Phytoremediation
of
CONTAMINATED
SOIL and WATER

Edited by
Norman Terry
Gary Bañuelos

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Preface

The need to synthesize, critically analyze, and put into perspective the ever-mounting body of new information on phytoremediation in the soil and water environment provided the impetus for the development of this book. It is a compilation of articles provided by speakers at a symposium entitled "Phytoremediation of Trace Elements in Contaminated Soil and Water" that was held in June 1997 as part of the Fourth International Conference on the Biogeochemistry of Trace Elements on the Clark Kerr campus of the University of California, Berkeley. Also included in the book are invited articles on special topics such as the phytoremediation of constructed wetlands and the role of microphytes.

Twenty eminent scientists from around the world spoke at the symposium on topics such as field demonstrations of phytoremediation in trace element cleanup; the role of hyperaccumulator plants in phytoextraction; the genetics, molecular biology, physiology, and ecology of trace element hyperaccumulation and tolerance; phytovolatilization of mercury and selenium in phytoremediation; the role of microbes; and the phytostabilization and immobilization of metals in contaminated soil. We are especially indebted to Dr. Jaco Vangronsveld who helped coordinate the symposium and who was instrumental in developing the list of excellent speakers from Europe. The papers represent the latest research in all of the major aspects of phytoremediation of trace elements in contaminated soil and water.

Norman Terry
Gary Bañuelos

Editors

Norman Terry is Professor of Environmental Plant Biology in the Department of Plant and Microbial Biology, and Researcher in the Agricultural Experiment Station at the University of California, Berkeley. Terry received his Ph.D. in Plant Physiology at the University of Nottingham, England, and was awarded a NRC (Canada) Post-doctoral Fellowship to carry out research on phloem translocation (Ottawa, 1966–1968). He joined the Berkeley faculty in 1972 and currently teaches advanced undergraduate courses on plant physiology, biochemistry, and environmental plant biology. During his research career, Terry authored over 120 scientific articles. His early research was on the regulation of photosynthesis *in vivo*, the environmental control of plant growth, mineral nutrition, and salinity.

In 1990, Terry's research interests shifted to phytoremediation. He developed a research program that is a multidisciplinary blend of environmental engineering, microbiology, plant biochemistry, and molecular biology. This approach is unique in phytoremediation research and has facilitated several innovative and creative solutions to environmental problems. He pioneered the use of constructed wetlands for the cleanup of selenium and other toxic elements from oil refinery effluents and agricultural irrigation drainage water. Using cutting edge molecular approaches, Terry developed transgenic plants with superior capacities for the phytoremediation of selenium and heavy metals (e.g., cadmium). And, by using sophisticated high energy x-ray absorption spectroscopy to monitor element speciation changes, he successfully demonstrated that plants have the ability to detoxify metals (e.g., chromium).

Gary S. Bañuelos is a plant/soil scientist at the USDA/ARS' Water Management Research Laboratory in Fresno, CA and an adjunct professor at California State University. Focusing his research activities on the phytoremediation of soil and water contaminated with selenium, boron, and salinity, Dr. Bañuelos is the principal author of over 60 refereed technical articles and a member of the American Chemical Society, American Society of Agronomy, and the International Soil Science Society, among others.

He received his German proficiency degree in 1977 from Middlebury College in Vermont, a B.A. degree in German from Humboldt State University in California (1979) and a German language certification at Goethe Institute in Germany in 1979. In 1984, he received a B.S. degree in crop science and Master's in agriculture from CalPoly Technical University, and in 1987 he was a National Science Foundation Fellow at Hohenheim University in Germany, where he acquired a Ph.D. in plant nutrition/agriculture.

Contributors

J. Scott Angle
University of Maryland
Dept. of Natural Resources and
  Landscape Architecture
College Park, MD 20742

Alan J. M. Baker
Dept. of Animal and Plant Sciences
Environmental Consultancy (ECUS)
University of Sheffield
Sheffield S10 2TN U.K.

Gary S. Bañuelos
USDA–ARS
Water Management Research
  Laboratory
2021 S. Peach Ave.
Fresno, CA 93727

Roland Bernhard
Dept. of Ecology and Ecotoxicology
Faculty of Biology
Vrije Universiteit
De Boelelaan 1087
Amsterdam, The Netherlands

William R. Berti
Environmental Biotechnology Program
DuPont Central Research and
  Development
Glasgow Business Community 301
Newark, DE 19714-6101

Michael J. Blaylock
Phytotech, Inc.
1 Deer Park Drive, #I
Monmouth Junction, NJ 08852

Sally L. Brown
University of Maryland
Dept. of Natural Resources and
  Landscape Architecture
College Park, MD 20742

Rufus L. Chaney
USDA–ARS
Environmental Chemical Laboratory
Beltsville, MD 20705

Mel Chin
Artist
New York, NY

H. Clijsters
Liverpool John Moores University
School of Biological and Earth Sciences
Byrom Street
Liverpool L3 3AF U.K.

P. Corbisier
Environmental Technology
Vlaamse Instelling voor Technologisch
  Onderzoek
VITO, Boeretang 200
B-2400 Mol, Belgium

R. L. Correll
CSIRO Mathematical and Information
  Sciences
PMB2 Glen Osmond
Adelaide 5064
Australia

Scott D. Cunningham
DuPont Company
Centre Road
Wilmington, DE 19805-0708

Keri L. Dandridge
Dept. of Biology
Furman University
Greenville, SC 29613

Mark deSouza
Dept. of Plant and Microbial Biology
University of California
Berkeley, CA 94720

L. Diels
Environmental Technology
Vlaamse Instelling voor Technologisch
  Onderzoek
VITO, Boeretang 200
B-2400 Mol, Belgium

S. J. Dunham
Soil Science Dept.
IACR-Rothamsted, Harpenden
Herts. AL5 2JQ U.K.

R. Edwards
Liverpool John Moores University
School of Pharmacy and Chemistry
Byrom Street
Liverpool L3 3AF U.K.

Teresa W.-M. Fan
Dept. of Land, Air, and Water Resources
University of California
Davis, CA 95616-8627

A. Gilis
Environmental Technology
Vlaamse Instelling voor Technologisch
  Onderzoek
VITO, Boeretang 200
B-2400 Mol, Belgium

Peter Goldsbrough
Dept. of Horticulture and Landscape
  Architecture
Purdue University
West Lafayette, IN 47907-1165

G. Gragson
Dept. of Genetics
Life Sciences Building
University of Georgia
Athens, GA 30602

S. K. Gupta
Institute for Environmental Protection
  and Agriculture
Swiss Federal Research Station for
  Agroecology and Agriculture
Schwarzenburgstrasse 155
CH-3003 Bern, Switzerland

T. Hari
Institute for Environmental Protection
  and Agriculture
Swiss Federal Research Station for
  Agroecology and Agriculture
Schwarzenburgstrasse 155
CH-3003 Bern, Switzerland

T. Herren
Division of Radiation Protection and
  Waste Management
Paul Scherrer Institut
CH-5232 Villigen-PSI
Switzerland

Richard M. Higashi
Crocker Nuclear Laboratory
University of California
Davis, CA 95616-8627

Faye A. Homer
University of Maryland
Dept. of Natural Resources and
  Landscape Architecture
College Park, MD 20742

Alex J. Horne
Ecological Engineering Group
Dept. of Civil and Environmental
  Engineering
University of California
Berkeley, CA 94720-1710

Edward M. Jhee
Dept. of Biology
Furman University
Greenville, SC 29613

M. K. Kandasamy
Dept. of Genetics
Life Sciences Building
University of Georgia
Athens, GA 30602

N. Kato
AgBiotech Center
Rutgers University
Cook College
New Brunswick, NJ 08903-0231

Leon V. Kochian
Plant, Soil, and Nutrition Laboratory
USDA–ARS
Cornell University
Ithaca, NY 14853

U. Krämer
Fakultät für Biologie-W5
Universität Bielefeld
Bielefeld, Germany

R. Krebs
AMT für Umweltschutz SG
Linsebühlstrasse 91
St. Gallen, Switzerland

Mitch M. Lasat
Plant, Soil, and Nutrition Laboratory
USDA–ARS
Cornell University
Ithaca, NY 14853

N. W. Lepp
Liverpool John Moores University
School of Biological and Earth Sciences
Byrom Street
Liverpool L3 3AF U.K.

Yin-Ming Li
USDA–ARS
Environmental Chemical Laboratory
Beltsville, MD 20705

Zhi-Qing Lin
Dept. of Plant and Microbial Biology
University of California
Berkeley, CA 94720

Mercè Llugany
Dept. of Ecology and Ecotoxicology
Faculty of Biology
Vrije Universiteit
De Boelelaan 1087
Amsterdam, The Netherlands

C. Lodewyckx
Environmental Technology
Vlaamse Instelling voor Technologisch
  Onderzoek
VITO, Boeretang 200
B-2400 Mol, Belgium

Mark R. Macnair
Dept. of Biological Sciences
University of Exeter
Prince of Wales Road
Exeter EX4 4PS U.K.

Minnie Malik
University of Maryland
Dept. of Natural Resources and
  Landscape Architecture
College Park, MD 20742

S. P. McGrath
Soil Science Dept.
IACR-Rothamsted, Harpenden
Herts. AL5 2JQ U.K.

R. B. Meagher
Dept. of Genetics
Life Sciences Building
University of Georgia
Athens, GA 30602

M. Mench
INRA Agronomy Unit
Bordeaux-Aquitaine Research Centre
BP 81
F-33883 Villenave d'Ornon cedex
France

M. Mergeay
Environmental Technology
Vlaamse Instelling voor Technologisch
  Onderzoek
VITO, Boeretang 200
B-2400 Mol, Belgium

Elizabeth Pilon-Smits
Dept. of Plant and Microbial Biology
University of California
Berkeley, CA 94720

A. Joseph Pollard
Dept. of Biology
Furman University
Greenville, SC 29613

I. Raskin
AgBiotech Center
Rutgers University
Cook College
New Brunswick, NJ 08903-0231

Roger D. Reeves
Dept. of Chemistry
Massey University
Palmerston North, New Zealand

C. L. Rugh
Dept. of Genetics
Life Sciences Building
University of Georgia
Athens, GA 30602

David E. Salt
Chemistry Department
Northern Arizona University
Flagstaff, AZ 86011-5698

Henk Schat
Dept. of Ecology and Ecotoxicology
Faculty of Biology
Vrije Universiteit
De Boelelaan 1087
Amsterdam, The Netherlands

J. A. C. Smith
Dept. of Plant Sciences
University of Oxford
South Parks Road
Oxford OX1 3RB U.K.

R. D. Smith
De Kalb Genetics Corp.
Mystic, CN 06355

Susanne E. Smith
Dept. of Biological Sciences
University of Exeter
Prince of Wales Road
Exeter EX4 4PS U.K.

N. Spelmans
Limburgs Universitair Centrum
Environmental Biology
Universitaire Campus
B3590 Diepenbeek, Belgium

S. Taghavi
Environmental Technology
Vlaamse Instelling voor Technologisch
  Onderzoek
VITO, Boeretang 200
B-2400 Mol, Belgium

Norman Terry
Dept. of Plant and Microbial Biology
University of California
Berkeley, CA 94720

Gavin H. Tilstone
Grupo de Oceanoloxia
Instituto de Investigacions Marinas-
  CSIC
Eduardo Cabello, 6
36208 Vigo, Spain

D. van der Lelie
Environmental Technology
Flemish Institute of Technological
  Research (VITO)
Boeretang 200
B-2400 Mol, Belgium

J. Vangronsveld
Limburgs Universitair Centrum
Environmental Biology
Universitaire Campus
B3590 Diepenbeek, Belgium

N. J. Wang
Dept. of Genetics
Life Sciences Building
University of Georgia
Athens, GA 30602

K. Wenger
Institute for Environmental Protection
  and Agriculture
Swiss Federal Research Station for
  Agroecology and Agriculture
Schwarzenburgstrasse 155
CH-3003 Bern, Switzerland

Adel Zayed
Dept. of Plant and Microbial Biology
University of California
Berkeley, CA 94720

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Michael J. Blaylock

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SUMMARY

Phytoremediation is a new technology that uses specially selected metal-accumulating plants to remediate 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 (e.g., *Brassica juncea*) with innovative soil amendments allows plants to achieve high biomass and metal accumulation rates from soils.

INTRODUCTION

The use of plants to remove toxic metals from soils (phytoremediation) is being developed as a method for cost-effective and environmentally sound remediation of contaminated soils (Baker et al., 1994; Chaney, 1983; Raskin et al., 1994). Metal (hyper)accumulating plants have been sought that have the ability to accumulate and tolerate unusually high concentrations of heavy metals in their tissue. Accumulators of nickel (Ni) and zinc (Zn), for example, may contain as much as 5% of these metals on a dry-weight basis (Baker et al., 1994, Brown et al., 1995). This process of extracting metals from the soil and accumulating and concentrating metals in the above-ground plant tissues enables plants to be used as part of a soil cleanup technology. For example, plants accumulating metals at the above-mentioned 5% (50,000 mg/kg) dry-weight concentration from a soil with a total metal concentration of 5000 mg/kg results in a 10-fold bioaccumulation factor. The metal-rich plant material can be swathed, collected, and removed from the site using established agricultural practices, without the extensive excavation and loss of topsoil associated with traditional remediation practices. Post-harvest biomass treatments (i.e., composting, compaction, thermal treatments) may also be employed to reduce the volume and/or weight of biomass for disposal. The metal bioaccumulation of the plant shoots above that of the soil concentration coupled with subsequent biomass reduction processes can greatly reduce the amount of contaminated material requiring disposal compared to soil excavation, thereby decreasing the remediation costs.

Successful implementation of phytoremediation in the field depends on a significant quantity of metal being removed from the soil through plant uptake to effectively decrease the soil metal concentration. Several conditions must be met in order for phytoremediation to be effective. The availability of metals in the soil for root uptake is the first critical factor for metal uptake. Soils containing metal contaminants that cannot be solubilized or made available for plant uptake will limit the uptake and therefore the success of phytoremediation.

Metal solubility is dependent on a number of soil characteristics and is strongly influenced by soil pH (Harter, 1983) and complexation with soluble ligands (Norvell, 1984). Chelating agents have been used extensively in the laboratory as extractants to estimate metal availability (Martens and Lindsay, 1990) and also to supply micronutrients in fertilizers. Numerous studies have been conducted to evaluate the effectiveness of soil-applied chelating agents to increase micronutrient availability to crop plants (Wallace, 1983 and references contained therein; Muchovej et al., 1986; Norvell, 1991; Sadiq and Hussain, 1993). The addition of synthetic chelated metals (predominantly polyaminopolycarboxylic acids) to the soil has generally been effective in diminishing micronutrient deficiencies in plants. The effectiveness of the chelate varies depending on soil conditions and the specific micronutrient of interest (Wallace and Wallace, 1983). Although the major portion of the chelate literature addresses amelioration of Fe deficiency, increases in heavy metal uptake have also been demonstrated. Wallace (1977) showed a yield reduction in bush bean (*Phaseolus vulgaris*) coupled with an increase in leaf cadmium concentrations (from 6.7 to 423 µg/g) through the soil application of 100 µg/g of EDTA (ethylenediamine tetraacetic acid) to soils spiked with 100 µg Cd/kg. A much smaller increase in Cd

leaf concentrations (from 6.7 to 12.8 µg/g) was observed with a similar treatment of NTA (nitrilotriacetic acid) instead of EDTA. Patel et al. (1977) showed an increase in Pb uptake in bush beans and barley with 100 µg/g additions of DTPA (diethylenetrinitrilopentaacetic acid) to soil spiked with Pb. The levels of uptake observed (477 µg Pb/g), however, were much less than those required for effective phytoremediation (>1000 mg/kg).

Blaylock et al. (1997) and Huang et al. (1997) have recently shown the effectiveness of applying synthetic chelates to the soil to increase lead solubility and plant uptake as part of the phytoremediation process. In their studies, the application of EDTA and other chelates (DTPA; CDTA, *trans*-1,2-cyclohexylenedinitrilotetraacetic acid; EGTA, ethylenebis[oxyethylenetrinitrilo] tetraacetic acid; and citric acid) to the soil resulted in enhanced shoot lead concentrations. Concentrations greater than 10,000 mg/kg were achieved with EDTA, DTPA, and CDTA while maintaining biomass production. Key factors involved in the increase of lead uptake were soil pH, chelate concentration, and the total soil lead concentration, as well as water soluble lead concentrations. Plants grown in soils at pH 5 and amended with EDTA accumulated nearly 2000 mg/kg more lead in their shoots than corresponding treatments in soil limed to pH 7.5. Shoot lead concentrations also dramatically increased as the total soil lead concentration increased from 150 to 300 mg/kg (Blaylock et al., 1997). Only when the added chelate (EDTA, DTPA, or CDTA) concentration exceeded 1 mmol/kg was substantial lead accumulation (>5000 mg/kg) in the shoots observed. The effectiveness of the chelator can be partially attributed to an increase in lead solubility in the soil coupled with an enhancement of the transport of lead from roots to shoots. EDTA was more effective than DTPA in increasing Pb uptake in the shoots, however, even when both produced equivalent concentrations of water soluble Pb in the soil. Huang et al. (1997) showed that Pb uptake varied with plant species as well as soluble lead concentrations. Lead concentrations in pea (*Pisum sativum* L. cv. Sparkle) were much greater (11,000 mg/kg) than corn (3500 mg/kg) receiving equivalent EDTA applications. In their studies, EDTA was substantially more effective than the other chelates tested at increasing Pb solubility in the soil solution and increasing Pb concentrations in the plant shoots. A correlation value (r^2) of 0.96 was obtained when comparing shoot Pb concentrations in corn to soil solution Pb in soils treated with chelates. From the data of Huang et al. (1997), the soil solution Pb concentration must be greater than 2000 mg/l to achieve substantial shoot Pb concentrations (>5000 mg/kg) in corn.

The plants selected for phytoremediation must also be responsive to agricultural practices and produce sufficient biomass coupled with high rates of metal uptake. The plant must also be adapted to the wide variety of environmental conditions that exist in contaminated soils and waste sites. One crop plant that produces high rates of biomass under field conditions and also has the capacity to accumulate substantial metal concentrations in its shoots is *B. juncea* or Indian mustard (Kumar et al., 1995; Blaylock et al., 1997), which has also been used successfully to decrease the selenium content of soils in central California (Bañuelos et al., 1993).

The application of phytoremediation in the field requires the integration of a variety of skills and techniques. The appropriate plant for the field conditions must be combined with agricultural techniques that support the application of soil amend-

ments to enhance plant availability of the metal contaminants in order to achieve a successful remediation program.

Two field demonstrations of phytoremediation were recently conducted at sites in the U.S. to demonstrate the technical feasibility of phytoremediation for remediating lead-contaminated soils. At both sites, total soil lead levels were significantly reduced during a single growing season. This chapter will detail the results of these two studies. A brief description of each site is below.

BAYONNE, NJ

The first site is an industrial site in Bayonne, NJ contaminated with various heavy metals, but predominantly high levels of total lead. Due to the shallow water table and potential site flooding, an elevated, plastic-lined lysimeter of approximately 1000 sq. ft in area and 3.5 ft deep was constructed and filled with lead-contaminated soil from the site for the purposes of the field trial. A sump was created at one end of the lysimeter to collect any excess drainage water. The source of metal contamination at this site has been attributed to cable manufacturing operations.

DORCHESTER, MA

The second site is located in a heavily populated, urban residential area in Dorchester, MA. The site is a backyard to young children who have been treated twice for lead poisoning. A 1081 sq. ft area was selected for the field trial. The source of lead at the site is unknown but is believed to be from paint and aerial deposition. The plot has been used as a home garden for a number of years.

METHODS

TREATABILITY STUDY

A preliminary site investigation was conducted for each site prior to the field studies to determine the distribution of lead in the soil and to collect bulk surface (0 to 15 cm depth) samples for a laboratory treatability study. The treatability study was conducted to assess the potential of phytoremediation to reduce the lead concentration of the soil. The study determines the forms and concentration of lead in the soil and evaluates plant growth and metal uptake from the soil under greenhouse conditions. The bulk soil samples were sieved to 2 mm and a subsample was submitted to the Rutgers University Soil Testing Laboratory for a standard soil fertility analysis. An additional sample was analyzed for total metals by EPA Method 3050 and also extracted sequentially (Ramos et al., 1994) to assess metal associations with operationally defined soil fractions (i.e., exchangeable, carbonates, oxides, organic matter, and residual). The remaining soil from the treatability sample was fertilized with urea (150 mg N/kg), potassium chloride (83 mg K/kg), and gypsum (70 mg $CaSO_4$/kg). The soil was then placed in 8.75-cm diameter pots (350 g soil/pot) and seeded with *B. juncea*. Phosphate fertilizer was added as a spot placement of triple super phosphate 1 cm below the seeds at planting at the rate of 44 mg P/kg. After seedling emergence, the pots were thinned to two plants per pot.

The plants were grown for 3 weeks in a growth chamber using a 16-h photoperiod and weekly fertilization treatments of 16 and 7 mg/kg N (urea) and K_2O (KCl), respectively. The potassium salt of EDTA (ethylenedinitrilo tetraacetic acid) was applied to the soil surface as a solution to equal 5 mmol EDTA/kg soil 3 weeks after seedling emergence using 4 replications of each treatment. The pots were placed in individual trays to prevent loss of amendments from leaching. The plants were harvested 1 week after the amendment treatment by cutting the stem 1 cm above the soil surface. The plant tissue was dried at 70°C and then wet ashed using nitric and perchloric acids. The resulting solution was analyzed for metal content by inductively coupled plasma spectrometry (ICP; Fisons Accuris, Fisons Instruments, Inc., Beverly, MA).

FIELD PLOTS

Initial Sampling

Based on the results of the treatability study, a field trial was planned and conducted at each site. An initial sampling of the site to obtain baseline soil data was conducted by sampling on a 3 m (10 ft) grid at three depths (0 to 15, 15 to 30, and 30 to 45 cm). The soil samples were collected using a hand-operated, 5 cm diameter, stainless-steel bucket auger. Duplicate samples were collected from 20% of the soil cores. The extracted soil core was mixed in a polyethylene bucket and transferred to a polyethylene bag. Soil samples were collected again at the end of the growing season on the same grid as the initial sampling to determine metal removal efficiency and to monitor changes in Pb concentration in the surface (0 to 15 cm) and subsurface soil (15 to 45 cm).

Site Preparation and Cultivation

The sites were fertilized according to the soil fertility test results and roto-tilled to a depth of 10 to 15 cm before seeding with *B. juncea* (cv. 426308). Tensiometers were installed at two depths (30 and 45 cm) to monitor soil water content. Irrigation was conducted using overhead impact sprinklers. Soil amendments containing EDTA were applied at a rate of 2 mmol/kg through the irrigation system to enhance metal uptake. The crop of *B. juncea* was harvested after 6 weeks of growth. Plant samples were collected randomly from 1 m² blocks for metal analysis, rinsed with water, and placed in paper bags for drying. The remaining biomass was harvested by mowing and removed from the plot for appropriate disposal. Roots were not collected and were left in the soil to decompose. After harvest, the plot was roto-tilled to a 10-cm depth and replanted within 1 week. A total of three crops were grown and harvested at each site during 1996.

Soil Analysis

The soil samples were air dried and sieved to 2 mm before analysis. Soil aggregates were crushed to pass through the sieve and the remaining rocks and debris were discarded. The sieved soil samples were extracted for total metals using a modifi-

cation of EPA SW-846 Method 3050 (U.S. EPA, 1983). The supernatant solution was analyzed for lead. Sequential extraction and fractionation of the soil lead was conducted according to the procedure of Ramos et al. (1994). Lead and total metal content of the soil extracts was determined using ICP by EPA SW-846 Method 6010 (U.S. EPA, 1983). Soil pH was measured in a 1:1 soil:water suspension. Duplicates and spikes were carried through the procedure in combination with National Institutes of Standards and Technology (NIST) Standard Reference Material 2711 to ensure the quality of the data. Contour maps of lead contamination at the site were plotted and areas corresponding to specific levels of metal concentration were calculated using Surfer 6.04 (1996).

PLANT TISSUE ANALYSIS

Plant tissue samples were dried in a forced-air oven at 60°C, ground to 20 mesh using a stainless steel Wiley Mill, and digested using nitric and perchloric acids. The sample was diluted to 25 mL and analyzed for total metals by ICP using EPA SW-846 Method 6010 (U.S. EPA, 1983). Appropriate duplicates and spikes were carried through the digestion procedure as well as the NIST Peach Leaf Standard (SRM 1547) as part of the Quality Assurance/Quality Control (QA/QC) plan.

RESULTS AND DISCUSSION

TREATABILITY STUDIES

Bayonne

The soil at the Bayonne site was an alkaline (pH 7.9) sandy loam soil with 2.5% organic matter. Slightly elevated Cu and Zn concentrations were present in the soil, although they did not exceed regulatory limits. Soil characteristics of the bulk sample collected for the treatability studies are presented in Table 1.1. The sequential extraction of the soil sample from the Bayonne site used for the treatability studies showed the soil lead to be predominantly associated with the carbonate fraction (66% of the total lead), with only 211 mg/kg of the 1608 mg/kg total lead associated

TABLE 1.1

Soil Characteristics and Total Metal Content of a Surface Soil (0 to 15 cm) Sample Collected at Each Site for the Treatability Study

Site	pH	Texture	Organic Matter %	Cd	Cr	Cu	Ni	Pb	Zn
						(mg/kg)			
Dorchester	6.1	Sandy loam	9.0	5	21	32	13	735	101
Bayonne	7.9	Sandy loam	2.5	8	33	139	19	1438	454

with the residual fraction (Table 1.2). Assuming that most of the lead associated with the exchangeable, carbonate, oxide, and organic fractions can be made plant available through soil amendments, enough available lead existed for plant uptake and removal to reduce the soil concentration to below the 400 mg/kg target level.

TABLE 1.2

Fractionation of Metal Contaminants Based on the Sequential Extraction of a Surface (0 to 15 cm Depth) Soil Sample Collected for the Treatability Study

Fraction	Dorchester, MA	Bayonne, NJ
	(mg/kg)	
Exchangeable	100	34
Carbonates	126	1064
Oxide	75	130
Organic	137	170
Residual	125	211
Sum of Fractions	563	1608

Dorchester

The soil at the Dorchester site is a sandy loam containing 9% organic matter in the surface horizon (0 to 15 cm). Soil characteristics of the bulk sample collected for the treatability studies are presented in Table 1.1. The sequential extraction of the bulk soil sample used for the treatability study showed the soil lead to be fairly evenly distributed between all fractions with the organic fraction containing the highest proportion of the total lead (24%; Table 1.2). Similar to the soil from the Bayonne plot, the lead concentration of the residual fraction (125 mg/kg) was much less than the 400 mg/kg target, indicating a suitable quantity of lead in the available/semi-available fractions (exchangeable, carbonate, oxide, and organic) to allow phytoremediation to be successful.

The greenhouse treatability studies indicated that *B. juncea* plants were capable of accumulating significant shoot concentrations of lead from these soils. Shoot lead concentrations of 2080 and 8240 mg/kg were achieved from the soils of the Dorchester and Bayonne sites, respectively, through the use of EDTA-containing amendments in the greenhouse experiments. The plant uptake data coupled with the soil chemical fractionation analysis indicating a low proportion of lead in the unavailable residual fraction (Table 1.2), suggested that the soil Pb could be made plant available through additions of chelators and solubilizing agents. Based on this data, the application of phytoremediation in the field as a means to reduce the surface soil lead concentrations to less than 400 mg/kg was selected.

Bayonne

The excavated soil in the lysimeter at the Bayonne site varied in pH from 7.3 to 8.7. Because surface soil (0 to 15 cm) was used to fill the lysimeter, the Pb contamination was distributed throughout the 3.5-ft deep profile. Initially, the surface (0 to 15 cm) samples ranged in lead concentration from 1000 to 6500 mg/kg with an average of 2055 mg/kg. Average soil Pb concentrations of the subsurface samples were similar (±800 mg/kg) to those of the surface soil samples and ranged from 780 to 2100 at the 15 to 30 cm depth and 280 to 8800 at the 30 to 45 cm depth. After three crops, the lead contamination in the surface soil ranged from 420 to 2300 mg/kg with an average concentration of 960 mg/kg. The average lead concentration in the 15 to 30 cm depth decreased slightly to 992 mg/kg (from 1280 mg/kg, initially) while the 30 to 45 cm depth concentrations remained relatively unchanged.

Dorchester

Initial total lead concentrations in the surface soil at the Dorchester site were lower than at the Bayonne site and ranged from 640 to 1900 mg/kg with an average of 984 mg/kg. The subsurface soil exhibited lower total Pb levels than the surface, averaging 538 mg/kg at the 15 to 30 cm depth and 371 mg/kg at the 30 to 45 cm depth. The Dorchester site exhibited a slightly narrower pH range than the Bayonne site, but was much more acidic with a pH range of 5.1 to 5.9. After three phytoremediation crops, the average concentration in the surface soil decreased from 984 to 644 mg/kg, while the 15 to 30 cm depth samples increased slightly to 671 mg/kg and the 30 to 45 cm depth decreased slightly to 339 mg/kg.

The change in lead concentrations in specific areas of the plot can be evaluated through the surface contour maps created by kriging the data. This allows interpretation of the data based on sample locations and the spatial variability that exists. It also allows one to calculate areas associated with particular Pb concentrations and by comparing the initial and final contour maps to evaluate an increase or reduction in concentration at particular areas. Areas in the plots where the soil exceeded defined Pb concentrations, i.e., 400, 600, 800, or 1000 mg/kg, were calculated based on the initial sampling and then the process repeated after the final sampling. At the Bayonne site, through the process of phytoremediation, the area with lead concentrations exceeding 1000 mg/kg was reduced from 73 to 32% of the plot of the total plot area. Figure 1.1 presents a contour map showing the areas corresponding to specific total soil Pb concentrations before and after one season of phytoremediation (three crops/season). A reduction in area where total soil Pb concentration exceeded the 600, 800, 1200, 1500, and 1700 mg/kg levels was also observed and is quantified in Table 1.3. The greatest reductions were observed in the areas contaminated at the 1000, 1200, and 1500 mg/kg levels.

The implementation of phytoremediation technology at the Dorchester site was also successful in reducing the area of lead-contaminated soil. Figure 1.2 presents
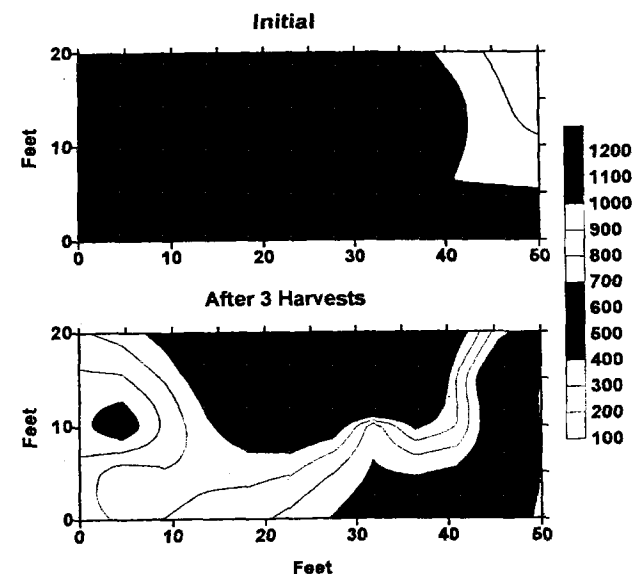
FIGURE 1.1 Contour plot showing the surface soil (0 to 15 cm) lead distribution at the Bayonne site before (top) and after (bottom) three phytoremediation crops. Color contours represent total soil Pb concentrations in mg/kg according to the values on the color scale.

TABLE 1.3

Effect of Phytoremediation on the Area of Surface Soil (0 to 15 cm) Pb Contamination at the Bayonne Site

Soil Pb Concentration (mg/kg)	Initial	After Third Harvest
	(% of Plot Area)	
>600	100	87
>800	80	66
>1000	73	32
>1200	67	20
>1500	49	10
>1700	24	6

Note: Values given are the percentage of the plot area that exceed the given total soil Pb concentrations before and after one season of phytoremediation (three harvests).
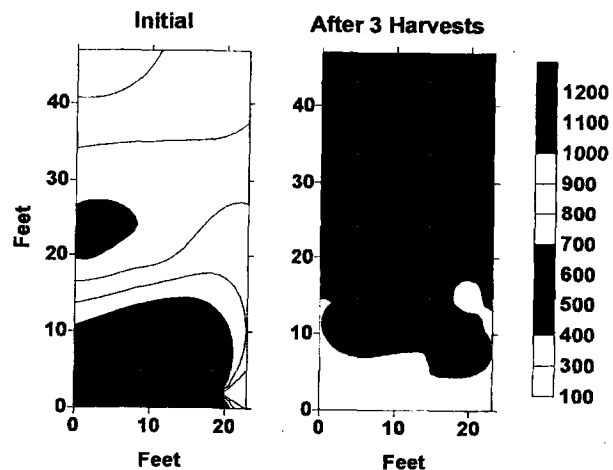
FIGURE 1.2 Contour plot showing initial soil surface lead concentrations (left) and the soil concentration after three phytoremediation crops (right) at the Dorchester site. Color contours represent soil lead concentrations in mg/kg according to the values on the color scale.

a contour map showing the initial soil lead concentration and the soil lead concentration after three phytoremediation crops. At the time of the initial sampling, 68% of the plot was above 800 mg/kg and about 25% of the plot exceeded 1000 mg/kg (Table 1.4). After three crops, none of the treated area exceeded 800 mg/kg.

TABLE 1.4

Effect of Phytoremediation on the Area of Surface Soil (0 to 15 cm) Pb Contamination at the Dorchester Site

Soil Lead (mg/kg)	Initial	After Third Harvest
	(% of Treated Area)	
>500	100	100
>600	100	100
>800	68	0
>1000	25	0

Note: Values given are the percentage of the plot area that exceed the given total soil Pb concentrations before and after one season of phytoremediation (three harvests).

Although none of the area was cleaned below the regulatory limit of 400 mg/kg at the Dorchester and Bayonne sites in the first year, the decrease in the average soil lead concentration shows the potential for phytoremediation to reduce the soil lead

concentrations and the associated hazards. An evaluation of the lead concentrations in the surface soil shows that the average concentration at the Bayonne site decreased from 2055 to 960 mg/kg. This is a substantial decrease — greater than one would expect from plant accumulation of Pb in three phytoremediation crops in one growing season. In fact, under ideal conditions based solely on plant uptake, one would generally predict a 50 mg/kg/crop decrease in the total soil Pb concentration. This assumes a perfectly homogeneous soil with Pb uniformly distributed in the <2 mm particle size fraction (a condition that does not exist at contaminated sites). Nevertheless, it is apparent that some processes occur as part of phytoremediation which enhances the reduction observed above that was predicted. Movement of soil lead from the surface to lower depths was not observed eliminating the effect of leaching or movement of the soil Pb to the subsurface. In addition, the results presented indicate the performance for one growing season only. Additional decreases in soil-metal content may be observed in subsequent seasons. Only with additional research can removal rates over longer periods of time be determined.

These results provide an important first step in establishing phytoremediation as a method to reduce soil Pb levels in the field. Phytoremediation, as implemented at these sites, is projected to be comparable in cost to nonpermanent remediation systems, such as capping, while eliminating the liability concerns and requirements for long-term monitoring. In addition, phytoremediation provides an environmentally compatible means of removing the contaminant. Although this technology may not be applicable to all contaminated soils, it is particularly effective for those sites where the average lead contamination is less than 1500 mg/kg. Phytoremediation has the potential to treat many of the urban and industrial sites containing metal concentrations above the required action limits. The substantial cost 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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2 Phytoremediation by Constructed Wetlands

Alex J. Horne

CONTENTS

SUMMARY

Constructed wetlands offer an unlimited potential for the phytoremediation of toxins and pollutants. Their unique advantage is complete low-cost treatment of large volumes of water. High capacity makes wetlands very different from terrestrial phytoremediation or conventional physical–chemical methods that deal with relatively small volumes of contaminated soils or groundwater. No post-treatment such as filtration is needed for wetlands differentiating them from algae-based systems. Another difference between wetlands and terrestrial phytoremediation is that harvesting of pollutant accumulator plants as yet plays only a small role in wetlands, which have a very limited flora. Harvesting large volumes of toxic plants in wetlands considerably increases the cost of treatment. At least for heavy metals and some organics, the anoxic soils that characterize wetlands immobilize pollutants while the oxidized soils of terrestrial phytoremediation mobilize them into plant tissue. Pollutants such as nitrate, some organics, and probably microbial pathogens can be destroyed or detoxified in wetlands. Phosphate, heavy metals, selenium, and organics are usually immobilized and held in nontoxic forms. The greatest drawback of most terrestrial or wetland phytoremediation is the creation of a toxic "attractive nuisance" to wildlife while the pollutant is moved between the source and final sink. A management problem for treatment of wetlands is pollutant release due to seasonal biotic cycles or when the wetland is fully loaded. Natural wetlands are inefficient, but constructed wetlands, designed for specific pollutants, can deliver reliable treatment and even meet strict discharge limits. All the while the wetland provides multiple use benefits ranging from aesthetic enjoyment to enhanced biodiversity. The combination of higher plants, some algae, and bacteria make wetlands an exciting prospect for detoxification and for the control of eutrophication.

Remediation of pollution requires large amounts of energy. As with other phytoremediation, wetlands become competitive with other cleanup methods by employing free solar energy. Wetland phytoremediation differs from other forms in that bacterial transformation rather than plant uptake dominates detoxification. Nonetheless, some combinations of plants increase efficiency. Wetland plants provide the litter layer that provides both microbial habitat and a source of labile organic carbon for bacterial processes. The key to efficient phytoremediation in constructed wetlands is manipulation of the partially decomposed litter layer and sediments whose high horizontal porosity (m/h) compares with cm/week in deeper sediments. Combinations of toxic and anoxic sites and wet and dry cycles aid remediation of recalcitrant toxics. The detoxification mechanisms involved in wetland phytoremediation differ with each class of pollutant. For example, both nitrate and phosphate must be removed to fully reverse eutrophication. Nitrate is best removed as a gas by denitrification, thus emphasizing the role of plants as providers of labile carbon for bacteria. In contrast, phosphate removal in wetlands is primarily by uptake into plant and algal cell material. Here uptake and burial combined with repressing nutrient recycling is most important. With heavy metals such as copper or lead, or metalloids such as selenium, emphasis is on creating conditions for immobilization in the highly reduced sulfite or metallic form. Selenium is unusual in that it can be volatilized as dimethylselenide gas. Less is known about toxic organics or pesticide removal,

although recent studies indicate that wetlands efficiently remove some chlorinated compounds present at low levels that are difficult to remove by other means. Finally, removal of bacteria, viruses, and protozoan cysts, currently of great importance in the water industry, would appear to be a major advantage of wetlands.

There are similarities between phytoremediation in wetlands, in soils using seeded crops, and groundwater bioremediation, but wetlands are less easily controlled. Thus, floods and higher trophic level interaction such as insect infestation must be considered if regulatory authorities impose effluent discharge limits.

INTRODUCTION

DEFINITIONS

Phytoremediation can be defined as the clean up of pollutants primarily mediated by photosynthetic plants. *Clean up* is defined as the destruction, inactivation, or immobilization of the pollutant in a harmless form. In this way, both higher plants and algae are included as prime phytoremediation agents, but the use of plants to create a suitable physiochemical environment for pollutant detoxification by bacteria and fungi is also specifically included. Small phytoplankton and attached algae can also be important in wetland phytoremediation (see Chapter 16). Larger wetland algae such as the skunkweed, *Chara*, or its close relative, *Nitella*, that may be 50 cm high, are here considered as part of the true wetlands flora.

Wetlands are shallow water bodies containing higher plants. Technically, jurisdictional wetlands are defined by three common components: shallow water coverage for at least a few weeks per year, permanent or temporarily anoxic soils, and characteristic vegetation (i.e., no roots or roots that can survive anoxia; Lyon, 1993). For the purposes of phytoremediation, however, wetlands are shallow waters with at least a 50% aerial cover of submerged or emergent macrophytes or attached algae. Unfortunately, by common usage, as well as the current European definition, small lakes or ponds surrounded by a thin fringe of aquatic macrophytes are termed wetlands. In practice, lakes and ponds are poor at remediation relative to wetlands. This is primarily because the large plants and a few large algae species that provide reduced carbon and the physical environment for wetland phytoremediation are not present in deeper, open lake waters. In terms of simple primary production, the least productive wetland bog exceeds the most eutrophic green lake or pond.

Wetlands are customarily divided into four groups based on their water regime (and often concomitant productivity) or the general kinds of vegetation plants present (Mitsch and Gosslink, 1993). Marshes are dominated by emergent macrophytes, swamps by trees, acid bogs by *Sphagnum* and other mosses, and alkaline fens by mosses and grasses (Horne and Goldman, 1994). Depending on the water depth and degree of shading, marshes and swamps also typically contain submerged macrophytes, often with abundant periphyton. Wetlands are characterized by anoxic reducing soils and consequently plant roots are very shallow, even absent, forcing pollutant treatment into the upper few centimeters of sediment or the litter layer. Productive seasonal wetlands dry out in summer and are thus distinguished from the less productive permanent wetlands. Tidal wetlands have some energetic advantages over

other wetlands since water is pumped through the system at no cost. Finally, the different chemistry and biology of marine and inland saltwater wetlands distinguishes them from the more usual freshwater wetlands. Many of the four classes overlap. For example, the selenium-polluted Kesterson system in central California was an inland, saline, seasonal marsh but it was converted into a freshwater permanent marsh as part of an experimental cleanup (Horne, 1991).

HISTORICAL BACKGROUND OF WETLANDS AND TRADITIONAL REMEDIATION TECHNIQUES

Natural wetlands have long been used for the disposal of wastes. In fact, marshes and bogs were called "wastes" in northern England up until this century. Any treatment occurring in early waste disposal wetlands was incidental and confined to some reduction in the biological oxygen demand (BOD). Currently, the U.S. government encourages the use of simple wetlands for economical treatment of sewage BOD from small communities of less than 5000 people. There are several recent volumes that detail the engineering design required for BOD removal as well as the removal of other pollutants, primarily phosphorus and nitrogen, but also including metals and pesticides (Hammer, 1988, 1996; Marble, 1992; Moshiri, 1993; USEPA, 1993; and a comprehensive survey by Kadlec and Knight, 1996). Given that most wetlands are basically water-saturated anoxic sediments with plants growing on top, they are the least obvious way to remove oxygen-demanding BOD, which is much more efficiently removed with other methods such as algae-based oxidation ponds or small "package" plants using bacteria-based activated sludge. Thus natural or constructed wetlands are best reserved for two purposes: (1) *polishing* of already partially treated (oxidized) industrial or domestic waste or (2) *removal of specific pollutants*, such as nitrogen, phosphorus, copper, lead, selenium, organic compounds, pesticides, viruses, or protozoan cysts from all wastes including agricultural and urban storm runoff.

Traditional remediation of wastes also has a long history (Tchobanoglous and Schroeder, 1985) and in the U.S. has been amplified over the past decade by the need to clean up U.S. EPA Superfund and other lesser-polluted sites (Mineral Policy Center, 1997). If pollution generated by domestic and industrial sewage, agricultural runoff, and storm runoff is added to that from abandoned mines and industrial sites, the range of pollution problems is large. Typical physiochemical remediation methods include addition of bases or metals such as iron that will neutralize and precipitate soluble acid-mine toxic metals such as copper and zinc. Other physiochemical methods are the extraction of polluted groundwater directly or following additions of steam or solvents. Groundwater bioremediation provides additional nutrients and perhaps bacteria to metabolize the toxicant *in situ*. When remediation is not economical, containment by grout walls or other impermeable barriers, including onsite burial, is common. Traditional methods of treating domestic or industrial sewage involve oxygenated activated sludge bacteria, trickling filters, or high rate oxidation ponds. The volumes of agricultural and storm runoff are so large that treatment is rare. Pollutant source control by best management practices (BMPs), usually involv-

ing soil conservation but also including wetlands, has been tried but with only moderate success (Meade and Parker, 1985). Finally, a new regulatory tool, total maximum daily load (TMDL) is being implemented to provide the quantitative tool lacking in previous BMP programs.

The most obvious advantage of phytoremediation over traditional techniques is cost. While most traditional remediation methods rely on electricity, pumping, or oxygen additions and often require large concrete or steel vessels, phytoremediation uses free solar energy and requires no sophisticated containment system. Other differences between conventional remediation, terrestrial phytoremediation, and wetlands phytoremediation are shown in Table 2.1.

TABLE 2.1

Similarities and Differences Between Conventional Bioremediation, Phytoremediation, and Wetlands Phytoremediation

Contamination	Conventional Bioremediation	Terrestrial Phytoremediation	Wetlands Phytoremediation
Waste liquid volume	Low	Low	High
Waste solid volume	High	Moderate (roots)	Low
Energy source	Added carbon	*In situ* generation	*In situ* generation
Containment	Tanks, pumps, grout curtains	Not needed on land	Earth berms
Remediation away from site	Yes and no	No	Yes and no
Agricultural runoff	No	No	Yes
Urban storm runoff	No	No	Yes
Domestic wastewater	No	No	Yes
Industrial wastewater	Yes	Yes?	Yes
Acid-mine drainage	No	No	Yes
Heavy metals	NA	Metal accumulation	Metal immobilization
Polluted soils	Yes	Yes	Rarely
Pumped polluted groundwater	Yes	No	Yes
Metals	No	Yes	Yes
Toxic organics	Yes	Potentially	Potentially
Nutrients	No	No	Yes
Pathogens	No	No	Maybe

Note: Conventional bioremediation has concentrated on toxic organics such as solvents and dissolved nonaqueous phase liquids (DNAPL), while terrestrial phytoremediation has focused on heavy metals. Major differences are also due to wetlands normally being used to treat external water inflows while terrestrial phytoremediation and *in situ* bioremediation restore contaminated soils or groundwater on site. The common method of groundwater cleanup "pump and treat," could use any of the three methods.

NA = not applicable.