

Brian J. Alloway
Editor

Heavy Metals in Soils

Trace Metals and Metalloids in Soils
and their Bioavailability

Third Edition



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Brian J. Alloway
Soil Research Centre
Department of Geography
and Environmental Science
School of Human and Environmental
Sciences
University of Reading
Whiteknights, Reading, UK

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Preface

An understanding of the occurrence and availability of heavy metals and metalloids in soils is of major importance to environmental health, crop and livestock production, food and water quality and ecotoxicology. The concentrations of heavy metal (loid)s in soils can vary widely, even in uncontaminated soils. Marked differences in the geochemical composition of the rocks which form the parent materials of soils and variations in the intensity of soil-forming processes can result in wide ranges of total and available concentrations of most elements in soils, even in those unaffected by contamination. Nevertheless, contamination from many sources can often give rise to some very high concentrations of heavy metal(loid)s which can cause toxicity in soil organisms and susceptible plants, but this depends on the factors affecting the bioavailability of the elements.

This book covers the general principles of the occurrence, soil chemical behaviour and soil-plant-animal aspects of heavy metal(loid)s and more detailed coverage of 21 individual elements, including: antimony, arsenic, barium, cadmium, chromium, cobalt, copper, gold, lead, manganese, mercury, molybdenum, nickel, selenium, silver, thallium, tin, tungsten, uranium, vanadium and zinc.

This is the third edition of this book which was previously published in 1990 and 1995 and it has involved a complete re-write with mainly new authors and several new chapters. The structure of the book is largely the same as in the first two editions with Part I covering 'Basic Principles' and Part II covering 'Key Heavy Metals and Metalloids'. However, the scope of Part I has been broadened with the addition of four new chapters dealing with toxicity in soil organisms (Chap. 5), soil-plant relationships (Chap. 6), heavy metal(loid)s as micronutrients for plants and/or animals (Chap. 7) and the modelling of Critical Loads of heavy metals for risk assessments and environmental legislation (Chap. 8). As in the previous editions, Part II covers arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium and zinc. However, a new Part III has been created to give expanded coverage on ten 'Other Heavy Metals and Metalloids of Potential Environmental Significance' which include antimony, barium, gold, molybdenum, silver, thallium, tin, tungsten, uranium and vanadium (with barium and tungsten being new additions).

As with the previous editions, this book will be of great value to advanced undergraduate and postgraduate students, research scientists and professionals in environmental science, soil science, geochemistry, agronomy, environmental health and specialists responsible for the management and clean-up of contaminated land.

January, 2012 University of Reading, UK

Brian J. Alloway (Editor)

Contributors

Brian J. Alloway Soil Research Centre, Department of Geography and Environmental Science, School of Human and Environmental Sciences, University of Reading, Whiteknights, Reading, UK

Olav Albert Christophersen Pensioned state stipendiate, Oslo, Norway

Rafael Clemente Department of Soil and Water Conservation and Organic Waste Management, CEBAS-CSIC, Murcia, Spain

Jan Colpaert Centre for Environmental Sciences, Environmental Biology, Hasselt University, Diepenbeek, Belgium

Ann Cuypers Centre for Environmental Sciences, Environmental Biology, Hasselt University, Diepenbeek, Belgium

Christine M. Davidson Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland, UK

Wim deVries Alterra, Wageningen University and Research, Wageningen, The Netherlands

Cristina Gonnelli Department of Evolutionary Biology, University of Florence, Florence, Italy

Jan Engelbert Groenenberg Alterra, Wageningen University and Research, Wageningen, The Netherlands

Anna Haug Department of Animal and Aquacultural Sciences, The Norwegian University of Life Sciences, Aas, Norway

Mark E. Hodson Environment Department, University of York, Heslington, York, UK

Nicholas W. Lepp School of Biological and Earth Sciences, Liverpool John Moore's University, Liverpool, UK

Steve Lofts Centre for Ecology and Hydrology, Lancaster Environment Centre, Lancaster, UK

Graham Lyons School of Agriculture, Food & Vine, University of Adelaide, Glen Osmond, SA, Australia

Paula Madejón Protection of the Soil-Water-Plant System, Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), CSIC, Sevilla, Spain

Jelle Mertens Division Soil and Water Management, Katholieke Universiteit Leuven, Leuven, Belgium

Koen Oorts ARCHE (Assessing Risks of CHEmicals), Ghent, Belgium

Maximilian Posch CCE, RIVM (National Institute for Public Health & the Environment), Bilthoven, The Netherlands

Tony Remans Centre for Environmental Sciences, Environmental Biology, Hasselt University, Diepenbeek, Belgium

Giancarlo Renella Department of Plant, Soil and Environmental Sciences, University of Florence, Florence, Italy

Erik Smolders Division Soil and Water Management, Katholieke Universiteit Leuven, Leuven, Belgium

Eiliv Steinnes Department of Chemistry, Norwegian University of Science and Technology, Trondheim, Norway

Ed Tipping Centre for Ecology and Hydrology, Lancaster Environment Centre, Lancaster, UK

Nicholas C. Uren Department of Agricultural Sciences, La Trobe University, Bundoora, VIC, Australia

Jaco Vangronsveld Centre for Environmental Sciences, Environmental Biology, Hasselt University, Diepenbeek, Belgium

Andon Vassilev Department of Plant Physiology & Biochemistry, Agricultural University of Plovdiv, Plovdiv, Bulgaria

Walter W. Wenzel University of Natural Resources and Life Sciences, Vienna, and Department of Forest and Soil Sciences, Institute of Soil Science, University & Research Centre Tulln (UFT), Tulln, Austria

Nele Weyens Centre for Environmental Sciences, Environmental Biology, Hasselt University, Diepenbeek, Belgium

Scott D. Young School of Biosciences, University of Nottingham, Loughborough, Leicestershire, UK

Abbreviations

AAS	atomic absorption spectrometry (analytical method)
ADI	acceptable daily intake ($\mu\text{g kg}^{-1} \text{ day}^{-1}$), the quantity of a compound to which a person can be orally exposed, on the basis of body weight, without experiencing adverse effects on health.
AFA	active fulvic acid
AFS	atomic fluorescence spectrometry
Ag	silver
Al	aluminium
AOC	active organic carbon
AOM	active organic matter
AR	<i>aqua regia</i> (acid digestion in pseudototal analysis)
AROMIS	European Commission concerted action project on ‘Assessment and Reduction of Heavy Metal Input into Agro-ecosystems’
As	arsenic
AsB	arseonobetaine
AsC	arsenocholine
AR	<i>Aqua regia</i> soluble metalloid concentration
ATP	adenosine triphosphate (high-energy compound in living cells)
Au	gold
B	boron
Ba	barium
BC	Before Christ
BCF	bio-concentration factor (also known and transfer coefficient)
BCR	Community Bureau of Reference (of the EU)
BLM	Biotic Ligand Model
BSI	British Standards Institute
Bt	billion tonnes (10^9 t)
β_{ML}	overall metal(M)-ligand(L) stability constant
C	carbon
Ca	calcium

CA	cacodylic acid
CCA	chromated copper arsenate (wood preservative)
CCD	charge coupled device
CCE	Coordination Centre for Effects (of the ICP Modelling and Mapping under the LRTAP Convention)
Cd	cadmium
Cd-U	Urinary cadmium
Ce	cerium
CEC	cation exchange capacity
CHUM-AM	model (which includes WHAM-VI) to simulate combined acidification and metal behaviour for catchments in Cumbria (north-west England)
Cl	chlorine
CL	critical load
$\text{cmol}_c \text{ kg}^{-1}$	centimoles charge per kilogram (units of cation exchange capacity)
Co	cobalt
Cr	chromium
CRM	certified reference material
Cu	copper
CVAAS	cold vapour atomic absorption spectrometry
Da	Daltons (molecular size) 1 Da=1 g/mol
D_{app}	apparent diffusion coefficient ($\text{m}^2 \text{ s}^{-1}$)
DBT	dibutyltin
DDT	damage delay time
DGT	diffusive gradients in thin films technique
DIN	Deutsches Institut für Normung (German Standards Institute)
DMA(V)	dimethylarsinate
DMT	dimethyltin
DNA	deoxyribonucleic acid
DOC	dissolved organic carbon
DOM	dissolved organic matter (mol kg^{-1})
DPT	diphenyltin
DTPA	diethylenetriaminepentaacetic acid (chelating agent used for soil tests)
DU	depleted uranium
DW	dry weight (also DM=dry matter)
EC10	effective concentration yielding 10% inhibition in response
eCEC	effective cation exchange capacity (at pH of the soil)
EDL	electrodeless discharge lamp
EDTA	ethylenediaminetetraacetic acid (chelating agent use for soil tests)
EDXRF	energy dispersive X-ray fluorescence
Eh	redox potential, which is the potential generated between a platinum electrode inserted into the solution to be measured and a standard hydrogen electrode (mV)

EMEP	Meteorological Synthesizing Centre East under the LRTAP Convention
EPS	extracellular polysaccharide (biofilm produced by roots)
ESR	electron spin resonance (spectroscopy)
ETAAS	electrothermal atomic absorption spectrometry
EU	European Union (comprising 27 member states and ~500 M inhabitants)
EXAFS	extended X-ray absorption fine structure (spectroscopy)
F	fluorine
FAAS	flame atomic absorption spectrometry
FAO	Food and Agriculture Organisation of the United Nations
Fe	iron
FE	Freundlich equation
FIAM	free ion activity model
FMI	free metal ion
FTIR	Fourier transformed infra-red spectroscopy
FW	fresh weight (or wet weight) usually in analysis of plant tissues
G-Base	British Geological Survey's Baseline Survey of the Environment
GI tract	gastro-intestinal tract in humans and higher animals
GPF	general purpose Freundlich equation
GPS	global positioning system
GPx	glutathione peroxidase (antioxidant enzyme containing selenium)
GSH	glutathione (tripeptide functioning as reducing substrate for GPx)
H	hydrogen
h	hour(s)
ha	hectare (10,000 m ²) equivalent to 2.471 acres
HA	humic acid
HCL	hollow cathode lamp
Hg	mercury
HGAAS	hydride generation atomic absorption spectrometry
Hi	hysteresis index
HIV	human immunodeficiency virus
IAA	indole acetic acid (growth regulating hormone in plants)
IAP	ion activity product
ICP-AES	inductively coupled plasma atomic emission spectrometry (multi-element analytical method)
ICP-MS	inductively coupled plasma mass spectroscopy
INAA	instrumental neutron activation analysis
ISO	International Organisation for Standardisation
IUPAC	International Union of Pure and Applied Chemistry
JRC	Joint Research Centre, Ispra (of the EU)
K	potassium
k _d	distribution coefficient (L kg ⁻¹)
k _F	Freundlich adsorption constant

K_L	Langmuir adsorption constant
K_s	solubility product
L/A	leaching-ageing factor
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
LDL	low-density lipoprotein
LFE	Langmuir-Freundlich equation
LIBS	laser-induced breakdown spectrometry
LMWOLs	low molecular weight organic ligands
LOAEL	the lowest observed adverse effect level: toxicological threshold
LOD	limit of detection
LOI	loss on ignition (%) a measure of organic matter content
LRTAP	long-range transboundary air pollution (convention of UNECE)
mg kg^{-1}	milligrams per kilogram (equivalent to micrograms per gram or 1 part per million (ppm))
mg L^{-1}	milligrams per litre (or 1 part per million (ppm) in liquids)
MA	mugineic acid (phytosierophores)
MAE	mean absolute error
MBT	monobutyltin
Mg	magnesium
mM	milli-moles
MMA(V)	monomethylarsonate
Mn	manganese
MPT	monphenyltin
Mo	molybdenum
MOS	margin of safety
N	nitrogen
Na	sodium
NADPH	reduced nicotinamide adenine dinucleotide (reducing substrate for the enzymes glutathione reductase and thioredoxin reductase)
NF- <i>kappa</i> B	Nuclear factor- <i>kappa</i> B (transcription factor enhancing expression of several proinflammatory genes and replication rate of HIV)
Ni	nickel
NICA-Donnan	the Non-Ideal Competitive Adsorption model
NIST	National Institute of Standards and Technology (of the United States)
NMR	nuclear magnetic resonance spectroscopy
NOEC	no observed effect concentrations, i.e. highest dose at which no significant inhibitory effect is observed
NPK	nitrogen, phosphorus and potassium compound fertilisers
O	oxygen
OTC	organotin compound
Os	osmium
P	phosphorus
Pb	lead

PBET	physiologically-based extraction test
Pd	palladium
PC	phytochelatins
pe	the negative logarithm ($-\log_{10}$) of electron activity
pH	$-\log_{10}$ (hydronium ion activity) – measure of acidity
pKa	$-\log_{10}$ (acid dissociation constant)
PNEC	predicted non-effect concentration (above which toxic effects may occur in sensitive species)
Pt	platinum
PT	pseudototal (incomplete chemical dissolution e.g., <i>Aqua regia</i> digestion)
PTFE	polytetrafluoroethylene (Teflon)
PVC	polyvinylchloride
Ra	radium
RDA	recommended dietary allowance (for humans)
RDI	recommended daily intake (of nutrients for humans)
RDT	recovery delay time
REE	rare earth elements
Rh	rhodium
RM	reference material
Rn	radon
ROS	reactive oxygen species
RSD	relative standard deviation
S	sulphur
Sb	antimony
SBET	simplified bioaccessibility extraction test
SDMM	simple dynamic model of metals (Centre for Ecology and Hydrology, UK)
Se	selenium
SEM-EDX	scanning electron microscope with energy dispersive X-ray analysis
Se-Met	selenomethionine
SeMCYS	Se-methylselenocysteine
SDMM	simple dynamic model for metals
Si	silicon
Sn	tin
SOD	superoxide dismutase (enzyme)
SSA	specific surface area
SUVA	specific ultra-violet absorbance
t	metric tonne (or megagrams, Mg) – 0.984 tons (Imperial)
$T_{1/2}$	half life (of a radioisotope)
TBT	tributyl tin
TBTO	tributyl tin oxide
TDI	tolerable daily intake (of a potentially toxic substance)

TETRA	tetramethyl arsonium ion
TGA	thymine guanine adenine (base triplet in DNA molecule)
TGF- <i>beta</i>	transforming growth factor <i>beta</i> (cytokine inhibiting immune functions and stimulating formation of the structural molecule collagen found in fibrous connective tissue)
Th	thorium
Tl	thallium
TL	target load
TMAO	trimethyl arsine oxide
TMT	trimethyltin
TOC	total organic carbon
TOTs	tetraorganotin compounds
TPN	total parenteral nutrition (supplying nutrients in solution into a vein and by- passing the GI tract)
TPT	triphenyl tin (compounds)
TPTA	triphenyltin acetate
t-RNA	transfer RNA
TSP	total suspended particles (in air)
U	uranium
UGA	uracil guanine adenine (base triplet in RNA molecule)
UKAS	United Kingdom Accreditation Service
UKSHS	United Kingdom Soil and Herbage Survey
UNECE	United Nations Economic Commission for Europe
USDA	United States Department of Agriculture
USDoE	United States Department of Energy
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
V	vanadium
W	tungsten
W6-MTC	customised program based on WHAM6
WDXRF	wavelength-dispersive X-ray fluorescence
WHAM6	version 6 of the Windermere Humic Aqueous Model designed to calculate equilibrium chemical speciation in surface/ground waters, sediments and soils
WW	wet (fresh) weight (same as FW)
XANES	X-ray adsorption near edge structure
XRD	X-ray diffraction (analysis of crystal structures)
XRF	X-ray fluorescence (spectrometry)
Zn	zinc
ZPC	zero point of charge

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Part I

Basic Principles