

Emerging Contaminants and Associated Treatment Technologies

Biljana Balabanova
Trajce Staflov *Editors*

Contaminant Levels and Ecological Effects

Understanding and Predicting with
Chemometric Methods

 Springer

Emerging Contaminants and Associated Treatment Technologies

Series Editors

Muhammad Zaffar Hashmi, Department of Chemistry, COMSATS University
Islamabad, Pakistan

Vladimir Strezov, Department of Environmental Sciences, Macquarie University
Sydney, NSW, Australia

Emerging Contaminants and Associated Treatment Technologies focuses on contaminant matrices (air, land, water, soil, sediment), the nature of pollutants (emerging, well-known, persistent, e-waste, nanomaterials, etc.), health effects (e.g., toxicology, occupational health, infectious diseases, cancer), treatment technologies (bioremediation, sustainable waste management, low cost technologies), and issues related to economic development and policy. The book series includes current, comprehensive texts on critical national and regional environmental issues of emerging contaminants useful to scientists in academia, industry, planners, policy makers and governments from diverse disciplines. The knowledge captured in this series will assist in understanding, maintaining and improving the biosphere in which we live. The scope of the series includes monographs, professional books and graduate textbooks, edited volumes and books devoted to supporting education on environmental pollution at the graduate and post-graduate levels.

More information about this series at <http://www.springer.com/series/16185>

Biljana Balabanova • Trajče Stafilov
Editors

Contaminant Levels and Ecological Effects

Understanding and Predicting
with Chemometric Methods

 Springer

Editors

Biljana Balabanova
Faculty of Agriculture
Goce Delčev University
Štip, North Macedonia

Trajče Stafilov
Institute of Chemistry, Faculty of Natural
Sciences and Mathematics
Saints Cyril and Methodius University
Skopje, North Macedonia

ISSN 2524-6402

ISSN 2524-6410 (electronic)

Emerging Contaminants and Associated Treatment Technologies

ISBN 978-3-030-66134-2

ISBN 978-3-030-66135-9 (eBook)

<https://doi.org/10.1007/978-3-030-66135-9>

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Switzerland AG 2021

This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

The biosphere is the medium that is naturally optimized for the growth and development of a huge number of biological organisms. Nature itself creates natural disasters that degrade the ecosystems and organisms that live in it. Humans, in spite of their existential question in nature, still continuously degrade nature and its living environment. This anthropogenic factor affects all segments of the environment, the lower parts of the atmosphere, the upper parts of the lithosphere, as well as the hydrosphere. Intensive technological development as well as the availability of natural raw materials for their utilization have significantly enabled the progress of these degradation processes in nature. On the other hand, the chemical and pharmaceutical industry, with their intensive development, have generated substances that are not only unnatural but also highly risky for the human population and the environment. Pollutants and potentially toxic substances are continuously introduced into all segments of the biosphere, shifting the natural balance of natural normal distributions. The environmental pollutants create abnormal media for living organisms. These days, we are increasingly faced with the fact of the ecological risk for the survival of many species. In recent decades, researchers have paid great attention to environmental risk, determining the pollution index and identifying polluted sites where it is necessary to prevent further degradation. Therefore, several critical aspects should be involved when we initiate and launch environmental research or monitoring. One of the aims of the modern environmental investigations is to obtain more objective data for the complex but silent environmental markers, which will be identified as typical pollutants in various parts of the environment. The modern analytical approaches involve sophisticated and sensitive instrumental technique, but the main question is how to create a corresponding data matrix and proper data analysis. Chemometrics is a routine chemical sub-discipline, which involves several mathematical methods for extracting more realistic and proper environmental information. The implementation of modern and novel chemometric methods becomes a critical point in the environmental studies these days. Therefore, this book summarizes the latest investigations of the concerning parts of the biosphere, affected with hazards substances. Moreover, selected case studies investigation with spacious applicability will create general framework of the opportunities, advantages,

weaknesses, and anomalies of the mathematical approaches of the analysts. Furthermore, a properly defined chemometric model of each environmental investigation will provide long-term applicability potential.

This book consists of 13 chapters contributed by relevant experts in various fields correlated with environmental issues. All the chapters are logically selected and arranged to provide comprehensive state-of-the-art information about the practical aspects of environmental chemometric approaches. In this volume, the introductory chapter gives an overview of the critical environmental issues, such as degradation, ecological risks, and silent hazards. The next five chapters are on air pollution aspects: pollutants, hazardous emissions, monitoring, indication, as well as spatial indication of emission sources. These chapters give attention to air pollution, air deposition, and distribution models. Certain emphasis is given to the moss effectiveness for bioindication of the potential ecological risk. Another chapter is dedicated to the application of lichens as the main indicator in biological monitoring of air quality. Water pollutants and their determination issues are the main topics in the next two chapters, covering key issues in spatial distribution of various metals in different parts of the environment. These chapters deal with improving effective analytical methodologies of GC-MS and ICP-MS for tracking potential contaminants. This is followed by research into the effective removal of toxic hazard from aquatic systems. The next group of chapters is dedicated to the state of chemical characterization of the plant food and endemic plant species as characteristic media that involves the potential ecological risks. The presented are multidisciplinary approaches which enable detailed and precise elaboration of the set research subject.

All the chapters and their contents are supported by extensive citation of available literature; calculation and assumptions are based on realistic facts and figures of the present status of research and development in this field. This book will provide a wealth of information based on a realistic evaluation of contemporary development in environmental investigations with special emphasis on the latest research studies. Furthermore, this book also highlights the potential and perspective use of the multidisciplinary aspect for enchaining environmental pollution and potential ecological risks.

Most of the chapters cover advanced research as well as the use of more sophisticated methodologies. Therefore, we believe that the usefulness of this book will be primarily directed to experienced researchers. But of course we also encourage young researchers to use the book, because in many of the chapters, the methodologies used by the authors are explained very basically. We also believe that certain institutions and state regulatory bodies can use this book as an initiator for critical issues related to environmental degradation, environmental risks and their determination, and future prevention.

Štip, Republic of North Macedonia
Skopje, Republic of North Macedonia

Biljana Balabanova
Trajče Stafilov

List of Abbreviations

AAS	Atomic absorption spectrometry
AED	Atomic emission detector
AES	Atomic emission spectrometry
AF	Attenuation factor
AFR	Revised attenuation factor
AFT	Log-transformed attenuation factor
ALA	Alpha linolenic acid
ANN	Artificial neural networks
ANOVA	Analysis of variance
APCI	Atmospheric pressure chemical ionization
ATP	Adenosine triphosphate
BAF	Biological accumulation factor
BTF	Biotransfer factor
CA	Cluster analysis
CART	Classification and regression trees
CDI	Chronic daily intake dose
CEC	Cation exchange capacity
CHCA	A-cyano-4-hydroxycinnamic acid
CR	Carcinogenic risk
CVAAS	Cold vapor atomic absorption spectrometry
DBCP	Dibromochloropropane
DCM	Dichloromethane
DHA	Docosahexaenoic
DMT	Digital terrain models
DRC	Dynamic reaction cell
DTPA	Diethylenetriamine pentaacetic acid
DW	Dry weight
EC	Elemental carbon
ECD	Electron capture
EDB	Ethylene dibromide
EDS	Energy dispersive X-ray spectrometry

EEA	European Environment Agency
ELISA	Enzyme-linked immunosorbent assay
EPA	Environmental Protection Agency
EPA	Eicosapentaenoic
ESI	Electrospray ionization
ETAAS	Electrothermal atomic absorption spectrometry
FID	Flame ionization detector
FS	Fluorescence spectroscopy
GC	Gas chromatography
GHG	Greenhouse gas
GLI	Global leachability index
GUS	Groundwater ubiquity score
GWCP	Groundwater contamination potential
HI	Hornsby index
HPLC	High-performance liquid chromatography
ICP–AES	Inductively coupled plasma – atomic emission spectrometry
ICP–MS	Inductively coupled plasma – mass spectrometry
IR	Infrared spectroscopy
IRMS	Isotope ratio spectrometry
LA	Linoleic acid
LC	Liquid chromatography
LDA	Linear discriminant analysis
LEACH	Leaching index
LIX	Screening leachability index
LLE	Liquid-liquid extraction
LOD	Limit of detection
LOQ	Limit of quantification
LPI	Leaching potential index
LSD	Least significant differences
MAC	Maximum permissible concentrations
MALDI	Matrix-assisted laser desorption/ionization
MS	Mass spectrometry
MSA	Multivariate statistical analysis
NMR	Nuclear magnetic resonance
ORS	Octopole reaction system
PC	Principal components
PCA	Principal component analysis
PDA	Photodiode array
PDO	Protected designation of origin
PGI	Protected geographical indication
PLP	Pesticide leaching potential index
PTFE	Polytetrafluoroethylene
PTH	Parathyroid hormone
PTR-MS	Proton transfer reaction mass spectrometry
RAF	Relative accumulation factors

REEs	Rare earth elements
RLP	Relative leaching potential index
SA	Sinapic acid
SEM	Scanning electron microscopy
TDS	Total dissolved solids
TEP	Thermoelectric power plant
TF	Translocation factor
TGA/DTA	Thermogravimetric and differential thermal analysis
TIN	Triangular irregular network
TLC	Thin layer chromatography
TOF	Time-of-flight
TPP	Triphenylphosphate
VI	Volatility index

Contents

1	General Aspects of Environmental Degradation vs. Technological Development Progression	1
	Biljana Balabanova	
2	Spatial Series and Multivariate Analysis in Assessing the Essential (Cu and Zn) and Toxic (As, Cd, Cr, Co, Hg, Ni and Pb) Metals Linked with Health Risk and Ecological Effects of Atmospheric Deposition by Using Bryophyte Moss as Bioindicator	33
	Shaniko Allajbeu, Lirim Bekteshi, Pranvera Lazo, Flora Qarri, and Trajče Stafilov	
3	Moss Biomonitoring of Air Pollution Around the Coal Mine and Bitola Thermoelectric Power Plant, North Macedonia	75
	Trajče Stafilov, Robert Šajin, Mila Arapčeska, and Ivan Kungulovski	
4	Lichens as the Main Indicator in Biological Monitoring of Air Quality	101
	Svetlana Ristić, Robert Šajin, and Slaviša Stamenković	
5	Proposing Chemometric Tool for Efficacy Surface Dust Deposition Tracking in Moss Tissue Cross Bioindication Process of Metals in Environment	131
	Biljana Balabanova, Maja Lazarova, Blažo Boev, Lucian Barbu-Tudoran, and Maria Suciu	
6	Evidence for Atmospheric Depositions Using Attic Dust, Spatial Mapping and Multivariate Stats	171
	Robert Šajin, Biljana Balabanova, Trajče Stafilov, and Claudiu Tănăselia	

7	Improving Quantitative Analysis of GC-MS for Tracking Potential Contaminants in Groundwater	213
	Biljana Kovacevik, Zoran Zdravkovski, Sasa Mitrev, and Natalija Markova Ruzdik	
8	Groundwater Pollution Under the Intensive Agriculture Production	239
	Biljana Kovacevik, Sasa Mitrev, Blažo Boev, Natalija Markova Ruzdik, and Vesna Zajkova Panova	
9	Removal of Chromium(VI) from Aqueous Solution by Clayey Diatomite: Kinetic and Equilibrium Study	263
	Hamdije Memedi, Katerina Atkovska, Stefan Kuvendziev, Mrinmoy Garai, Mirko Marinkovski, Dejan Dimitrovski, Blagoj Pavlovski, Arianit A. Reka, and Kiril Lisichkov	
10	Chemometric Determination of Macro- and Microelements in Barley Genotypes with Different Origin Grown in the Republic of North Macedonia	283
	Natalija Markova Ruzdik, Verica Ilieva, Ljupcho Mihajlov, Sonja Ivanovska, Sasa Mitrev, Darina Vulcheva, Dragomir Vulchev, Biljana Kovacevik, and Mite Ilievski	
11	Chemical Composition and Nutritional Properties of Functional Food	311
	Violeta Ivanova Petropulos and Biljana Balabanova	
12	Characterization of Multi-element Profiles and Multi-isotope Ratio Records as a Tool for Determination of the Geographical Origin of Various Plant Species	353
	Liping Fan, Minxiu Yan, Meicong Wang, Yanqiu Liang, Xiaoguang Kong, Chong Li, and Biljana Balabanova	
13	Accumulation Abilities of Endemic Plant Species from the Vicinity of an As-Sb-Tl Abandoned Mine, Allchar, Kožuf Mountain	375
	Katerina Bačeva Andonovska, Trajče Stafilov, and Vlado Matevski	
	Index	403

Chapter 6

Evidence for Atmospheric Depositions Using Attic Dust, Spatial Mapping and Multivariate Stats



Robert Šajn, Biljana Balabanova, Trajče Stafilov, and Claudiu Tănăselia

Abstract Atmospheric deposition poses significant ecological concerns. It is very important in air pollution researches to provide fast and efficient access to qualitative and quantitative characterization. Case study was introduced in order to implement the multidisciplinary approach in the investigations. When monitoring the distribution of certain substances in the air, it is necessary to choose very carefully the medium that will reflect not only the current but also the long-term atmospheric deposition. Attic dust was examined as historical archive of anthropogenic emissions, with the aim of elucidating the pathways of enrichments associated with exploitation of Cu, Pb and Zn minerals in the Bregalnica river basin region. Attic dust samples were collected from 84 settlements. At each location for attic dust sampling, topsoil samples from the house yards were also collected. Mass spectrometry with inductively coupled plasma (ICP-MS) was applied as an analytical technique for multi-element determination. The universal kriging method with linear variogram interpolation was applied for the construction of spatial distribution maps. Data interpretation was considered in correlation with dominant geological units. Significantly enriched contents for Cd, Cu, Pb and Zn have been correlated with the lithogenic dominance of Rifeous shales. Both Pb-Zn mine environs were identified as the most affected areas with lead and zinc enrichments, due to the

R. Šajn
Geological Survey of Slovenia, Ljubljana, Slovenia

B. Balabanova
Faculty of Agriculture, University “Goce Delčev”,
Krstе Misirkov bb, Štip, Republic of Macedonia

T. Stafilov (✉)
Institute of Chemistry, Faculty of Science, Ss. Cyril and Methodius University,
Skopje, Republic of Macedonia
e-mail: trajcest@pmf.ukim.mk

C. Tănăselia
INCDO-INOE 2000 Research Institute for Analytical Instrumentation (ICIA),
Cluj-Napoca, Romania