **Figure 1** presents a schematic of a typical phytoremediation process.

Phytoremediation has been used to treat wastewater for more than 300 years, and plant-based remediation methods for slurries of dredged material and soils contaminated with heavy metals have been proposed since the 1970's [1,2]. Phytoremediation can be developed for different applications in environmental cleanups, and can be classified into three areas: phytoextraction, phytostabilization and rhizofiltration. Phytoremediation can be applied not only for treatment of organic contaminants in contaminated media but also for removal and stabilization of metals in soil and groundwater. This paper will deal with the application of phytoremediation technology for soils contaminated with metals.

1.2 Applicability

Phytoremediation is most applicable at sites with low to moderate metals concentrations, relatively shallow depths of contamination, and soil media favorable to plant growth. In many cases, phytoremediation may be used as a follow-up technique to remediate low level concentrations remaining from initial phase remedial approaches. If metal concentrations in soil exceed certain threshold limits, plant growth may not occur, however, without the addition of soil amendments.

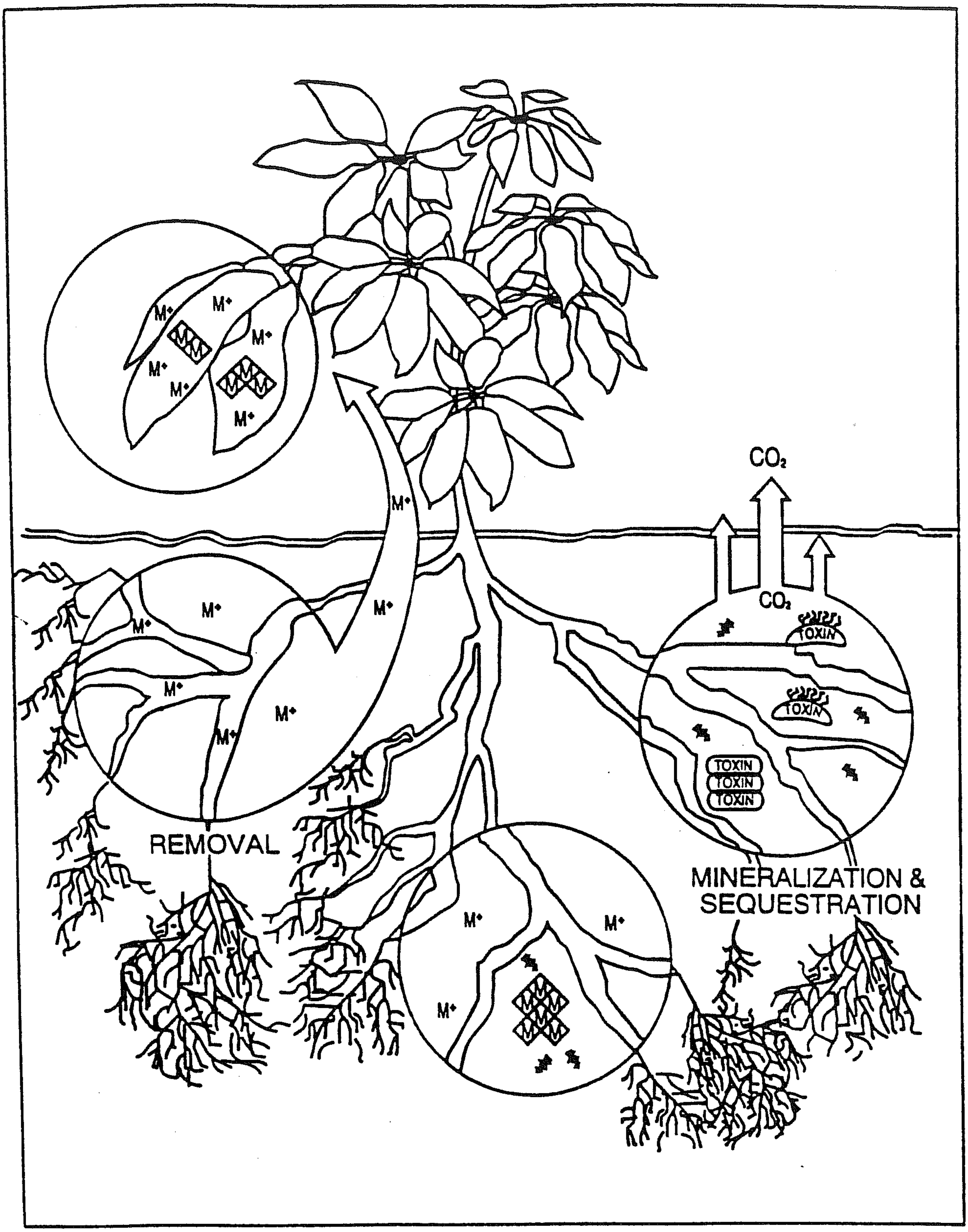


Figure 1. Diagram of Phytoremediation. Source: U.S. Department of Energy, 1994. "Summary Report of a Workshop on Phytoremediation Research Needs." Santa Rosa, California. July 24-26 [3]

1.3 Potential Advantages and Limitations of Phytoremediation

Advantages

The overall application of phytoremediation will likely be driven by its technical and economic advantages over alternative approaches; advantages include:

- Phytoremediation may be applied over large surface areas cost effectively.
- The low cost of phytoremediation should allow for on-site remediation of many sites currently being neglected due to the prohibitively high costs of currently available remedial technologies.
- The mass of contaminated media generated as a result of the cleanup may be dramatically reduced due to the preservation of top soil and site soils.
- The environmentally friendly nature of phytoremediation should be attractive to the public, responsible parties and regulatory agencies.
- Application of phytoremediation technology may result in a potentially recyclable metal-rich residue.
- The technology is applicable to a wide range of metals, radionuclides and organics.
- In-situ application may result in the elimination of secondary air or water-borne wastes.
- The need for excavation of soil may be minimized or eliminated.

Limitations

- For moderately to heavily contaminated soil, remediation may take several years.
- Soil texture, pH, salinity, pollutant concentrations and the presence of other toxins must be within the limits of plant tolerance for successful growth to occur.
- Plants provide an imperfect barrier against leaching; highly soluble contaminants may leach outside the root zone and migrate downward to the saturated zone.
- The depth of treatment is limited by the penetration depths of the specific plant and/or tree roots used. If the contamination is deeper than the root zone, additional remediation may be needed.

2.0 APPROACHES TO PHYTOREMEDIATION TECHNOLOGY

2.1 General

It has been recognized for more than 14 years that plant uptake could be exploited for the biological cleanup of various polluted rooting media including soils, compacted materials, effluents and drainage waters. The concept of phytoremediation of metal contaminated soils is further described by Baker *et al.* [3]:

".... where soils are contaminated with heavy metals, from industrial waste or metal-enriched sewage spread on the slurries, it might be possible to remove the toxic metals by growing several crops of hyperaccumulator plant. Once the plant has drawn out the metal, the land would be suitable for horticulture or agriculture."

The concept of phytoremediation has been studied extensively by Professor Ilya Raskin's group at the AgBiotech Center at Rutgers University, New Brunswick, NJ. Other notable workers in this field include Cunningham, Berti and Huang from DuPont Central Research & Development, and Ensley from Phytotech Inc. [3,4,5,6].

Phytoextraction is the use of plant roots to absorb, concentrate and precipitate toxic metals from soils into the harvestable portions of roots and surface biomass (shoots, leaves, etc.). Rhizofiltration is the use of plant roots to absorb, concentrate and precipitate toxic metals from polluted aqueous streams. Unlike phytoextraction, metals are primarily retained in the root system, and not moved into the plant shoots. Rhizofiltration, which is effective only in aqueous media, is not described in this report since it is generally used for slurries and sediments contaminated with metals, rather than soils.

The most recent emerging phytoremediation technology is called phytovolatilization. Metals such as selenium, arsenic and mercury can potentially be vented to the atmosphere through plants. Although it has been known for a long time that microorganisms play an important role in the volatilization of selenium and mercury, the practicality of using plants to volatilize these contaminants has yet to be established; research is currently in the initial stages.

Phytostabilization is a technology which uses plants to limit the mobility and bioavailability of toxic metals in soils. This technology is particularly useful in situations where there is a need for rapid immobilization of metals to prevent migration into ground and surface waters. Phytostabilization can also be used as follow-up treatment when phytoextraction or conventional excavation methods are initially utilized. In biologically active soils, contaminants form chemical and biological associations which can effectively decrease their availability and reduce the likelihood of leaching (Baker et al., 1989). Phytostabilization exploits sequestration processes to decrease bioavailability further with the aim of eliminating environmental and human health risks posed by contaminants at the site. Ideally, phytostabilizing plants should exhibit low levels of accumulation of heavy metals in the shoots, to eliminate the possibility of harvested residues becoming hazardous wastes (Dushenov et al., 1994).

At sites where metals contamination prevents vegetative growth, metal-tolerant plants may be used to prevent erosion and leaching. After field applications were conducted by a group in Liverpool, England, cultivars of three grasses were made commercially available for phytostabilization: *Agrosits tenuis*, cv *Parys* for copper wastes, *Agrosas tenuis*, cv *Cogina*n for acid lead and zinc wastes and *Festuca ruba, c*v *Merlin* for calcareous lead and zinc wastes (Blaylock et al., 1995).

Soil amendments, including phosphates and other plant nutrients, lime, ash and metal (Fe / Mn) oxyhydroxides, can be useful in stabilizing metals, and may be applied prior to planting. Plant species are selected based upon their ability to tolerate site conditions and maximize plant growth and ground cover.

Of the three main phyto-technologies prevalent in environmental applications, phytoextraction may be the most viable due to the size and scope of environmental problems associated with metal-contaminated soils, and the competitive advantage offered by a plant based remediation technology. *This document is focused primarily on phytoextraction technologies due to their applicability to soils contaminated with metals.*

2.2 Phytoextraction

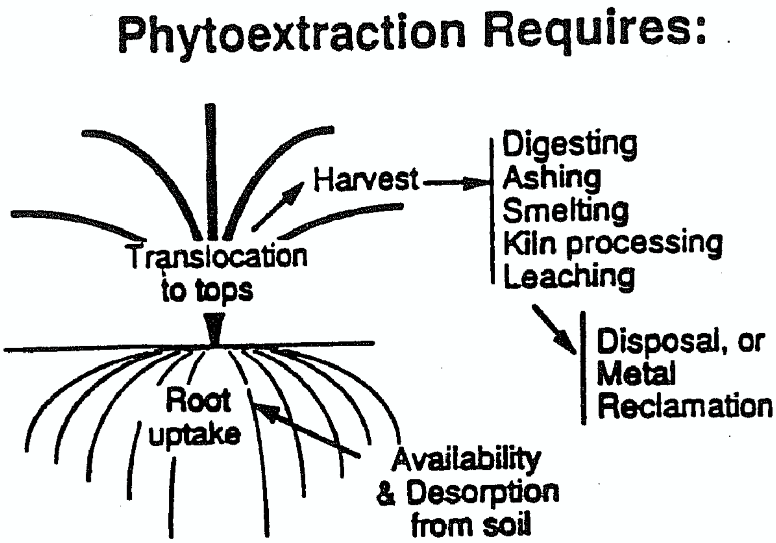
The inspiration for the development of phytoextraction came from the discovery of hyperaccumulator plants endemic to naturally mineralized soils that concentrate essential and nonessential heavy metals in their foliage. The degree of accumulation of metals such as nickel, zinc, and copper often reaches 1-5% of the dry weight of the plant. This concentration is an order of magnitude greater than the concentration of these metals in non-accumulating plants growing nearby [3,6,9,10].

The processes involved in phytoextraction are shown in **Figure 2** [2] on the following page. These processes will be limited by a number of factors:

- Metal availability within the rhizosphere
- Rate of metal uptake by roots
- Proportion of metal "fixed" within roots
- Rate of xylem loading and translocation to shoots
- Cellular resistance to toxic metals
- The form of the metals (particulate vs. molecular)

The amount of metal available for root uptake from soil is usually dramatically lower than the total metal content of the soil. Significant uptake of metal is only expected from the portion of metals that are in molecular form. "Soil-bound," or immobile metals must first be dissolved into soil water before they can be taken up by plants. To temporarily allow for metal uptake, synthetic chelating agents, such as ethylene-diamine-tetracetic acid (EDTA), can be added to the soil. In the future it may be possible to genetically engineer plants to produce metal-specific and biodegradable chelating agents capable of transferring metals from the soil matrix to plant roots for uptake.

Figure 2. Phytoextraction schematic (adapted from Cunningham and Berti, 1993)



For phytoextraction to be economically feasible, the contaminant must be accessible to the plant root. Roots, which account for 20-50% of plant biomass, extract elements from the soil and deliver most of the elements composing plant tissues to the shoots, with the exception of carbon. Most of the work on the mechanism of root and plant uptake has focused on the study of nitrogen, phosphorus, sulfur, iron, calcium, potassium and chlorides (Dushenov et al., 1994). These studies produced some understanding of processes involved in the acquisition of these essential elements.
Little is known about the mechanisms of mobilization, uptake and transport of environmentally hazardous heavy metals. It is clear that many of these metals remain sorbed to the solid soil constituents. To acquire these "soil bound" metals, plants have to mobilize them into soil water. Metal accumulation in plants can range from slightly elevated metal concentrations relative to background plants, to highly metal-concentrated plant tissue such that metals constitute a significant percentage of the dry plant matter.

Some plant species endemic to metalliferous soils have accumulated exceptionally high metal concentrations. The term "hyperaccumulator" was coined for serpentine plants capable of concentrating nickel to more than 1000 ug/g (0.1%) in their leaf dry matter (Akman et al., 1979). Hyperaccumulating plants have been identified for several metals but their utility for remediation is limited by several factors (Marschner, 1995):

- Hyperaccumulators often accumulate only specific elements and have not been developed for all elements of interest.
- Most hyperaccumulators grow slowly and have small biomass.
- There is little data regarding their agronomic characteristics, that is, pest management, breeding potential, and physiology.
- The plants are often rare and grow in remote regions.
- The use of wild plants as a seed source is unreliable.

Despite these limitations, efforts are being made to develop traditional crop plants with hyperaccumulator tendencies.

2.3 Current Applications of Phytoremediation

Phytoremediation technologies are not presently commercially available. Several research projects and field tests of the technology have been conducted to date. One of the most promising prospects for this technology is the combination of phytoremediation with traditional remedial strategies, such as soil excavation and offsite disposal or treatment.

The application of the technology depends on the type and degree of contamination and the cleanup levels that must be achieved at a particular site. Phytoextraction and rhizofiltration are the two most frequent applications of phytoremediation. Rhizofiltration is currently being used to remove organics from groundwater. Several field demonstrations using poplar trees to remove organic contaminants from groundwater are currently ongoing. Phytoextraction of heavy metals and radionuclides from contaminated soils represents one of the largest economic opportunities for phytoremediation. A number of sites are undergoing phytoextraction of soils contaminated with lead, copper and zinc. The Magic Marker site in Trenton, NJ, is utilizing phytoremediation under evaluation by the USEPA SITE Program. A final report is expected by February 1998.

3.0 RESEARCH AND DEVELOPMENT - FUTURE NEEDS

Molecular and plant biologists have begun to address some of the inherent limitations of existing plant species for phytoremediation. An integrated approach involving a broad range of basic and applied research, along with consideration of legal, safety and policy issues, will be necessary to establish phytoremediation as a viable remedial alternative. According to the 1994 US DOE "Summary Report of a Workshop on Phytoremediation Research Needs" the following broad areas of research and development have been identified:

- **The uptake, transport and accumulation mechanisms of plants**: Phytoremediation as a stabilization technology needs input from soil chemists and microbiologists to determine the relative degree of stabilization and the amount of potential offsite migration of contaminants that occurs.

- **Genetic evaluation of hyperaccumulators**: Research is being conducted to collect plants growing in soils that contain high levels of metals and screen them for specific traits potentially useful in phytoremediation.

- **Field evaluation and validation**: Research and field testing is being conducted to accelerate implementation of phytoremediation technologies and to provide data to research programs. Work in establishing protocols, standards, and application techniques for the research, engineering, and regulatory authorities is also needed. In order to facilitate the deployment of phytoremediation it is important that systems be developed to ensure that accessible, centralized verification data be made available to researchers, regulators, and the general public.

- **Soil amendments:** Research is needed to assess the potential human health and environmental risks due to the possible effects of increased bioavailability and /or migration of metals from the addition of soil amendments.

Other important areas for future research are:

- **Process optimization**: By evaluating agronomic practice and applied soil science, it may be possible to increase plant uptake of soil metals and reduce the duration of phytoremediation projects. Localized rhizosphere mobilization via chemical amendments could facilitate metal uptake with minimal risk of vertical dispersion or off-site migration.

- **Application of the technology to other media**: Growth and cropping of hyperaccumulator plants raised directly in polluted wastes and effluent waters is needed. This end-of-pipe approach may offer yet another mechanism for remediation of metal contaminants.

4.0 REGULATORY ISSUES

In order for the successful installation and operation of phytoremediation systems to occur, compliance with applicable regulations is mandatory. This section includes various regulatory and technical concerns regarding the application of phytoremediation technology. These concerns are not meant to discourage the use of phytoremediation as a remedial option, but rather to encourage discussion so that regulators, vendors and stakeholders can foresee potential problems and adjust their strategies accordingly. Wherever possible, responses to these concerns are presented based on discussions with academia, vendors, and ITRC Team members. In the near future, the ITRC plans to develop a “Technical and Regulatory Guidance Document” for deployment of phytoremediation technology. A handbook for the application of phytoremediation is also under development by the EPA.

- **If the effective depth of remediation is the root zone, which, for many plants is relatively shallow (two feet), how are other remedial strategies incorporated for contaminant levels at greater depths?**

Basic plowing methods can relocate contaminated soils at a depth of approximately three feet closer to the surface so that phytoremediation may work. Soils deeper than three feet could be excavated and brought to the surface for planting. Research is continuing to identify plant species and phytoextraction techniques which are capable of extracting contaminants at greater depths.

- **Is the projected time for cleanup to appropriate standards acceptable to the public and regulatory agencies?**

To illustrate this concern, consider the following example. Phytotech, Inc., a phytoremediation technology developer, estimates that lead in soil may be reduced at a rate of approximately 50 - 70 mg/kg/crop. Three crops/yr is a typical growth rate in the mid-Atlantic states; at a reduction rate of 200 mg/kg of lead in soil per year, it would take five years to reduce lead levels from 2000 mg/kg to 1000 mg/kg. While at first glance this rate may seem unacceptable, for many contaminated sites, time is not a critical factor. Voluntary cleanup sites and inactive or abandoned "Brownfields" sites may remain unremediated for many years. For sites that must be remediated but do not pose immediate health threats, long term, low cost treatment technologies such as phytoremediation may present an excellent solution. It may be appropriate and desirable to deploy phytoremediation at many sites, regardless of the contaminant levels, as an initial remedial effort because it is relatively low cost and relatively simple to implement. Phytoremediation offers the added benefit of erosion and contaminant migration control until such time as a site may be fully remediated.

- **Is phytoremediation a "single contaminant" remedy? If so, how are other remedial strategies incorporated for sites with multiple contaminants?**

Phytoremediation can potentially be used for multiple contaminants. Plants which can hyperaccumulate zinc, nickel and copper simultaneously have already been identified and research is ongoing in this area. It may also be possible to plant multiple species of plants, each of which extracts different metals, in the same contaminated area. Progress has also been made in the development of plants which can mineralize organics. Where multiple contaminants exist, phytoremediation may be used as part of a technology suite or treatment train approach.

- **What is the possible effect of plants "discharging" metals or organics to the atmosphere?**

Phytovolatilization is a technology that uses plants to remove contaminants such as mercury from soil and discharge the contaminant directly to the atmosphere. Studies are underway to clearly understand the potential applicability of phytovolatilization as a remediation tool. Volatilization of mercury, selenium and other metals to the atmosphere is a natural phenomenon which may not be of regulatory concern if the metals are present in site soils at natural background levels. However, if primary contaminants in the soils include volatile organics or metals which are subject to phytovolatilization, air discharge of these contaminants should be evaluated during bench or pilot scale studies. Engineering controls to capture contaminant emissions from the plants may also be developed.

- **Is it possible to set definitive post remedial sampling strategies, in light of the "non-uniform" growth patterns of plants? What should they be?**

Since phytoremediation usually would require several crop growths, any untreated soil due to non-uniform growth can be treated by subsequent crops. Regulatory criteria specifying a minimum crop coverage could also be developed to address this concern. It may be appropriate to use post remedial sampling strategies that would apply to any other in-situ treatment technology to verify effectiveness. Lack of treatment due to any non-uniform growth would be determined by the post remedial samples.

- **Since, to some extent, mixing of contaminated soils will occur as soils are prepared and amended during cropping cycles, is it possible that "hot spots" of contamination, which might be better treated separately or with another technology, will be mixed with more moderately contaminated soils?**

It may be appropriate to develop guidelines which would recommend upper limits of contamination, above which phytoremediation may not be applicable. To guard against contaminants being mixed rather than treated, mass-based treatment goals could be developed, which, along with post remedial sampling, should provide adequate certainty that the technology was effective.

- **If metals are mobilized to enhance the effectiveness of phytoextraction, what measures will be taken to prevent migration of the metals deeper into the soil column or into groundwater?**

Academia and technology developers have studied this issue and claim that water infiltration and metal mobility can be effectively controlled. Nearly all of the additives used in phytoremediation are also used in common agricultural practices. Post remedial soil sampling at depth, ground water monitoring, or leachability testing on representative post remedial soil samples could be required to verify that metal migration has not occurred.

- **If soils are amended to enhance the effectiveness of phytoextraction, what measures will be taken to ensure that soils which have been remediated to acceptable regulatory levels, but still contain metals, will not continue to provide a source of metals which may be taken up by plants that continue to grow naturally in the treated soils?**

To gain confidence that treated soils will not provide an ongoing source of metals after soil remediation is completed, a final crop may be planted to ensure that there are negligible levels of metals in the plants. This would also ensure that naturally occurring metals have not been mobilized by the addition of soil amendments.

- **Can metals in plants enter the food chain?**

Academia and technology developers both believe that animal foraging can be prevented through proper control and mitigation practices including restricted access to areas under remediation. In general, plants used for phytoremediation are not consumed by animals. Concerns such as these must be balanced against alternatives such as on-site containment, which can result in a long term, persistent threat to human health and the environment.

- **What is the fate of root bound lead or other metals? Are there any innovative technologies on the horizon for the harvesting of roots? Once the root biomass degrades, are the toxins released back to the subsurface?**

It is expected that the root material will decay and subsequent crops will remove any earlier root bound metals. At present, roots are not harvested. Replanting usually takes place immediately after harvest. The timing of the root decay is a concern, but the presence of significant root-bound metals should be detected in post-remedial soil samples. Analytical methods may have to be modified to ensure that root material is not excluded from the sample, or requirements to sample root tissue separately could be included.

- **Would it be necessary to comply with state / federal discharge permits with respect to irrigation and watering of the plants?**

As mentioned earlier, the amount of water needed for irrigation for phytoremediation is in conformity with common agricultural practices. However, if soil amendments which increase water solubility of the metal are used, groundwater monitoring may be required.

5.0 COST

Phytoremediation projects involve costs related to the treatment of hazardous materials, extensive sampling and analysis, and handling and disposal of plants containing metal residues. Due to the limited availability of information on completed projects, little cost data is available. According to Phytotech, Inc., cleanup costs, including treatment and disposal, can range from $20 - $80 per cubic yard of contaminated soil. This cost estimate includes incineration of plants and ash disposal at a hazardous waste incinerator at a cost of $500 per cubic yard of plant material. If the plants can be recycled at a smelter, costs near the low end of the range can be expected. The cost of phytoremediation for one acre of sandy loam soil to a depth of 50 cm is estimated to range from $60,000 to $100,000. This is considerably lower than the approximate cost of $400,000 for excavation and disposal of the contaminated soil at a landfill.

The cost of plant disposal can be significantly less than the cost of disposal of metal-contaminated soils because contaminants have been concentrated in the much smaller plant biomass. However, the total cost of phytoremediation will depend on the rates of uptake from the soil and the number of crops which are needed to meet cleanup levels. Analysis of the costs of phytoremediation must include the entire remedial process, from growing and harvesting the plants to disposing or recycling the metals in the plants. Table 5-1 on the following page contains additional cost comparison information [10].

6.0 PUBLIC AND STAKEHOLDER ACCEPTANCE & CONCERNS

Phytoremediation is an in-situ technology which potentially minimizes the risk and cost associated with excavation and transport of contaminated soils. While physical-chemical processes for treating metals in soil can potentially remove nutrients and humic matter, sterilize soil, or reduce biological activity, phytoremediation can selectively remove targeted contaminants while leaving remaining soil constituents in a natural state. Please refer to the EPA "Citizen's Guide to Phytoremediation" for assistance in communicating phytoremediation issues to the public.

Table 5-1 Cost Comparison

Type of Treatment	Cost / m^3 ($)	Time (Months) Required	Additional Factors/Expense	Safety Issues
Fixation	**90 - 200**	**6 - 9**	**Transport, excavation, long-term monitoring**	**Leaching**
Landfilling	**100 - 400**	**6 - 9**	**Long-term monitoring**	**Leaching**

Soil Extraction / Leaching	**250 - 300**	**8 - 12**	**Minimum project volumes, chemical recycling**	**Residue disposal**
Phytoextraction	**20 - 80**	**18 - 60**	**Time / land commitment**	**Residue**

6.1 Issues to be Addressed

Listed below are some major issues that must be clearly understood by tribal and community stakeholders in order to gain full acceptance of phytoremediation.

- The use of plants to treat contaminated soil may result in long-term treatment at the site.
- Phytoremediation may create additional environmental concerns by introducing contaminants into the food chain.
- When leaves or other plant tissue containing heavy metals fall or blow away, contaminants may be redeposited on site soils, or an offsite contaminant migration pathway may be created. Proper management of contaminated plants can eliminate this pathway.
- Community stakeholders have expressed concern regarding the use of soil amendments to enhance metal absorption by plants. Mobilization of metals in soil may cause additional human health and environmental risks due to the increased amounts of metals potentially bioavailable in the surface and subsurface soil. In addition, increased human health and environmental risks may result from the migration of mobilized metals to groundwater. It is important to explain the purpose of these amendments and any controls put in place to ensure that their use results in no additional threat to human health or the environment.
- Stakeholders and tribal representatives raised a variety of concerns when phytoremediation was discussed at the Hanford DOE Site in Washington State. The presence of several endangered species and protected animals, most notably the bald eagle, increased the level of attention the project received from community members. Tribal members were concerned about impacts on species of cultural significance. Major concerns included the potential introduction of contaminants into the food chain, and subsequent impacts on animal species as well as human consumers.

The concerns above have been included not to discourage the use of phytoremediation at any given site, but rather as a point of reference for stakeholders, regulators, technology developers and technology users. For successful technology deployment, it is essential that these issues be identified and addressed when applicable to a particular site.

7.0 CONCLUSION

The use of plants for remediation is not a new scientific concept. Current research efforts are focusing on the expansion of the technology to address contaminated soils and groundwater. For the remediation of soils, phytoextraction and phytostabilization are two applicable techniques which show considerable promise. Preliminary results of several laboratory and field experiments have produced positive results which indicate that the technology may be relatively cost effective. A suggested model workplan for phytoremediation has been developed as part of the effort to produce this document; it is presented in Appendix D.

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APPENDIX A

Acronyms

ACRONYMS

EDTA	Ethylene-diamine-tetracetic acid
Fe	Iron
IINERT	In-Place Inactivation and Natural Ecological Restoration Technologies
ITRC	Interstate Technology and Regulatory Cooperation Working Group
mg/kg	milligrams per kilogram
Mn	Manganese
NJ	State of New Jersey
RCRA	Resource Conservation and Recovery Act
RTDF	Remediation Technologies Development Forum
ug/g	Micrograms per gram
USEPA	United States Environmental Protection Agency
USDOE	United States Department of Energy

APPENDIX B

ITRC Work Team Contacts
ITRC Fact Sheet
Product Information
User Survey

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APPENDIX C

Case Study

Phytotech

Phytoremediation of Lead Contaminated Soil at a Brownfield Site in New Jersey

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Abstract

Phytoremediation is a new technology which uses specially selected metal-accumulating plants to clean up soil contaminated with heavy metals and radionuclides. Phytoremediation offers an attractive and economical alternative to currently practiced soil removal and burial methods. The integration of specially selected metal-accumulating crop plants (*Brassica juncea*) with innovative soil amendments allows plants to achieve high biomass and metal accumulation rates from soils. The use of these techniques will facilitate reclamation of many contaminated sites. Phytotech Inc. is developing this technology with particular attention to the remediation of lead contaminated Brownfields. A demonstration of this technology is being conducted at the former Magic Marker site in Trenton, New Jersey. In the studies conducted at the Trenton site, approximately 75% of the treated area has been cleaned below the regulatory limit of 400 parts per million (ppm) in one cropping season. Projected costs of phytoremediation indicate a substantial cost savings compared to alternative remediation techniques, further enhancing the attractiveness of this technology for remediation of contaminated soils.

Introduction

The use of plants to remove toxic metals from soils (phytoremediation) is emerging as a strategy for cost effective and environmentally sound remediation of contaminated soils (1-4). Certain plants, known as metal hyperaccumulators, have been discovered that contain unusually high concentrations of heavy metals in their tissue. Hyperaccumulators of Ni and Zn, for example contain as much as 5% of these metals on a dry weight basis (5, 1). Phytoremediation as a soil clean-up technology seeks to exploit the ability of metal accumulating plants to extract metals from the soil with their roots and to concentrate these metals in above ground plant parts. The process of concentration greatly reduces the amount of contaminated material that requires disposal, thereby decreasing the

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associated disposal fees. The metal-rich plant material can be safely harvested and removed from the site without extensive excavation, disposal costs, and loss of topsoil associated with traditional remediation practices. Phytoremediation also provides an attractive, environmentally friendly remediation process.

The success of phytoremediation is dependent on several factors. Plants must produce sufficient biomass while accumulating high concentrations of metal. The metal accumulating plants also need to be responsive to agricultural practices to allow repeated planting and harvesting of the metal rich tissues. The ability to cultivate a high biomass plant with a high content of toxic metals on a contaminated soil will be a determining factor in the success of phytoremediation.

In addition, the availability of metal in the soil for plant uptake is another limitation for successful phytoremediation. For example, Pb, one of the most important environmental pollutants has limited solubility in the soil and is not generally available for plant uptake. The solubility of Pb in soils is often controlled by carbonate or phosphate minerals in equilibrium with the soil solution. These minerals have very low solubilities, resulting in very low concentrations of soluble lead in the soil solution (6) In most soils capable of supporting plant growth, the soluble Pb levels will remain very low and will not allow substantial uptake by the plant. Vegetation growing in heavily contaminated areas often has less than 50 µg/g Pb in the shoots (7). In addition, many plants retain Pb in their roots via sorption and precipitation with only minimal transport to the above ground harvestable portions (8, 4). Recently, Phytotech, Inc. has developed technology which combines high biomass producing metal accumulator plants (Brassica juncea) with innovative soil and plant amendments. This technology has accelerated the development of phytoremediation for metals such as Pb and created the opportunity to apply this appealing remediation technique in the field.

Methods

The application of this technology was recently demonstrated at a Brownfields site in Trenton, New Jersey with Pb contaminated soil. The site is located in a residential/commercial area of the city and is adjacent to a school, churches and residences. A 4500 sq. ft area at the abandoned Magic Marker factory was selected for the study. The site is part of property formerly occupied by Gould Battery Inc., before being purchased by Doral Industries (the predecessor to Magic Marker Industries) in 1981. Magic Marker abandoned the property in 1989 after declaring bankruptcy. The soil at the site is contaminated with Pb.

A preliminary site investigation was conducted in October of 1995 to determine the distribution of Pb in the soil and collect surface (0-15 cm depth) samples for a laboratory treatability study. The soil samples were sieved to 4 mm and a subsample was submitted to the Rutgers University Soil Testing Laboratory for a standard soil fertility analysis. An additional sample was analyzed at Phytotech for total metals by EPA Method 3050 (Table 1) and also extracted sequentially to assess metal associations with operationally defined soil fractions (i.e. exchangeable, carbonates, oxides, organic matter, and residual) according to the procedure of Ramos et al. (9) (Table 2). The remaining soil was fertilized and potted in 3.5 inch diameter pots and planted with *Brassica juncea*. The soil was treated with Phytotech Inc.'s proprietary amendments to induce metal uptake by the plants. After 4 weeks growth, the plants were harvested and analyzed for metal content.

Based on the results of the treatability study a field trial was planned and conducted at the site in Trenton. An initial sampling of the site to obtain baseline soil data was conducted by sampling every 5 ft. at three depths (0-15, 15-30, and 30-45 cm). Contour maps describing the surface contamination were plotted using Surfer™ (10). The site was tilled and fertilized according to the soil fertility test results and seeded with B. juncea. Soil solution lysimeters and tensiometers were installed at 4 depths (6", 12", 24" and 36") to collect soil solution samples and monitor soil water content. Irrigation was conducted according to a hydrogeological model developed specifically for the Magic Marker site. Soil amendments were added based on the results obtained in the treatability study to optimize plant growth and metal uptake. The crop of B. juncea was harvested after 6 weeks growth and the plot was replanted within one week of the harvest. The harvested biomass was dried and removed from the plot.

Soil samples were collected again at three depths after the second crop to determine metal removal efficiency. The soil samples were air dried and analyzed for total metal content using a modification of EPA Method 3050. Contour maps of the contaminated areas were again plotted in the same manner as the initial sampling. The areas corresponding to specific levels of metal concentration were calculated using Surfer™.

Results and Discussion

The soil at the Magic Marker site had significant variation in pH Pb contamination. The soil pH varied from 5.1 to 7.1. Surface Pb concentrations ranged from 200 to 1800 mg/kg (Figure 1). Soil characteristics from the sample used for the treatability study are presented in Tables 1 and 2. The soil Pb was predominantly associated with the organic fraction (33% of the total Pb) with the residual and oxide fractions containing 28% and 22%, respectively (Table 2).

Table 1. Soil characteristics and total metal content of a surface soil sample collected at the Magic Marker site.

pH	Texture	Organic Matter	Cd	Cr	Cu	Ni	Pb	Zn
		%	----------	----------	mg/kg	----------	----------	----------
7.1	loamy sand	11.8	8	22	92	22	927	138

Figure 1. Initial surface soil Pb concentrations and distribution at the Magic Marker site in Trenton, New Jersey.

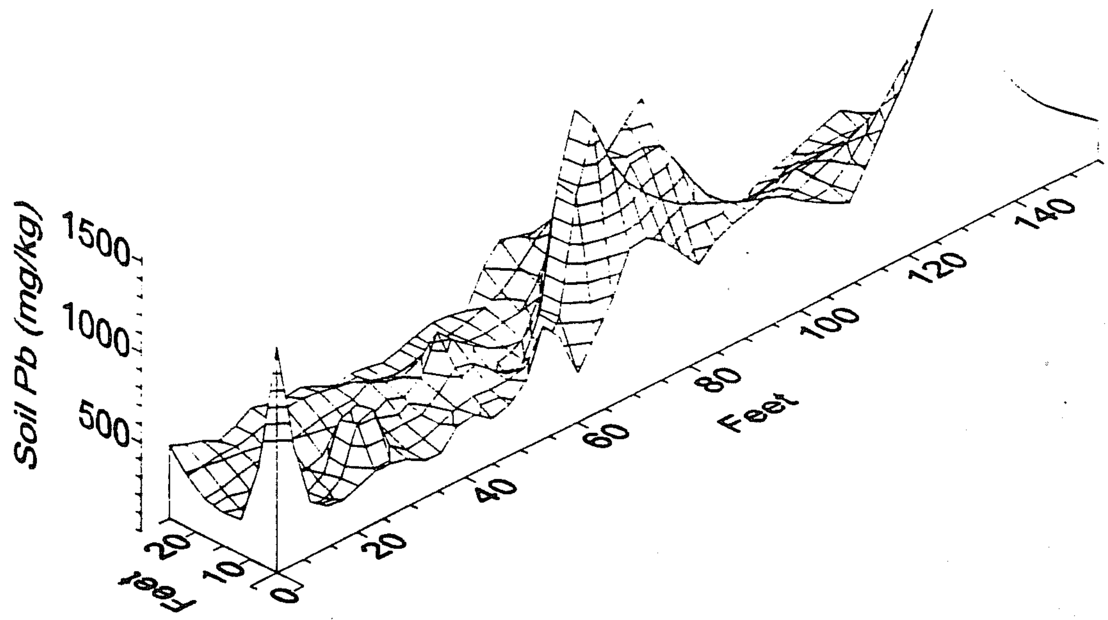


Table 2. Fractionation of metal contaminants based on sequential extraction of the surface soil (0 to 15 cm depth) collected from the Magic Marker site in Trenton, New Jersey.

	Cd	Cr	Cu	Ni	Pb	Zn
Fraction	-----------------	------	mg/kg	------	------	-----------------
Exchangeable	2	0	1	1	33	14
Carbonates	0	0	4	0	92	9
Oxide	0	1	14	2	152	23
Organic	1	6	79	6	232	62
Residual	6	14	45	17	196	81
Sum of Fractions	9	22	142	26	704	190

The greenhouse treatability study indicated that B. juncea plants were capable of removing significant quantities of Pb from the soil. Shoot Pb concentrations of 3900 mg/kg were achieved through the use of proprietary amendments in the greenhouse scale system. This data coupled with the soil analysis indicating that less than 200 mg/kg of the soil Pb remained in the residual fraction after the sequential extraction, encouraged the application of phytoremediation as a means to reduce the surface soil Pb concentrations to less than 400 mg/kg.

The implementation of phytoremediation technology at the field site was successful in reducing the area of Pb contaminated soil. At the time of the initial sampling, 46% of the selected area exceeded the regulatory limit of 400 mg Pb/kg and approximately 7% of the selected area exceeded 1000 mg/kg (Table 3). After two phytoremediation crops, the area that exceeded 400 mg/kg decreased from 46% to 26% of the treated area. In addition, none of the treated area exceeded 1000 mg/kg at the end of the second crop.

Table 3. Reduction in surface area of soil contaminated with Pb. Values given are the percent of the treated area that exceed the given soil concentration.

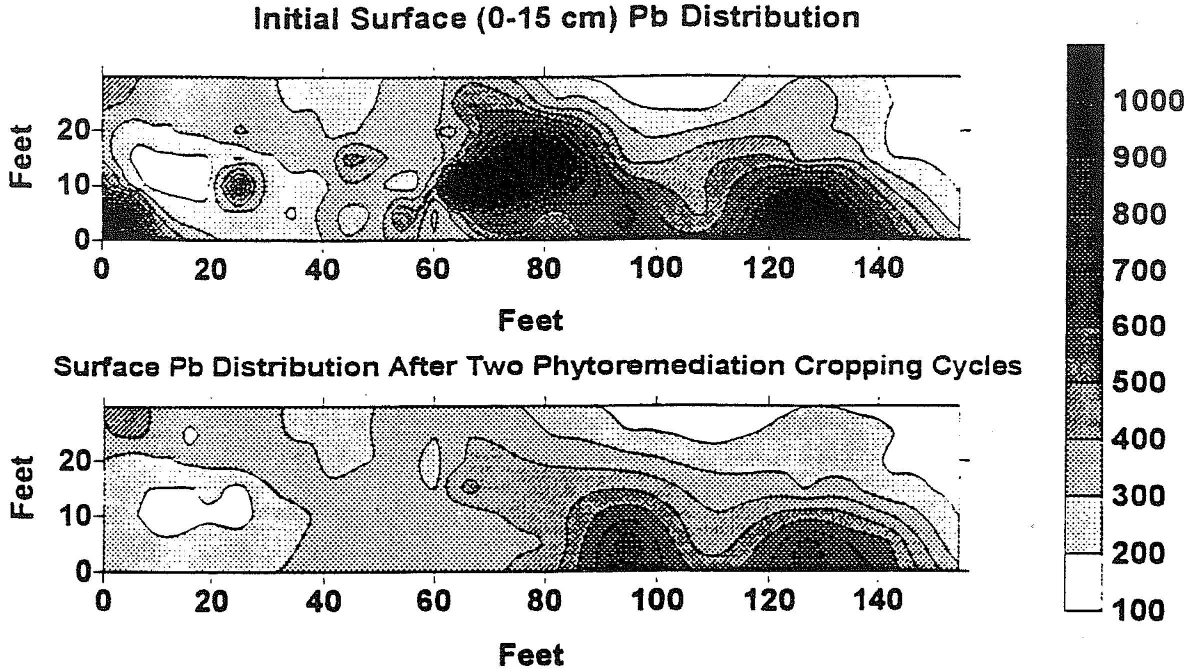
	% of Treated Area	
Soil Pb Concentration (mg/kg)	Initial	After 2nd Harvest
>400	41%	26%
>450	36%	18%
>500	31%	13%
>600	23%	8%
>800	12%	1%
>1000	7%	0%

Figure 2 presents the soil Pb surface contour map showing the initial soil Pb concentrations (top) and the soil Pb distribution after two phytoremediation crops (bottom). Phytoremediation also reduced the surface area of Pb contamination at the 400, 450, 500, 600, 800, and 1000 mg/kg levels (Table 3).

A further analysis of water soluble Pb in the soil showed that the phytoremediation process did not increase the amount of water soluble Pb in the soil at the 15-30 cm and 30-45 cm depths. Total subsurface soil Pb concentrations also did not measurably increase as a result of remediation.

The successful phytoremediation of Pb contaminated soil at the Magic Marker site has important implications for Brownfields and other contaminated sites requiring a low cost remediation approach. Phytoremediation, as implemented at the Magic Marker site, is projected to cost between 25 to 50% of traditional permanent remediation approaches and be comparable in cost to non-permanent remediation systems such as capping while eliminating the liability concerns and requirements for long term monitoring. In addition, phytoremediation provides an environmentally friendly means of removing the contaminant. Although phytoremediation may not be applicable to all contaminated soils, it is particularly effective for those sites where Pb

Figure 2. Contour plot showing initial surface soil Pb concentrations (top) and the soil Pb concentration after two phytoremediation cropping cycles (bottom).



contamination is less than 1500 mg/kg. Phytoremediation has the potential to treat many of the urban and industrial sites containing metal concentrations just above the required action limits. The substantial savings will result in the ability of cities and private industry to remediate many more sites than would otherwise be economically possible.

Acknowledgments

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APPENDIX D

A Typical Workplan for Phytoremediation

A TYPICAL WORK PLAN FOR PHYTOREMEDIATION

1.0 INTRODUCTION

The introduction should provide a very brief description of the technology.

2.0 OBJECTIVE

Work plan should clearly define the objectives of the remediation goal and regulations that must be followed during the operation. If the remediation is an interim action / treatability test / pilot scale test, the objective should clarify it and define the expected future path of the project.

3.0 SCOPE OF WORK: The work scope is broken down into the following

3.1 Remedial And Experimental Design

Task 1. Soil Characteristics
(identify the soil types, contaminant levels, specify other soil types that are going to affect the test / remediation objectives)

Task 2. Treatment by Chemical Additives
(Effect of potential soil treatment on soil metal content)

3.2 Quality Analysis and Control

(EPA/ASTM methodologies shall be utilized for all parameters)

Task 1. **Experiments / Analysis And Sampling QA/QC**

Task 2. **Vegetation Experiments**

Task 3. **Plant Analysis**
(Including the biological evaluation of phytotoxicity)

Task 4. **Soil Analysis**
(Including total species and bioavailability management)

Task 5. **Monitoring Requirements And Parameters**
(Identify sample frequency, number of verification samples, etc.)

Task 6. **Harvesting and Sampling**

Task 7. **Statistical Analysis**

4.0 GENERAL QA/QC

All QA/QC required by the analytical method shall be completed. Lab QA/QC summary documentation (including non-conformance summary report and chain of custody) shall be submitted with analytical results. Full QA/QC deliverables as specified by the analytical method shall be maintained and shall be made available for request for at least three years. Ultimate responsibility for QA/QC documentation belongs with the responsible party of a site or the vendor conducting the demonstration. However, the responsible party may contract with another entity, such as an analytical laboratory, to house the actual QA/QC data.

5.0 HEALTH AND SAFETY

The work plan should provide details on health and safety issues related to the entire operation. Various exposure scenarios must be analyzed and strategies to handle the related health and safety issues must be discussed.

6.0 DISCUSSION OF RESULTS AND INTERPRETATION

7.0 CONCLUSIONS