

TRACE ELEMENTS AS CONTAMINANTS AND NUTRIENTS

TRACE ELEMENTS AS CONTAMINANTS AND NUTRIENTS

Consequences in Ecosystems and Human Health

Edited by

M. N. V. Prasad



A JOHN WILEY & SONS, INC., PUBLICATION

Copyright © 2008 by John Wiley & Sons, Inc. All rights reserved

Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

Prasad, M. N. V. (Majeti Narasimha Vara), 1953–
Trace Elements as Contaminants and Nutrients: Consequences in Ecosystems and Human Health /
M.N.V. Prasad.
p. cm.
Includes index.
ISBN 978-0-470-18095-2 (cloth)
1. Trace elements—Environmental aspects. I. Title.
QH545.T7P73 2008
613.2'85—dc22

2007050456

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

CONTENTS

Foreword	xix
Preface	xxiii
Acknowledgments	xxv
Contributors	xxvii

1 The Biological System of Elements: Trace Element Concentration and Abundance in Plants Give Hints on Biochemical Reasons of Sequestration and Essentiality	1
---	----------

Stefan Fränzle, Bernd Markert, Otto Fränzle and Helmut Lieth

1. Introduction	1
1.1 Analytical Data and Biochemical Functions	1
2. Materials and Methods	6
2.1 Data Sets of Element Distribution Obtained in Freeland Ecological Studies: Environmental Analyses	6
2.2 Conversion of Data Using Sets of Elements with Identical BCF Values	8
2.3 Definition and Derivation of the Electrochemical Ligand Parameters	10
3. Results	11
3.1 Abundance Correlations Among Essential and Nonessential Elements	11
3.2 (Lack of) Correlation and Differences in Biochemistry	14
3.3 Implication for Biomonitoring: Corrections by Use of Electrochemical Ligand Parameters and BCF-Defined Element Clusters	14
4. Discussion	15
5. Conclusion	18
References	19

2 Health Implications of Trace Elements in the Environment and the Food Chain	23
--	-----------

Nelson Marmiroli and Elena Maestri

1. Trace Elements Important in Human Nutrition	24
2. The Main Trace Elements: Their Roles and Effects	25

2.1	Arsenic	25
2.2	Cadmium	29
2.3	Chromium	30
2.4	Cobalt	30
2.5	Copper	30
2.6	Fluorine	30
2.7	Iodine	31
2.8	Iron	31
2.9	Lead	31
2.10	Manganese	32
2.11	Mercury	32
2.12	Molybdenum	32
2.13	Nickel	32
2.14	Selenium	33
2.15	Silicon	33
2.16	Tin	33
2.17	Vanadium	34
2.18	Zinc	34
2.19	Hypersensitivity Issues	34
3.	Issues of Environmental Contamination of the Food Chain	37
4.	Legislation Concerning Trace Elements	38
4.1	Elements in Soils and the Environment	38
4.2	Elements in Foods	39
4.3	Supplementation of Minerals to Foods	41
5.	Food Chain Safety	42
5.1	Soil and Plants	42
5.2	Animal Products	43
5.3	Geological Correlates	44
5.4	Intentional Contamination	45
5.5	Availability of Minerals	46
6.	Biofortification	47
7.	Concluding Remarks	48
	Acknowledgments	49
	References	49
3	Trace Elements in Agro-ecosystems	55
	<i>Shuhe Wei and Qixing Zhou</i>	
1.	Introduction	55
2.	Biogeochemistry of Trace Elements in Agro-ecosystems	56
2.1	Input and Contamination	56
2.2	Translation, Translocation, Fate, and Their Implication to Phytoremediation	60
3.	Benefit, Harmfulness, and Healthy Implication of Trace Elements	65
3.1	Benefit to Plant/Crop	65
3.2	Harmfulness to Plant/Crop Physiology	65

3.3	Soil Environmental Quality Standards and Background of Trace Elements	66
4.	Phytoremediation of Trace Element Contamination	68
4.1	Basic Mechanisms of Phytoremediation	68
4.2	Research Progress of Phytoextraction	72
4.3	Discussion on Agro-Strengthen Measurements	73
	Acknowledgments	76
	References	76
4	Metal Accumulation in Crops—Human Health Issues	81
	<i>Abdul R. Memon, Yasemin Yildizhan and Eda Kaplan</i>	
1.	Introduction	81
2.	The Concept of Ionomics and Nutriomics in the Plant Cell	83
3.	The Trace Element Deficiencies in the Developing World	84
4.	Improvement of Trace Metal Content in Plants Through Genetic Engineering	85
5.	Genetic Engineering Approaches to Improve the Bioavailability of Iron and Zinc in Cereals	88
6.	Decreasing the Content of Inhibitors of Trace Element Absorption	91
7.	Increasing the Synthesis of Promoter Compounds	92
8.	Conclusions	93
	Acknowledgments	93
	References	93
5	Trace Elements and Plant Secondary Metabolism: Quality and Efficacy of Herbal Products	99
	<i>Charlotte Poschenrieder, Josep Allué, Roser Tolrà, Mercè Llugany and Juan Barceló</i>	
1.	Coevolutionary Aspects	99
2.	Environmental Factors and Active Principles	102
3.	Influence of Macronutrients	102
4.	Influence of Micronutrients	104
5.	Trace Elements as Elicitors of Active Principles	106
6.	Trace Elements as Active Components of Herbal Drugs	107
7.	Trace Elements in Herbal Drugs: Regulatory Aspects	111
	Acknowledgments	112
	References	112
6	Trace Elements and Radionuclides in Edible Plants	121
	<i>Maria Greger</i>	
1.	Introduction	121
2.	Plant Uptake and Translocation of Trace Elements	122
3.	Distribution and Accumulation of Trace Elements in Plants	124

viii CONTENTS

4. Vegetables, Fruit, and Berries	125
5. Cereals and Grains	128
5.1 Cadmium in Wheat	128
5.2 Arsenic in Rice	129
6. Aquatic Plants	129
7. Fungi	130
8. How to Cope with Low or High Levels of Trace Elements	131
References	132
7 Trace Elements in Traditional Healing Plants—Remedies or Risks	137
<i>M. N. V. Prasad</i>	
1. Introduction	137
2. The Indigenous System of Medicine	138
3. Herbal Drug Industry	139
4. Notable Medicinal and Aromatic Plants that have the Inherent Ability of Accumulating Toxic Trace Elements	141
5. Cleanup of Toxic Metals from Herbal Extracts	149
6. Polyherbal Preparation and Traditional Medicine Pharmacology	150
7. Conclusions	152
References	155
8 Biofortification: Nutritional Security and Relevance to Human Health	161
<i>M. N. V. Prasad</i>	
1. Introduction	161
2. Bioavailability of Micronutrients	168
3. Social Acceptability of Biofortified Crops	169
4. Development and Distribution of the New Varieties	169
5. Selected Examples of Biofortified Crops Targeted by Harvestplus in Collaboration with a Consortium of International Partners	169
5.1 Rice	170
5.2 Wheat	171
5.3 Maize	172
5.4 Beans	173
5.5 <i>Brassica juncea</i> (Indian Mustard)	174
6. Selenium-Fortified Phytoproducts	175
7. Sources of Selenium in Human Diet	175
8. Selenium (Se) and Silica (Si) Management in Soils by Fly Ash Amendment	175
9. Chromium for Fortification Diabetes Management	176
10. Silica Management in Rice—Beneficial Functions	177
11. Conclusions	178
Acknowledgments and Disclaimer	179
References	179

9	Essentiality of Zinc for Human Health and Sustainable Development	183
	<i>M. N. V. Prasad</i>	
1.	Biogeochemical Cycling of Zinc	185
2.	Distribution of Zinc Deficiency in Soils on a Global Level	186
3.	Zinc Intervention Programs	188
4.	Zinc-Transporting Genes in Plants	191
5.	Addressing Zinc Deficiency Without Zinc Fortification	204
6.	Zinc Deficiency is a Limitation to Plant Productivity	204
	Acknowledgments and Disclaimer	205
	References	205
10	Zinc Effect on the Phytoestrogen Content of Pomegranate Fruit Tree	217
	<i>Fatemeh Alaei Yazdi and Farhad Khorsandi</i>	
1.	Introduction	217
2.	Materials and Methods	220
3.	Results and Discussions	222
3.1	Pomegranate Yield	222
3.2	Pomegranate Zinc Content	223
3.3	Phytoestrogen Content	225
4.	Summary and Conclusions	227
	Acknowledgments	227
	References	228
11	Iron Bioavailability, Homeostasis through Phytoferritins and Fortification Strategies: Implications for Human Health and Nutrition	233
	<i>N. Nirupa and M. N. V. Prasad</i>	
1.	Introduction	233
2.	Iron Importance	234
3.	Iron Toxicity	235
4.	Interactions with Other Metals	235
5.	Iron Acquisition by Plants	238
6.	Translocation of Iron in Plants	238
7.	Iron Deficiency in Humans	239
8.	Amelioration of Iron Deficiencies	241
9.	Ferritin	242
10.	Ferritin Structure	243
11.	Mineral Core Formation	247
12.	Ferritin Gene Family and Regulation	248
13.	Developmental Regulation	249
14.	Role of Ferritin	251
15.	Metal Sequestration by Ferritin: Health Implications	254

16. Overexpression of Ferritin	254
Acknowledgments	257
References	257
12 Iodine and Human Health: Bhutan's Iodine Fortification Program	267
<i>Karma Lhendup</i>	
1. Role of Iodine	267
2. Iodine Deficiency Disorders (IDD)	268
3. Sources of Iodine	269
4. Recommended Intake of Iodine	270
5. Indicators for Assessment of Iodine Status and Exposure	270
6. Control of IDD	271
7. IDD Scenario in Bhutan: Past and Present	272
8. Toward IDD Elimination in Bhutan: Highlights of the IDD Control Program	273
8.1 IDD Survey	273
9. 1996 Onward: Internal Evaluation of the IDDCP through Cyclic Monitoring	277
10. Conclusion	278
References	278
13 Floristic Composition at Kazakhstan's Semipalatinsk Nuclear Test Site: Relevance to the Containment of Radionuclides to Safeguard Ecosystems and Human Health	281
<i>K. S. Sagyndyk, S. S. Aidossova and M. N. V. Prasad</i>	
1. Introduction	281
2. Kazakhstan: Semipalatinsk Nuclear Test Site	283
3. Flora of Nuclear Test Site	286
4. Fodder Plants	292
5. Conclusions	293
Acknowledgments and Disclaimer	293
References	293
14 Uranium and Thorium Accumulation in Cultivated Plants	295
<i>Irina Shtangeeva</i>	
1. Introduction: Uranium and Thorium in the Environment	295
2. Uranium and Thorium in Soil	296
2.1 Soil Characteristics Affecting Uranium and Thorium Plant Uptake	297
2.2 Effects of Soil Amendments	300
3. Radionuclides in Plants	301

3.1	Accumulation of Uranium and Thorium in Plant Roots	302
3.2	Differences in U and Th Uptake by Different Plant Species (in the example of wheat <i>Triticum aestivum</i> and Rye <i>Secale cereale</i>)	303
3.3	Effects of U and Th Bioaccumulation on Distribution of Other Elements in Rye and Wheat	311
3.4	Relationships Between U and Th in Soils and in Different Plant Parts	312
3.5	Phytotoxicity of U and Th	314
3.6	Effects of U and Th on Leaf Chlorophyll Content and the Rhizosphere Microorganisms	321
3.7	Temporal Variations of U and Th in Plants	325
3.8	Effects of Thorium on a Plant During Initial Stages of the Plant Growth	328
4.	Potential Health Effects of Exposure to U and Th	333
	References	336
15	Exposure to Mercury: A Critical Assessment of Adverse Ecological and Human Health Effects	343
	<i>Sergi Díez, Carlos Barata and Demetrio Raldúa</i>	
1.	Human Health Effects	343
1.1	Introduction	343
1.2	Sources and Cycling of Mercury to the Global Environment	344
1.3	Methylmercury	346
2.	Adverse Ecological Effects	349
2.1	Laboratory Toxicity Studies	349
2.2	Biochemical Approaches to Study Bioavailability and Effects	351
2.3	Methods	353
2.4	Results and Discussion	354
3.	Case Study: Mercury-Cell Chlor-Alkali Plants as a Major Point Sources of Mercury in Aquatic Environments—The Case of Cinca River, Spain	357
3.1	Introduction	357
3.2	The Case of Mercury Pollution in Cinca River, Spain	358
	References	364
16	Cadmium as an Environmental Contaminant: Consequences to Plant and Human Health	373
	<i>Saritha V. Kuriakose and M. N. V. Prasad</i>	
1.	Introduction	373
2.	Cadmium is Natural	374
3.	Past and Present Status	375
3.1	Natural Sources	376
3.2	Technogenic Sources	376
3.3	In Agricultural Soils: Cadmium from Phosphate Fertilizers	378

xii CONTENTS

3.4	Induction of Oxidative Stress as a Fall-Out of Cadmium Toxicity	378
3.5	Oxidative Damage to Membranes	378
3.6	Oxidative Damage to Chloroplasts	379
3.7	Protein Oxidation	379
3.8	Oxidative Damage to DNA	380
3.9	Antioxidant Defense Mechanisms in Response to Cadmium Toxicity	382
3.10	Cadmium Availability and Toxicity in Plants	384
3.11	Metal–Metal Interactions	387
3.12	Uptake and Transport of Cadmium by Plants	388
3.13	Consequences to Human Health	389
3.14	Options for Cadmium Minimization	392
3.15	Molecular and Biochemical Approaches	392
3.16	Breeding Strategies	394
3.17	Soil Cadmium Regulation	394
4.	Conclusions	396
	References	397

17 Trace Element Transport in Plants **413**

Danuta Maria Antosiewicz, Agnieszka Sirko and Paweł Sowiński

1.	Introduction	413
2.	Short-Distance Transport	416
2.1	Metal Uptake Proteins	416
2.2	Metal Efflux Proteins	423
2.3	Alternative Plant Metal Transporter	433
3.	Intercellular and Long-Distance Transport	433
4.	The Importance of Plant Mineral Status for Human Health	438
	Acknowledgments	438
	References	439

18 Cadmium Detoxification in Plants: Involvement of ABC Transporters **449**

Sonia Plaza and Lucien Bovet

1.	Cadmium in Plants	449
1.1	Cadmium Effects in Plants	449
1.2	Genes Regulated by Cd Stress	450
2.	ABC Transporters	451
2.1	Functions of ABC Transporters in Plants	451
2.2	Characteristics of ATP-Binding Cassette Transporters	451
2.3	Subfamilies of ATP-Binding Cassette Proteins	452
2.4	Involvement of ABC Transporters in Cadmium Detoxification in Plants	452
3.	Conclusion	462
	Acknowledgments	463
	References	463

19 Iron: A Major Disease Modifier in Thalassemia	471
<i>Sujata Sinha</i>	
1. Introduction	471
1.1 Hemoglobin: The Tetramer Molecule	472
1.2 Erythropoiesis and Erythroid Differentiation	472
1.3 Pathophysiology of Thalassemia	474
2. Iron Metabolism: Current Concepts and Alterations in Thalassemia	474
2.1 Iron Absorption and Uptake	476
2.2 Regulation of Expression of Transferrin Receptors	477
2.3 Alterations in Iron Absorption and Uptake in Thalassemia	479
3. Heme Synthesis and Its Role in Regulation of Erythropoiesis	480
3.1 Role of Heme in Globin Regulation and Erythroid Differentiation	481
3.2 Pivotal Role of HRI in Microcytic Hypochromic Anemia	481
3.3 Role of HRI in Beta Thalassemia Intermedia	482
3.4 Iron and Pathobiology of Thalassemia	482
3.5 Iron Storage and Its Effects on Parenchymal Tissues and Organs	483
4. Effect of Transfusional Iron Overload on Iron Homeostasis and Morbidity and Mortality	484
4.1 Iron Homeostasis in Transfusional Iron Overload	484
4.2 Transfusion Iron Overload-Associated Morbidity and Mortality	485
4.3 Endocrinopathy in Thalassemia	485
4.4 Liver Disease	485
4.5 Heart Disease	486
5. Evaluation and Management of Iron Overload	486
5.1 Evaluation of Iron Overload	486
5.2 Basis of Iron Chelation Therapy and Iron Chelator Drugs	487
5.3 Potential Role of Iron Chelation Therapy in Improving Basic Pathophysiology of Beta Thalassemia	488
6. Summary	488
References	489
20 Health Implications: Trace Elements in Cancer	495
<i>Rafael Borrás Aviñó, José Rafael López-Moya and Juan Pedro Navarro-Aviñó</i>	
1. Introduction	495
1.1 General Nutritional and Medical Benefits	496
2. Toxic Heavy Metals	496
2.1 Mercury	497
2.2 Arsenic	500
2.3 Chromium	508
2.4 Cadmium	511
2.5 Lead	515
2.6 Benefits in Cancer	517

3. General Conclusions	519
References	519
21 Mode of Action and Toxicity of Trace Elements	523
<i>Arun K. Shanker</i>	
1. Introduction	523
2. Mode of Action and Toxicity of Trace Elements in General	525
3. Specific Mode of Action of Major Trace Elements	528
3.1 Arsenic	528
3.2 Cadmium	532
3.3 Chromium	537
4. Specific Mode of Action of Other Metals	542
4.1 Nickel	542
4.2 Lead	544
4.3 Mercury	545
5. Mode of Action: What is the Future?	549
References	550
22 Input and Transfer of Trace Metals from Food via Mothermilk to the Child: Bioindicative Aspects to Human Health	555
<i>Simone Wuenschmann, Stefan Fränze, Bernd Markert and Harald Zechmeister</i>	
1. Introduction	555
2. Aims and Scopes	556
3. Principles	558
3.1 Transfer of Chemical Elements	558
3.2 Physiology of Lactation	559
3.3 Transfer of Chemical Elements into Human Milk	560
4. Materials and Methods	561
4.1 A Comparison of the Two Experimental Regions Euroregion Neisse and Woivodship Małopolska with Respect to Factors that Cause Environmental Burdens	561
4.2 Origins and Sampling of Food and Milk Samples	564
4.3 Analytical Methods	567
4.4 Quality Control Measures for Analytic Data	569
4.5 Calculation of Transfer Factors in the System Food/Mother's Milk	570
5. Results	570
5.1 A Comparison of Element Concentrations Detected in Colostrum and Mature Milk Sampled in Different Countries	570
5.2 Transfer Factors for All the Investigated Elements (Specific Ones) in the Food/Milk System and Extent of Partition of Elements into Mother's Milk	574

6. Discussion	577
6.1 Physiological and Dynamic Features of Chemical Elements in the Food/Milk System	577
6.2 Lack of an Effect of Regional Pollution on Chemical Element Composition in Mother's Milk	582
7. Conclusion: Is There a Role for Human Milk in Metal Bioindication?	584
References	588
23 Selenium: A Versatile Trace Element in Life and Environment	593
<i>Simona Di Gregorio</i>	
1. What is Selenium?	593
1.1 Selenium Industrial Applications	593
1.2 Selenium in the Environment	594
2. Biological Reactions in Selenium Cycling	596
2.1 Microbial Assimilatory Reduction	597
2.2 Microbial Dissimilatory Reduction	597
2.3 Detoxification of Se Oxyanions by Reduction Reactions in Aerobiosis	599
2.4 Regulation of Reducing Equivalents	601
2.5 Oxidation of Reduced Se Forms	602
2.6 Selenium Volatilization, Se Methylation and Demethylation	602
3. Selenium in Humans and Animals	603
4. Selenium in Plants	605
5. Selenium of Environmental Concern: Exploitation of Biological Processes for Treatment of Selenium Polluted Matrices	607
5.1 Microbe-Induced Bioremediation	608
5.2 Selenium Plant-Assisted Bioremediation (Phytoremediation)	609
5.3 Plant–Microbe Interaction: Selenium Phytoremediation Processes	611
References	612
24 Environmental Contamination Control of Water Drainage from Uranium Mines by Aquatic Plants	623
<i>Carlos Paulo and João Pratas</i>	
1. Introduction	623
2. Uranium Mining: Environmental and Health	624
2.1 Uranium Toxicity	627
2.2 Uranium Mining History in Portugal	629
3. Phytoremediation of Metals with Aquatic Plants as Strategies for Mine Water Remediation	631
3.1 Uranium Accumulation in Aquatic Plants and Phytoremediation Studies	632

4.	Case Study: Water Drainage from Uranium Mines Control by Aquatic Plants in Central Portugal	634
4.1	Selection of Aquatic Macrophytes: Field Studies	634
4.2	Laboratory Experiments: Uranium Accumulation by <i>C. stagnalis</i>	640
4.3	Phytoremediation Laboratory Prototype	644
5.	Future Prospects of Water Phytoremediation	646
	Acknowledgments	647
	References	647
25	Copper as an Environmental Contaminant: Phytotoxicity and Human Health Implications	653
	<i>Myriam Kanoun-Boulé, Manoel Bandeira De Albuquerque, Cristina Nabais and Helena Freitas</i>	
1.	Copper and Humans: A Relation of 10,000 Years	653
2.	Copper: Identity Card, Main Sources, and Environmental Pollution	654
2.1	Copper in the Atmosphere	654
2.2	Copper in the Hydrosphere	654
2.3	Copper in the Lithosphere and Pedosphere	655
3.	Copper in Plants	656
3.1	Metabolic Functions of Copper	656
3.2	Toxicity of Copper	657
3.3	Copper and Human Health	663
4.	Further Research Topics	670
	References	671
26	Forms of Copper, Manganese, Zinc, and Iron in Soils of Slovakia: System of Fertilizer Recommendation and Soil Monitoring	679
	<i>Bohdan Jurani and Pavel Dlapa</i>	
1.	Forms of Trace Elements in Heterogeneous Soil Materials	679
2.	Concept of Micronutrients Used in Agriculture of Former Czechoslovakia	682
3.	Determination of Available Forms of Some Micronutrients in Soil Based on the Rinkis Method	682
4.	Results of Modified Rinkis Method of Available Copper, Manganese, and Zinc in Soils of Slovakia	685
5.	More Suitable Method for Determination of Plant Available Forms of Copper, Manganese, Zinc, and Iron in Soils	686
6.	Limits to Lindsay—Norvell Method	687
7.	Some Results Concerning Using Lindsay—Norvell Method	690
8.	System of Micronutrients Application: Copper, Manganese, Zinc, and Iron for Agricultural Crops, Recommended in Slovakia	692

9. Remarks to the System used for Copper, Manganese, Zinc, and Iron Available Forms Determination and Fertilizers Recommendation	694
10. New Priorities in Research of Trace Elements in Soils of Slovakia—Soil Monitoring	695
References	697
27 Role of Minerals in Halophyte Feeding to Ruminants	701
<i>Salah A. Attia-Ismail</i>	
1. Introduction	701
2. Ash and Mineral Contents of Halophytes	702
3. Factors Affecting Mineral Contents of Halophytes	702
4. Salt-Affected Soils	706
5. Irrigation with Saline Water	706
6. Salinity Level	706
7. Plant Species	708
8. Mineral Role in Ruminant Nutrition	708
9. Recommended Mineral Allowances	708
10. Minerals Deficiency in Halophyte Included Diets	710
11. Excessive Minerals in Livestock Rations in Dry Areas	713
12. Effect of Halophytes Feeding on Mineral Utilization	713
13. Effect of Minerals on Rumen Function	714
14. Effect of Minerals on Feed Intake	715
15. Effect of Minerals on Water Intake and Nutrient Utilization	716
16. Effect of Minerals on Microbial Community in the Rumen	717
References	717
28 Plants as Biomonitors of Trace Elements Pollution in Soil	721
<i>Munir Ozturk, Ersin Yucel, Salih Gucel, Serdal Sakçali and Ahmet Aksoy</i>	
1. Introduction	721
2. Soils and Trace Elements	722
3. Plants as Biomonitors of Trace Elements	725
4. Conclusions	735
References	735
29 Bioindication and Biomonitoring as Innovative Biotechniques for Controlling Trace Metal Influence to the Environment	743
<i>Bernd Markert</i>	
1. Introduction	743
2. Definitions	745

xviii CONTENTS

3. Comparison of Instrumental Measurements and the Use of Bioindicators with Respect to Harmonization and Quality Control	746
4. Examples for Biomonitoring	748
4.1 Mosses for Atmospheric Pollution Measurements	748
4.2 Is There a Relation Between Moss Data and Human Health?	750
5. What do Bioaccumulation Data Really Tell Us?	752
6. Future Outlook: Breaking “Mental” Barriers Between Ecotoxicologists and Medical Scientists	754
References	757
Biodiversity Index	761
Subject Index	769

FOREWORD

From the very beginning, metals such as gold, silver, copper, and iron have played a major role in the development and history of human societies and civilizations. Metals are dispersed on and in the Earth's crust, and methods for obtaining them from natural deposits have evolved over time. The distribution of metals is not uniform, and localized deposits serve as ores for metals, usually found as compounds, combined with other minerals and inorganic anions. If the concentration of the desired metal is high enough in the deposit for an economical extraction, then the ore can be exploited for a short or long period, depending on the state of the art and technology of mining. Most metals have to be purified or refined and then reduced to the metallic state before use. For example, the production of steel from iron requires the elimination of impurities present in the rocks, followed by the addition of other metals to obtain steel with the desired properties, such as hardness and resistance to corrosion. The science and technology of metals is precisely called metallurgy. Our post-modern society is still based on the use of metals, and some major applications are briefly mentioned below:

- Potassium chloride is used as a fertilizer, and potash (K_2CO_3) is used in making soft soaps, pottery, and glass. Potassium hydroxide is an electrolyte in alkaline batteries, and NaOH is the most important base for industry. Soda ash (Na_2CO_3) is mainly used to make glass, but is also required to prepare chemicals, paper, and detergents. $NaHCO_3$ is an additive to control water pH in swimming pools, as well as to provide the fizz and neutralize excess stomach acid in analgesic drugs.
- Magnesium and calcium are good heat and electricity conductors. Alloyed with aluminum, Mg produces a strong structural metal. Another use of Mg is in fireworks. Epsom salt ($MgSO_4$) is useful in the tanning of leather and to treat fabrics. Milk of magnesia ($Mg(OH)_2$) has antacid and laxative properties. $CaCl_2$ is used to remove moisture from very humid places; CaO is a major ingredient in Portland cement, and partially dehydrated $CaSO_4$ (gypsum) produces plaster of Paris.
- Chromium is resistant to corrosion and is excellent as a protective coating over brass, bronze, and steel. Chromium is also needed to produce alloys such as stainless steel or nichrome; the latter is often used as the wire heating element in various devices such as toasters. Compounds of Cr have many practical

applications, such as for pigments production and leather tanning. The main use of manganese is as an additive to steel and in the preparation of different alloys.

- Iron and its alloys have such physical properties that they have been put to more uses than any other metal. Nickel is one of our most useful metals; in its pure state, it resists corrosion, and it is thus frequently layered on iron and steel as a protective coating by electrolysis. When alloyed with iron or with copper, Ni makes the metal more ductile and resistant to corrosion and to impact.
- Copper has a very high electrical and thermal conductivity and is thus used in electrical wiring. It is also resistant to corrosion and thus appropriate to carry hot and cold water in buildings. Cu does oxidize slowly in air; and when CO₂ is also present, its surface becomes coated with a green film.
- Zinc provides a protective coating on steel, in a process called galvanizing. It is also used in various alloys, like brass (Cu and Zn) and bronze (Cu, Sn, and Zn). Zinc is important in the manufacture of zinc-carbon dry cells and other batteries. Zinc oxide is used in sunscreens and to make quick-setting dental cements. Zinc sulfide is suitable to prepare phosphors that glow when submitted to UV light or high-energy electrons of cathode rays, like the inner surface of TV picture tubes and the displays of computer monitors. Cadmium is useful as a protective coating on other metals and for making Ni-Cd batteries.
- In the past, lead was used for pipes and as an additive to gasoline. Nowadays, Wood's metal consists of an alloy of Bi, Pb, Sn, and Cd, melting at 70°C only, used to seal the heads of overhead sprinkler systems: A fire triggers the system automatically by melting the alloy. Different lead oxides are also needed in making pottery glazes and fine lead crystal; in corrosion-inhibiting coatings applied to structural steel; and as the cathode in lead storage batteries.

However, metals not only play an essential role in our daily life, but also are released into the environment in an uncontrolled way and become contaminants, or even pollutants. A contaminant is present where it would not normally occur, or at concentrations above natural background, whereas a pollutant is a contaminant that cause adverse biological effects to ecosystems and/or human health. In such a context, green plants play a key role in the availability and mobility of metals. Plants can remove metals from contaminated soils and water for cleanup purposes. Several plant species, hyperaccumulating elements like nickel, gold, or thallium, can be used for phytomining. On the other hand, crops with a reduced capacity to accumulate toxic metals in edible parts should be valuable to improve food safety. In contrast, crop plants with an enhanced capacity to accumulate essential minerals in an easily assimilated form can help to feed the rapidly increasing world population and improve human health through balanced mineral nutrition. Because many metals hyperaccumulated by plants are also essential nutrients, food fortification and phytoremediation are thus two sides of the same coin. The different chapters of this book

do address the dual role of trace elements as nutrients and contaminants and review the consequences for ecosystems and health.

DR. JEAN-PAUL SCHWITZGÜBEL

*Chairman of COST Action 859
Laboratory for Environmental Biotechnology (LBE)
Swiss Federal Institute of Technology Lausanne (EPFL),
Station 6, CH 1015, Lausanne, Switzerland*

PREFACE

It is a general belief that the fruits and vegetables that our parents ate when they were growing up were more nutritious and enriched with essential mineral nutrients and were less contaminated with toxic trace elements than the ones that are being consumed by us currently. A study of the mineral content of fruits and vegetables grown in Great Britain between 1930 and 1980 has added weight to that belief with findings of such decreases in nutrient density. The study, conducted by scientists in Great Britain, found significantly lower levels of calcium, magnesium, copper, and sodium in vegetables, as well as significantly lower levels of magnesium, iron, copper and potassium in fruits. Research studies are showing that the reducing nutritional value and the problem of contamination associated with food quality is increasing at an alarming rate. The decline in quality of agricultural produce has corresponded to the period of increased industrialization of our farming systems, where emphasis has been on cash crop cultivation that demands high doses of agrochemicals—that is, fertilizers and pesticides.

Several of the trace elements are essential for human as well as animal health. However, nutritionally important trace elements are deficient in soils in many regions of the world and the health problems associated with an excess, deficiency, or uneven distribution of these essential trace elements in soils are now a major public health issue in many developing countries. Therefore, the development of “foods and animal feeds” fortified with essential nutrients is now one of the most attractive research fields globally. In order to achieve this, knowledge of the traditional forms of agriculture, along with conservation, greater use of native bio-geo-diversity, and genetic diversity analysis of the cultivable crops, is a must.

A number of trace elements serve as cofactors for various enzymes and in a variety of metabolic functions. Trace elements accumulated in medicinal plants have the healing power for numerous ailments and disorders. Trace elements are implicated in healing function and neurochemical transmission (Zn on synaptic transmission); Cr and Mn can be correlated with therapeutic properties against diabetic and cardiovascular diseases. Certain transition group elements regulate hepatic synthesis of cholesterol. Nutrigenomics, pharmacogenomics, and metallomics are now emerging as new areas of research with challenging tasks ahead.

Soil, sediment, and urban dust, which originate primarily from the Earth’s crust, is the most pervasive and important factor affecting human health and well-being. Trace element contamination is a major concern because of toxicity and the threat to human life and the environment. A variety of elements commonly found in the urban environment originate technogenically. In an urban environment, exposure of

human beings to trace elements takes place from multiple sources, namely, water transported material from surrounding soils and slopes, dry and wet atmospheric deposition, biological inputs, road surface wear, road paint degradation, vehicle wear (tyres, body, brake lining, etc.), and vehicular fluid and particulate emissions. Lead and cadmium are the two elements that are frequently studied in street dust, but very little attention has been given to other trace elements such as Cr, Cu, Zn, and Ni, which are frequently encountered in the urban environment.

Street dusts often contain elevated concentrations of a range of toxic elements, and concerns have been expressed about the consequences for both environmental quality and human health, especially of young children because of their greater susceptibility to a given dose of toxin and the likelihood to ingest inadvertently significant quantities of dust. Sediment and dust transported and stored in the urban environment have the potential to provide considerable loadings of heavy metals to receiving water and water bodies, particularly with changing environmental conditions. On land, vegetables and fruits may be contaminated with surficial deposits of dusts. Environmental and health effects of trace metal contaminants in dust are dependent, at least initially, on the mobility and availability of the elements, and mobility and availability is a function of their chemical speciation and partitioning within or on dust matrices. The identification of the main binding sites and phase associations of trace metals in soils and sediments help in understanding geochemical processes and would be helpful to assess the potential for remobilization with changes in surrounding chemistry (especially pH and Eh). Sophisticated analytical and speciation techniques and synchrotron research are being applied to this field of research in developed nations.

This book covers both the benefits of trace elements and potential toxicity and impact of trace elements in the environment in the chosen topics by leaders of the world in this area.

M. N. V. PRASAD

*University of Hyderabad
Hyderabad, India*

ACKNOWLEDGMENTS

I am thankful to Padmasri Professor Seyed Ehtesham Hasnain, Vice-Chancellor, University of Hyderabad for inspiring me to focus research in the area of health and nutritional science which gained considerable momentum under his dynamic leadership. I am grateful to all authors for cogent reviews which culminated in the present form.

Thanks are due to Anita Lekhwani, Senior Acquisitions Editor, Chemistry and Biotechnology for laying the foundation for this fascinating subject in 2005. I wish to place on record my appreciation for Rebekah Amos, Senior Editorial Assistant; Kellsee Chu, Senior Production Editor at John Wiley and Sons for superb and skillful technical assistance in production of this work punctually.

Dr K. Jayaram and Mr. H. Lalhrulaitluanga helped in the preparation of the Index and their assistance is greatly appreciated. Last, but not least, I must acknowledge the excellent cooperation of my wife, Savithri.

CONTRIBUTORS

S. S. AIDOSSOVA, Botany Department, Biology Faculty, Kazakh National al-Farabi University, Almaty 050040, Republic of Kazakhstan

AHMET AKSOY, Biology Department, Faculty of Science & Arts, Erciyes University, 38039 Kayseri, Turkey

JOSEP ALLUÉ, Department of Plant Physiology, Bioscience Faculty, Autonomous University of Barcelona, E-08193 Bellaterra, Spain

DANUTA MARIA ANTOSIEWICZ, Department of Ecotoxicology, Faculty of Biology, The University of Warsaw, 02-096 Warsaw, Poland

SALAH A. ATTIA-ISMAIL, Desert Research Center, Matareya, 11753 Cairo, Egypt

RAFAEL BORRÁS AVINÖ, ABBA Chlorobia S.L., Citriculture Department, School of Agronomists, Polytechnic University of Valencia, 46022 Valencia, Spain

MANOEL BANDEIRA DE ALBUQUERQUE, Center for Functional Ecology, Department of Botany, University of Coimbra, 3001-455 Coimbra, Portugal

JUAN BARCELÓ, Department of Plant Physiology, Bioscience Faculty, Autonomous University of Barcelona, E-08193 Bellaterra, Spain

CARLOS BARATA, Environmental Chemistry Department, IIQAB-CSIC, 08034 Barcelona, Spain

LUCIEN BOVET, Philip Morris International R & D, Philip Morris Products SA, 2000 Neuchatel, Switzerland

SIMONA DI GREGORIO, Department of Biology, University of Pisa, 56126 Pisa, Italy

SERGI DÍEZ, Environmental Geology Department, ICTJA-CSIC, 08028 Barcelona, Spain; and Environmental Chemistry Department, IIQAB-CSIC, 08034 Barcelona, Spain

PAVEL DLAPA, Department of Soil Science, Faculty of Natural Sciences, Comenius University, 842 15 Bratislava, Slovak Republic

OTTO FRANZLE, Christian-Albrechts-University Kiel, Ecology Centre, Olshausenstr. 40, D-24089 Kiel, Germany

STEFAN FRANZLE, International Graduate School (IHI) Zittau, Department of Environmental High Technology, D-02763 Zittau, Germany

HELENA FREITAS, Center for Functional Ecology, Department of Botany, University of Coimbra, 3001-455 Coimbra, Portugal

MARIA GREGER, Department of Botany, Stockholm University, 106 91 Stockholm, Sweden

SALIH GUCEL, Centre for Environmental Studies, Near East University, Nicosia, 33010 North Cyprus

BOHDAN JURANI, Department of Soil Science, Faculty of Natural Science, Comenius University, 842 15 Bratislava, Slovak Republic

MYRIAM KANOUN-BOULĚ, Center for Functional Ecology, Department of Botany, University of Coimbra, 3001-455 Coimbra, Portugal

EDA KAPLAN, Department of Biology, Istanbul University, 34134 Eminou, Istanbul, Turkey

FARHAD KHORSANDI, Department of Agronomy, Islamic Azad University Darab Branch, Darab, Fars Province, I.R. of Iran

SARITHA V. KURIAKOSE, Department of Plant Sciences, University of Hyderabad, Hyderabad 500 046, India

KARMA LHENDUP, Faculty of Agriculture, College of Natural Resources, Lobesa, PO Box Wangduephodrang, Bhutan

HELMUT LIETH, Wipperfurther Strasse 147, D-51515 Kurten, Germany

MERCÈ LLUGANY, Department of Plant Physiology, Bioscience Faculty, Autonomous University of Barcelona, E-08193 Bellaterra, Spain

JOSÉ RAFAEL LÓPEZ-MOYA, ABBA Chlorobia S.L., Citriculture Department, School of Agronomists, Polytechnic University of Valencia, 46022 Valencia, Spain

ELENA MAESTRI, Division of Genetics and Environmental Biotechnologies, Department of Environmental Sciences, University of Parma, Parma 43100, Italy

BERND MARKERT, International Graduate School (IHI) Zittau, Department of Environmental High Technology, D-02763 Zittau, Germany

NELSON MARMIROLI, Division of Genetics and Environmental Biotechnologies, Department of Environmental Sciences, University of Parma, Parma 43100, Italy

ABDUL R. MEMON, Institute of Genetic Engineering and Biotechnology, 41470 Gebze, Kocaeli, Turkey

CRISTINA NABAIS, Center for Functional Ecology, Department of Botany, University of Coimbra, 3001-455 Coimbra, Portugal

JUAN PEDRO NAVARRO-AVINO, ABBA Chlorobia S.L., Citriculture Department, School of Agronomists, Polytechnic University of Valencia, 46022 Valencia, Spain; and Department of Agrarian Sciences and of the Natural Environment,

School of Technology and Experimental Sciences, University Jaume I, 12071 Castellón, Spain

N. NIRUPA, Department of Plant Sciences, University of Hyderabad, Hyderabad 500 046, India

MUNIR OZTURK, Botany Department, Science Faculty, Ege University, 35100 Bornova, Izmir, Turkey

CARLOS PAULO, Earth Sciences Department, Faculty of Sciences and Technology of the University of Coimbra, 3000-272 Coimbra, Portugal

SONIA PLAZA, Plant Biology, University of Fribourg, 1700 Fribourg, Switzerland

CHARLOTTE POSCHENRIEDER, Department of Plant Physiology, Bioscience Faculty, Autonomous University of Barcelona, E-08193 Bellaterra, Spain

M. N. V. PRASAD, Department of Plant Sciences, University of Hyderabad, Hyderabad 500 046, India

JOAO PRATAS, Earth Sciences Department, Faculty of Sciences and Technology of the University of Coimbra, 3000-272 Coimbra, Portugal

DEMETRIO RALDŮA, Laboratory of Environmental Toxicology (UPC), 08220 Terrassa, Spain

K. S. SAGYNDYK, Botany Department, Biology Faculty, Kazakh National al-Farabi University, Almaty 050040, Republic of Kazakhstan

SERDAL SAKCALI, Biology Department, Faculty of Science & Arts, Fatih University, 34500 Hadimkoy, Istanbul, Turkey

ARUN K. SHANKER, Central Research Institute for Dryland Agriculture (CRIDA), Indian Council of Agricultural Research (ICAR), Santoshnagar, Hyderabad, 500 059, India

IRINA SHTANGEEVA, Chemical Department, St. Petersburg University, St. Petersburg 199034, Russia

SUJATA SINHA, BPS LAB-Centre for Diagnostic Hematology, Sankatmochan, Varanasi-221005 (UP), India

AGNIESZKA SIRKO, Institute of Biochemistry and Biophysics, Polish Academy of Sciences, 02-106 Warsaw, Poland

PAWE SOWIŃSKI, Department of Plant Physiology, Institute of Botany, Faculty of Biology, University of Warsaw, 02-096 Warsaw, Poland; and Plant Biochemistry and Physiology Department, Plant Breeding and Acclimatization Institute, 05-870 B onie, Radzików, Poland

ROSER TOLRÀ, Department of Plant Physiology, Bioscience Faculty, Autonomous University of Barcelona, E-08193 Bellaterra, Spain

SHUHE WEI, Key Laboratory of Terrestrial Ecological Process, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, People's Republic of China

SIMONE WUENSCHMANN, Fliederweg 17, D-49733 Haren, Germany

FATEMEH ALAEI YAZDI, Department of Agronomy, Yazd Agricultural and Natural Resources Research Center, Yazd, Yazd Province, I.R. of Iran

YASEMIN YILDIZHAN, Institute of Genetic Engineering and Biotechnology, 41470 Gebze, Kocaeli, Turkey

ERSIN YUCEL, Biology Department, Science Faculty, Anadolulu University, 26470 Eskisehir, Turkey

HARALD ZECHMEISTER, University of Vienna, Faculty of Life Sciences, Department of Conservation Biology, Vegetation, and Landscape Ecology, A-1090, Vienna, Austria

QIXING ZHOU, Key Laboratory of Terrestrial Ecological Process, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, People's Republic of China; and College of Environmental Science and Engineering, Nankai University, Tianjin 300071, People's Republic of China