



NATO Science for Peace and Security Series - C:
Environmental Security

Application of Phytotechnologies for Cleanup of Industrial, Agricultural and Wastewater Contamination

Edited by
Peter A. Kulakow
Valentina V. Pidlisnyuk

 Springer



*This publication
is supported by:*

The NATO Science for Peace
and Security Programme

Application of Phytotechnologies for Cleanup of Industrial, Agricultural, and Wastewater Contamination

edited by

Peter A. Kulakow

Kansas State University
Manhattan, Kansas, U.S.A.

and

Valentina V. Pidlisnyuk

Kremenchug Technical University
Kremenchug, Ukraine

 Springer

Published in cooperation with NATO Public Diplomacy Division

Proceedings of the NATO Advanced Research Workshop on
Application of Phytotechnologies for Cleanup of Industrial, Agricultural, and
Wastewater Contamination to Enhance Environmental and Food Security
Kamenetz-Podlisky, Ukraine
4–7 June 2007

Library of Congress Control Number: 2009937942

ISBN 978-90-481-3591-2 (PB)
ISBN 978-90-481-3590-5 (HB)
ISBN 978-90-481-3592-9 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springer.com

Printed on acid-free paper

All Rights Reserved
© Springer Science + Business Media B.V. 2010
No part of this work may be reproduced, stored in a retrieval system, or transmitted
in any form or by any means, electronic, mechanical, photocopying, microfilming,
recording or otherwise, without written permission from the Publisher, with the exception
of any material supplied specifically for the purpose of being entered and executed on
a computer system, for exclusive use by the purchaser of the work.

CONTENTS

Preface	v
General Factors Influencing Application of Phytotechnology Techniques	1
<i>T. Vansk, R. Podlipna, and P. Soudek</i>	
1. Introduction	1
2. Phytoremediation	2
2.1. Phytoremediation of Metal Contaminants	3
2.1.1. Phytoextraction	3
2.1.2. Rhizofiltration	3
2.1.3. Phytostabilization	4
2.2. Phytoremediation of Organic Contaminants	4
2.2.1. Phytodegradation	4
2.2.2. Rhizodegradation	5
2.2.3. Phytovolatilization	5
3. Advantages and Limitations of Phytoremediation	5
3.1. Advantages of Phytotechnologies	6
3.2. Limitations to Phytotechnologies	6
4. Performance	7
5. Cost	7
6. Recent Developments in Phytotechnologies	9
7. Conclusions	9
Acknowledgements	10
Capacity Building in Phytotechnologies	15
<i>N. Marmiroli, B. Samotokin, M. Marmiroli, E. Maestri, and V. Yanchuk</i>	
1. European Research in Phytoremediation	15
1.1. COST Actions	16
1.1.1. COST Action 837	17
1.1.2. COST Action 859	18
2. Dissemination and Education in Phytoremediation	18
2.1. Dissemination	18
2.2. Education and Capacity Building	19
2.2.1. The International University Master Course on Science and Technology for Sustainable Development of Contaminated Sites	20
3. NATO ASI School "Advanced Science and Technology for Biological Decontamination of Sites Affected by Chemical and Radiological Nuclear Agents"	21
4. Conclusions	23
Acknowledgements	24
Perspectives on Sustainable Agriculture in Ukraine: The Public View	25
<i>V. Pidlisnyuk, L. Sokol, and T. Stefanovska</i>	
1. Introduction	25

2. Materials and Methods	28
3. Results and Discussion	28
3.1. Governmental Officials	28
3.2. Citizens of Rural Communities	30
4. Conclusions	30
A Review of Recent Research Developments into the Potential for Phytoextraction of Persistent Organic Pollutants (POPs) from Weathered, Contaminated Soil	
<i>M. Whitfield Aslund and B. A. Zeeb</i>	
1. Introduction	35
2. Why Phytoextraction?	36
3. Researching the Potential of POPs Phytoextraction from Soil	38
3.1. The Search for POPs Hyperaccumulating Plants	38
3.2. Understanding the Mechanisms of POPs Uptake into <i>Cucurbita pepo</i> ssp <i>pepo</i>	40
3.3. Identification of Soil Amendments and Other Treatment Processes that could Increase Contaminant Bioavailability to Plants	44
3.3.1. Soil Amendment with Low Molecular-Weight Organic Acids (LMWOAs)	44
3.3.2. Nutrient Amendments	46
3.3.3. Planting Density	47
3.3.4. Surfactants	48
3.3.5. Mycorrhizal Fungi	49
3.3.6. Other Growth Conditions (Fruit Prevention, Soil Moisture Content, and Intercropping)	50
3.4. Impediments to the Practical Application of this Technology	51
4. Conclusions	53
Elimination of Acute Risks from Obsolete Pesticides in Moldova: Phytoremediation Experiment at a Former Pesticide Storehouse	
<i>O. Bogdevich and O. Cadocinicov</i>	
1. Introduction	62
2. Materials and Methods	64
2.1. Initial Site Characterization and Site Selection	64
2.2. Method of Risk Assessment	65
2.3. Analytical Determination	66
2.4. Spatial Analysis	67
2.5. Phytoremediation Study	67
3. Results	69
3.1. Site Selection and Risk Assessment	69
3.2. Characterization of Soil Pollution Impact on Surrounding Agricultural Land at the Balceana and Bujor Sites	71
3.2.1. Balceana Site	71
3.2.2. Bujor Site	74
3.3. Phytoremediation Experiment	76
3.3.1. Zucchini	76
3.3.2. Pumpkin	78

CONTENTS

xi

3.3.3. Total Pesticide Accumulation	78
3.3.4. Pesticide Uptake by Wild Carrot	81
4. Conclusions	84
Obsolete Pesticides Pollution and Phytoremediation of Contaminated Soil in Kazakhstan	87
<i>A. Nurzhanova, P. Kulakov, E. Rubin, I. Rakhimbayev, A. Sedlovskiy, K. Zhabbakin, S. Kalugin, E. Kolysheva, and L. Erickson</i>	
1. Introduction	89
2. Methods and Results	91
2.1. Task 1: Inventory Former Obsolete Pesticide Warehouses to Document Obsolete Pesticide Stockpiles and to Characterize Levels of Soil Contamination	91
2.2. Task 2: Study Genotoxicity of Organochlorine Pesticides	95
2.3. Task 3: Identify Pesticide-Tolerant Plant Species Using Surveys of Plant Community Structure at Selected Hot Points	98
2.4. Task 4: Describe Physiological and Biochemical Characteristics of Pesticide-Tolerant Plants Grown in Pesticide-Contaminated Soil	99
2.4.1. Ratio of Chlorophyll a to Chlorophyll b	100
2.4.2. Transpiration Rate	100
2.5. Task 5: Document Pesticide Accumulation Patterns in Pesticide-Tolerant Plants	102
2.5.1. Histological Analysis to Locate Pesticides in Plant Tissue	105
2.6. Task 6: Study the Fate and Transport of Pesticides in Soil and Plants in the Greenhouse Using soil Collected from Hot Points	105
2.7. Task 7: Study the Effect of Fertilization on Phytoremediation Potential in the Greenhouse and Field	107
2.7.1. Greenhouse Study	107
2.7.2. Field Plot Study	108
2.7.3. Phytoremediation Field Test Trial at Hot Point 2	109
Phytoremediation of Soil Polluted with Obsolete Pesticides in Ukraine	113
<i>L. Mokhyachuk, I. Gorodiska, O. Siobodenjuk, and V. Petryshyna</i>	
1. Introduction	114
1.1. Obsolete Pesticide Problem in Ukraine	114
1.2. Cleanup Technologies for Pesticide-Polluted Soil	115
1.3. Phytoremediation – A Promising Soil Remediation Method	116
2. Materials and Methods	116
3. Results and Discussion	117
3.1. Site Characterization	117
3.2. Testing Phytotoxicity of DDT-Contaminated Soil	118
3.3. Plant Uptake of DDT	119
3.4. Identification of Pesticide-Tolerant Plant Genotypes	120
4. Conclusions	122
Acknowledgments	123

Belarus Experience in Reduction of Radionuclides and Heavy Metals Content in Plants Following the Chernobyl Disaster	125
<i>M. Kalinin, Y. Trybul'skaya, and N. Chubrik</i>	
1. Introduction	125
2. Soil Rehabilitation Technology	126
3. Conclusions	134
Arsenic Content in and Uptake by Plants from Arsenic-Contaminated Soil	135
<i>A. C. Zolnowski, Z. Cieciko, and T. Najmowicz</i>	
1. Introduction	136
2. Materials and Methods	136
3. Results and Discussion	138
4. Conclusions	144
Long-Term Effect of Coal Fly Ash Application on Soil Total Nitrogen and Organic Carbon Concentrations	147
<i>Z. Cieciko, A. C. Zolnowski, and A. Chelstowski</i>	
1. Introduction	148
2. Materials and Methods	148
3. Results and Discussion	149
3.1. Organic Carbon	150
3.2. Total Nitrogen	152
3.3. C:N Ratio	154
4. Conclusions	157
Phytoremediation of Loess Soil Contaminated by Organic Compounds	159
<i>K. Zhu, H. Chen, and Z. Nan</i>	
1. Introduction	159
2. Land Issues in China	160
3. Availability of Phytoremediation for Cleanup of Soils Contaminated with Organic Pollutants	163
3.1. Review of Published Literature	163
3.2. Limitations in Applications of Phytoremediation	165
3.3. Technical Considerations	166
4. Application of Phytoremediation for Petroleum-Contaminated loess Soils in China	166
4.1. Characteristics of Loess Plateau	166
4.2. Characterization of Petroleum-Contaminated Land	168
4.3. Possibilities to Apply Phytoremediation on Petroleum-Contaminated Land	168
4.4. Experimental Study of Phytoremediation by Selected Plants in Loess Plateau	170
5. Conclusions	172
Acknowledgements	173
Phytoremediation of Contaminated Groundwater	177
<i>I. Newman</i>	
1. Introduction and History	177

CONTENTS

xiii

2. Plant Selection.....	179
3. Plant Contaminant Interactions.....	180
4. Designing a Site and Other Factors to Consider.....	181
4.1. Most Common Problem and Solution.....	181
4.1.1. Deep Rooting Methods.....	182
4.1.2. Pump and Irrigate.....	183
4.2. Monitoring.....	183
5. Genetic Manipulation of Plants.....	185
6. Plants and Bacteria.....	185
7. Acceptance by the Public and Regulators.....	186
Evapotranspiration Covers for Landfills.....	189
<i>S. A. Rock</i>	
1. Background.....	190
2. ET Cover Design Considerations.....	191
3. Regulation.....	194
4. Economics.....	197

Chapter

Application of Phytotechnologies for Cleanup of Industrial, Agricultural, and Wastewater Contamination

Part of the series *NATO Science for Peace and Security Series C: Environmental Security* pp 87-111

Obsolete Pesticides Pollution and Phytoremediation of Contaminated Soil in Kazakhstan

- A. Nurzhanova
- P. Kulakow
- E. Rubin
- I. Rakhimbayev
- A. Sedlovskiy
- K. Zhambakin
- S. Kalugin
- E. Kolysheva
- L. Erickson

Abstract

In Kazakhstan, a deepening ecological crisis has been caused by contamination of the environment with obsolete and expired pesticides. Large-scale physical and chemical technologies for managing pesticide-contaminated soils are expensive and unacceptable for Kazakhstan because of limited financial resources. Phytoremediation is a promising innovative technology for managing pesticide-contaminated soils. Pesticide contamination is common on land surrounding destroyed warehouses that were part of the official plant protection service of the former Soviet Union.

We surveyed substances stored in 76 former pesticide warehouses in Almaty and Akmola oblasts of Kazakhstan to demonstrate an inventory process needed to understand the obsolete pesticide problem throughout the country. The survey areas were within 250 km of Almaty (the former capitol of Kazakhstan) and within 100 km of Astana (the new capitol). In Almaty oblast, a total of 352.6 t of obsolete pesticides and 250 pesticide containers were observed. In Akmola oblast, 36.0 t of obsolete pesticides and 263 pesticide containers were observed. Persistent organic pollutants (POPs) pesticides contaminated soil around 26 of the former storehouses where the concentration of POPs exceed the Kazakhstan MAC (maximum allowable concentration) for soil contaminated

by tens to hundreds of times. The POPs pesticides include metabolites of DDT (dichlorodiphenyltrichloroethane) and isomers of HCH (hexachlorocyclohexane).

We studied plant community structure at six "hot points" contaminated sites with three located in Almaty oblast and three in Akmola oblast. From these studies, 17 pesticide-tolerant plant species were selected from colonizing plants that grew near the centers of the hot points.

A greenhouse experiment using the pesticide-tolerant species showed some plant species have the ability to change plant growth characteristics when grown in contaminated versus uncontaminated soil. These characteristics include biomass production, rate of phenological development, peroxidase activity in roots and leaves, ratio of chlorophyll a to chlorophyll b, rate of evapotranspiration, and phytoaccumulation of organochlorine pesticides and their metabolites (4,4 DDE, 2,4 DDD, 4,4 DDT, α -HCH, β -HCH and γ -HCH).

We observed pesticide accumulation was influenced by plant species, plant biomass, and soil pesticide concentrations. Among the investigated species, four accumulated metabolites of DDT and isomers of HCH in plant tissue concentrations exceeding the Kazakhstan MAC (maximum acceptable concentration) for plant tissue by 400 times. The Kazakhstan MAC for DDT and HCH metabolites in plant tissue is 20 $\mu\text{g}/\text{kg}$. Species in this category included: *Artemisia annua* L., *Kochia sieversiana* (Pall.) C.A. Mey., *Kochia scoparia* (L.) Schrad., and *Xanthium strumarium* L. Three species exceeded the MAC by up to 90 times including *A. annua*, *Ambrosia artemisiifolia* L., and *Erigeron canadensis* L. Most pesticides accumulated in the root systems; however, among the species investigated, *K. scoparia*, *A. annua*, *Barbarea vulgaris* W. T. Aiton, and *A. artemisiifolia* demonstrated capabilities to translocate pesticides from roots to aboveground tissues.

To help identify the location of accumulated pesticides within plant tissue, we employed histological analysis whereby a few species indicated pesticides were distributed unevenly within different plant tissues. If a species had a dorsiventral and isolateral leaf type, then pesticides appeared to accumulate in palisade mesophyll tissue. If a species had homogeneous mesophyll, then pesticide appeared to accumulate in mesophyllous cells around conducting bunches. For example, *X. strumarium* has a dorsiventral type of leaf; thus, pesticides collected in the palisade mesophyll. In the stem, pesticides accumulated in walls of xylem cells. In root tissue, pesticides accumulated in parenchymous cells and xylem walls.

We investigated cultivation methods to enhance plant uptake of pesticides. Use of mineral fertilizers resulted in stimulation of growth and biomass accumulation that increased phytoextraction. The concentration of DDT metabolites and isomers of HCH in soil and the application of fertilizers lengthened the rate of phenological development increasing plant height and biomass. In a greenhouse experiment using fertilizer applications to pesticide-contaminated soil, tolerant species showed increased phytoextraction of pesticides. Phytoextraction by *X. strumarium* increased from 0.3% to 0.6%, *A. annua* from 0.5% to 0.7%, and *Cucurbita pepo* L. *pepo* from 0.4% to 0.7%. *K. scoparia* and *Amaranthus retroflexus* L. showed high bioaccumulations factors but showed low biomass compared to other species and thus weak phytoextraction. *A. annua*, *K. scoparia*, *A. retroflexus*, and *X. strumarium* decreased pesticide

concentration of rhizosphere soil 11–24% more in treatments with fertilizer compared to treatments without fertilizer. Field experiments using selected wild species demonstrated reduction of pesticide concentrations in soil in excess of reductions observed without plants and without fertilizers. Additional work is needed to determine if practically useful phytotechnology applications can effectively manage pesticide-contaminated soil at former storehouse sites.

Keywords

obsolete pesticides phytoremediation DDT HCH pesticide tolerance inventory

References

- Bauer, L. D. Grill. 1977. Problems of pigment analysis for diagnosing smoke damage. *J. Angew. Bot.* 51:241–250.
- Bismildin, F. 1997. Pesticides and health of the population. Protection of plants in azakhstan. No. 1. pp. 8–9.
- Bykov, B. A. 1978. Geobotany. Almaty: Nauka.
- Esau, K. 1977. Anatomy of seed plants. New York: Wiley, pp. 556.
- Gao, J., A. W. Garrison, C. Hoehamer, C. S. Mazur, N. L. Wolfe. 2000. Uptake and phytotransformation of o,p'-DDT by axenically cultivated aquatic plants. *J. Agric. Food Chem.* 48:6121–6127.
[CrossRef \(http://dx.doi.org/10.1021/jf990956x\)](http://dx.doi.org/10.1021/jf990956x)
- Gavrilenko, V. F., M. E. Ladygina, L. M. Khandobina. 1975. Practicum on plant physiology. Moscow: Vysshaya Schkola, pp. 380.
- Huang, Y., X. Zhao, S. Luan. 2007. Uptake and biodegradation of DDT by 4 ectomycorrhizal fungi. *Sci. Total Environ.* 385:235–241.
[CrossRef \(http://dx.doi.org/10.1016/j.scitotenv.2007.04.023\)](http://dx.doi.org/10.1016/j.scitotenv.2007.04.023)
- Kamanavalli, C. M., H. Z. Ninnekar. 2004. Biodegradation of DDT by a *Pseudomonas* species. *Curr. Microbiol.* 48:10–13.
[CrossRef \(http://dx.doi.org/10.1007/s00284-003-4053-1\)](http://dx.doi.org/10.1007/s00284-003-4053-1)
- Karthikeyan, R., L. Davis, L. E. Erickson, K. Al Khatib, P. A. Kulakow, P. L. Barnes, S. L. Hutchinson, A. A. Nurzhanova. 2004. Potential of plant-based remediation of pesticide-contaminated soil and water using non-target plants such as trees, shrubs, and grasses. *Crit. Rev. Plant Sci.* 23:1–11.
[CrossRef \(http://dx.doi.org/10.1080/07352680490273310\)](http://dx.doi.org/10.1080/07352680490273310)
- Langenhoff, A. A. M., J. J. M. Staps, C. Puls, A. Alphenaar, G. Zwiep, H. H. M. Rijnaarts. 2002. Intrinsic and stimulated in situ biodegradation of hexachlorocyclohexane (HCH). *Water Air Soil Pollut.* 2:171–181.
[CrossRef \(http://dx.doi.org/10.1023/A:3A1019943410568\)](http://dx.doi.org/10.1023/A:3A1019943410568)
- Medved, L. I. 1977. Directory of pesticides. Kiev: Crop, pp. 376.
- Nazhmetdinova, A. S. 2001. Pesticides and their application in Kazakhstan. *Health and Illness.* No. 1. pp. 36–39.
- Paucheva, Z. P. 1974. Practicum on plant cytology. Moscow: Kolos, pp. 288.
- Phillips, T., A. Seech, H. Lee, and J. Trevors. 2005. Biodegradation of hexachlorohexane (HCH) by microorganisms. *Biodegradation* 16:363–392.
[CrossRef \(http://dx.doi.org/10.1007/s10532-004-2413-6\)](http://dx.doi.org/10.1007/s10532-004-2413-6)
- Prozina, M. 1960. Botanical microtechnique. Moscow: Vysshaya Schkola, pp. 208.
- Quintero, J. C. M. T. Moreira, J. M. Lema, G. Feijoo. 2006. An anaerobic bioreactor allows the efficient degradation of HCH isomers in soil slurry. *Chemosphere* 63:1005–1013.
[CrossRef \(http://dx.doi.org/10.1016/j.chemosphere.2005.08.043\)](http://dx.doi.org/10.1016/j.chemosphere.2005.08.043)
- Raina, V., M. Suar, A. Singh, O. Prakash, M. Dadhwal, S. K. Gupta, C. Dogra, K. Lawlor, S. Lal, J. R. van der Meer, C. Holliger, R. Lal. 2008. Enhanced biodegradation of hexachlorocyclohexane (HCH) in contaminated soils via inoculation with *Sphingobium indicum* B90A. *Biodegradation* 19:27–40.

CrossRef (<http://dx.doi.org/10.1007/s10532-007-9112-z>)

Republic of Kazakhstan. 1996. No. 439 Regarding prohibition of use in Republic Kazakhstan of ecologically harmful pesticides and the order of their burial place. No. 439 from 15 April 1996.

Republic of Kazakhsan. 2001. Resolution on the Stockholm Convention on Persistent Organic Pollutants. 18 May 2001.

Republic of Kazakhstan. 2003. Decree of the President of the Republic of Kazakhstan Regarding the concept of ecological safety of Republic of Kazakhstan for 2004–2015.

Sandermann, H. J. 1992. Plant metabolism of xenobiotics. *Trends Biochem. Sci.* 17:82–84.

CrossRef ([http://dx.doi.org/10.1016/0968-0004\(92\)90507-6](http://dx.doi.org/10.1016/0968-0004(92)90507-6))

Tahtadjan, A. L. 1987. Systematization magnoliophyta. Leningrad: Nauka.

UNEP. 2004. Report on enabling activities for the Stockholm Convention on Persistent Organic Pollutants.

USEPA. 2007. Organochlorine pesticides by gas chromatography. <http://www.epa.gov/waste/hazard/testmethods/sw846/pdfs/8081b.pdf> (<http://www.epa.gov/waste/hazard/testmethods/sw846/pdfs/8081b.pdf>) .

White, J. C. 2002. Differential bioavailability of field-weathered p,p-DDE to plants of the *Cucurbita* and *Cucumis* genera. *Chemosphere* 49:143–152.

CrossRef ([http://dx.doi.org/10.1016/S0045-6535\(02\)00277-1](http://dx.doi.org/10.1016/S0045-6535(02)00277-1))

Wu, W. Z., Y. Xu, K. W. Schramm, and A. Ketrup. 1997. Study of sorption, biodegradation and isomerization of HCH in stimulated sediment water system. *Chemosphere* 35:1887–1894.

CrossRef ([http://dx.doi.org/10.1016/S0045-6535\(97\)00266-X](http://dx.doi.org/10.1016/S0045-6535(97)00266-X))

Zeeb B., A. Lunney, and K. Reimer K. 2003. The potential for phytoremediation of DDT: Greenhouse studies. Seventh International HCH and Pesticides Forum, Kyiv, Ukraine, pp. 125–127.

About this Chapter

Title

Obsolete Pesticides Pollution and Phytoremediation of Contaminated Soil in Kazakhstan

Book Title

Application of Phytotechnologies for Cleanup of Industrial, Agricultural, and Wastewater Contamination

Pages

pp 87-111

Copyright

2010

DOI

10.1007/978-90-481-3592-9_6

Print ISBN

978-90-481-3591-2

Online ISBN

978-90-481-3592-9

Series Title

NATO Science for Peace and Security Series C: Environmental Security

Series ISSN

1874-6519

Publisher

Springer Netherlands

Copyright Holder

Springer Science+Business Media B.V.

Additional Links

- [About this Book](#)

Topics

- [Environmental Management](#)
- [Environmental Engineering/Biotechnology](#)
- [Ecotoxicology](#)
- [Waste Management/Waste Technology](#)
- [Waste Water Technology / Water Pollution Control / Water Management / Aquatic Pollution](#)

Keywords

- obsolete pesticides
- phytoremediation
- DDT
- HCH
- pesticide tolerance
- inventory

eBook Packages

- [eBook Package english full Collection](#)
- [eBook Package english Earth & Environmental Science](#)

Editors

- [Peter A. Kulakow](#) ⁽¹⁾
- [Valentina V. Pidlisnyuk](#) ⁽²⁾

Editor Affiliations

1. Kansas State University
2. Kremenchug Technical University

Authors

- [A. Nurzhanova](#) ⁽³⁾
- [P. Kulakow](#) ⁽⁴⁾
- [E. Rubin](#) ⁽⁵⁾
- [I. Rakhimbayev](#) ⁽³⁾
- [A. Sedlovskiy](#) ⁽³⁾
- [K. Zhabakin](#) ⁽³⁾
- [S. Kalugin](#) ⁽³⁾
- [E. Kolysheva](#) ⁽⁶⁾
- [L. Erickson](#) ⁽⁴⁾

Author Affiliations

3. Institute of Plant Biology and Biotechnology, 45 Timiryazev St., Almaty, 050040, Kazakhstan
4. Center for Hazardous Substance Research, 104 Ward Hall Kansas State University, Manhattan, KS, 66506, USA
5. USEPA, 1200 Pennsylvania Ave, Washington, DC, NW, (1400F), 20460, USA
6. Biomedpreparat, Biomonitoring Laboratory, Micro District 9, Building 3, Stepnogorsk, Akmolinsk, 021500, Kazakhstan