The Handbook of Environmental Chemistry 40 Series Editors: Damià Barceló · Andrey G. Kostianoy

Andrea Scozzari Elissavet Dotsika *Editors*

Threats to the Quality of Groundwater Resources

Prevention and Control



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Volume Editors: Andrea Scozzari · Elissavet Dotsika

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Aims and Scope

Since 1980, The Handbook of Environmental Chemistry has provided sound and solid knowledge about environmental topics from a chemical perspective. Presenting a wide spectrum of viewpoints and approaches, the series now covers topics such as local and global changes of natural environment and climate; anthropogenic impact on the environment; water, air and soil pollution; remediation and waste characterization; environmental contaminants; biogeochemistry; geoecology; chemical reactions and processes; chemical and biological transformations as well as physical transport of chemicals in the environment; or environmental modeling. A particular focus of the series lies on methodological advances in environmental analytical chemistry.

Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last three decades, as reflected in the more than 70 volumes of *The Handbook of Environmental Chemistry*, there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry*, the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of

x Series Preface

"pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of Environmental Chemistry* provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of The Handbook of Environmental Chemistry by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló Andrey G. Kostianoy Editors-in-Chief

Editorial Note and Acknowledgements

We intend this book for a wide audience of readers, such as students, researchers, policy-makers, and stakeholders at various levels. In particular, it is intended for those experts who want to widen their vision to contiguous fields of expertise. This approach can also be useful in order to enhance the mutual understanding between researchers having different backgrounds. Without the aim to be exhaustive, this book is intended as a stimulus for a multidisciplinary vision of the many interconnected aspects of groundwater protection, exploitation, monitoring, and the risks associated with the management of groundwater resources.

Chapters of this book have been peer-reviewed by two reviewers per each chapter. In some cases, more than one review round was needed. Reviewers have been selected partly internal and partly external to the book project. Some of the reviewers chose to remain anonymous. The editors are very indebted to the reviewers for their great contribution to the overall quality of the book.

Those who agreed to be acknowledged are listed here:

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Andrea Scozzari and Elissavet Dotsika

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Introduction

Andrea Scozzari and Elissavet Dotsika

Abstract Groundwater is the only source of water supply for some countries in the world and the main source for many other countries. Especially in the European Union and in the United States of America, the role of high-quality groundwater is fundamental for the drinking water supply, and this is true also for some countries in Asia, Africa and Australia. Thus, in a growing number of contexts, safeguarding drinking water supplies is strictly linked with the protection of local groundwater resources. The usage of groundwater for irrigation has also a relevant share in many countries, sometimes contributing to stress the resource. The assessment of groundwater vulnerability and the individuation of potential hazards are thus becoming common and often compelling issues. Given this particular background, this introductory chapter illustrates the motivational framework of this book and outlines its contents.

Keywords Freshwater pollution, Groundwater management, Water quality, Water resources protection

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There are known scenarios of incrementing attention and general concerns about worldwide freshwater resources. The trend of global water usage and withdrawal, the impact of climate change on the availability and on the exploitation possibilities of water resources and the impact of men activities on freshwater supplies are among the various aspects that people involved in the water sector have to deal with, systematically. The many challenges regarding this complicated context involve a diversified array of communities, which include stakeholders at various levels, scientists, technologists, industrial companies, water managers and policy-makers, encouraging the idea that a wide multidisciplinary framework can actively enhance communication, assist decision-making and mitigate the consequences of anthropic pressure on water resources, which are often combined with climate effects. Indeed, decision-makers who understand the scientific aspects of emerging water risks and the existing countermeasures are in a better position to determine policy and legal frameworks, in order to promote sound environmental management and protection. This is also in accordance with the demand for a global water governance [1], due to the general acknowledgment that technology and infrastructures alone are not enough to deal with the complexity of water management practices.

Despite the increasing general awareness about the arising issues, there are different degrees of perception towards water problems in the involved communities, which are also variable on a regional basis. Notwithstanding the wide literature produced, there's still some underestimation of the potential environmental security risks (and their implications) for the near and the middle-term future at regional levels, while local issues are typically more tangible. Nevertheless, there is an already well-established literature about a variety of risks, such as the eventuality of conflicts involving shared water bodies, the increased hazards for the health of populations, possible migratory movements and more general trans-boundary issues, which are often discussed in the frame of the prospected climate change scenarios [2–5]. The interested reader can expand the research much beyond the cited literature, which is just proposed as a possible starting point, given the wide availability of books, journal articles, reports and project deliverables focused on the various aspects of securing water supplies.

According to the "World Water Development Report 4" by UNESCO [6], "Water quality is inextricably linked with water quantity as both are key determinants of supply. Compared to water quality, water quantity has received far more investment, scientific support and public attention in recent decades. However, water quality is just as important as water quantity for satisfying basic human and environmental needs". The consciousness of the threats to the quality of water resources, the assessment of regulatory frameworks and the development of techniques to monitor and mitigate such threats play a key role for the preservation and the future availability of the resources under exploitation. This aspect is an essential component in the frame of minimising the environmental stress and its consequent security issues [7]. The issue of managing and securing water supplies represents a general challenge involving a large part of the world, and it's not limited to the areas which are considered more exposed to problems of scarcity. According to the

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data acquired by the Europarometer (European Commission) in 2006, "when asked to list the five main environmental issues that Europeans are worried about, averaged results for the EU25 show that nearly half of the respondents are worried about 'water pollution' (47%), with figures for individual countries going up as far as 71%" [8]. Even if Europeans are beginning to perceive the risks concerning the water supply for human consumption, in most of the developed and industrialised countries, the majority of people take safe drinking water for granted. As yet, about 800 million people in the world are lacking safe drinking water from improved sources, according to the latest UN-Water Annual Assessments [9-11] and the relating Thematic Factsheets. The deficit of improved sources of drinking water is not necessarily related with scarcity: it's instead commonly due to the lack of infrastructures and, in many cases, to various forms of pollution threatening the existing resources, in a context where the risk posed by climate change represents an additional threat [10]. The general mismatch between pro capita renewable freshwater and percentage of population accessing to safe water can be observed in several maps, which are currently available online [12-14]. Both geogenic and anthropogenic contamination sources participate in this complex scenario, where agricultural activities, industrial sites and human settlements represent the major anthropogenic threats to the quality of water. Also, the major problems of pollution are not necessarily individuated in the most industrialised countries (e.g. 80% of sewage in developing countries is discharged untreated into water bodies, according to the UN-Water Thematic Factsheet "Water Quality" [15]).

It is well known that about 96.5% of the water on the Earth is ocean water, while the total amount of freshwater storage is about 2.5%, being the remaining classified as other saline water. According to Shiklomanov [16, 17], 68.7% of the existing freshwater lies in the icecaps, in the glaciers or permanent snow cover, while about 30.1% of the total freshwater is groundwater. Inland water (including rivers, lakes, soil moisture, swamps) is representing only about 0.3% of the existing freshwater, keeping ground ice and permafrost out of the calculated budget. Despite its proportionally small amount, the surface water storage represents a strategic resource, which historically had a major impact over civilisation and still plays a fundamental role in many countries, besides being easily in the focus of trans-boundary water problems. Still, the above figures say that groundwater represents about 99% of the freshwater available for use, justifying its enormous importance, and it's characterised by an uneven global distribution and a very diversified role on a geographical basis [18]. Despite the heterogeneous patterns in terms of availability, usage, qualitative and quantitative characteristics, the exploitation of groundwater aquifers presents common issues regarding their susceptibility to degradation. Potential vulnerabilities of groundwater reservoirs actually depend on various factors, e.g. the hydrogeological and geochemical contexts, the abstraction rates, the policy of usage and the surrounding human activities, which are among the most influencing variables. In particular, the policy of exploitation and the distribution among the various categories of users (i.e. agricultural, domestic, industrial) is very specific to each country [19, 20], and also the environmental stressors potentially affecting the availability and quality of groundwater are often peculiar to each territory. For this reason, all the aspects linked with the exploitation and protection of the resource should ideally be managed at different scales, from regional to local, aiming at a truly sustainable use, which takes into account the environmental factors characterising each analysed scenario and the connected aspects of vulnerability.

At a global level, surface water is still largely prevailing over groundwater in terms of withdrawn quantities (source: FAO AQUASTAT [19]), but high figures of abstracted groundwater (including non-renewable one) are widespread in countries which are prone to problems of scarcity, especially for what regards the agricultural use. The balance between exploitation of surface water and groundwater reservoirs is very variable on a geographical basis, and it is not necessarily driven by the local abundance of surface water. Various additional factors, including the degree of economic development in the region and the state of degradation of surface water bodies, contribute to determine such balance. In the future, this heterogeneity in the distribution, exploitation and usage of freshwater storage will still be present and probably exacerbated by the demographic trends, the industrial development and climate change scenarios [17].

According to UNESCO [21], "groundwater is the only source of water supply for some countries in the world (e.g., Denmark, Malta, Saudi Arabia). Groundwater in Tunisia is 95% of the total water resources withdrawn, in Belgium it is 83%, in the Netherlands, Germany and Morocco it is 75%". Also, "in most European countries (Austria, Belgium, Denmark, Hungary, Romania and Switzerland) groundwater use exceeds 70% of the total water consumption".

The role of high-quality groundwater is fundamental for the drinking water supply and for domestic uses in general [22]. According to the Statistical Office of the European Union (Eurostat), groundwater is the main source of municipal water supplies in most European countries [20]. Latest cumulated values of water abstraction by source and by sector of use, referred to EU28 plus Switzerland, indicate that groundwater abstraction for the public water supply is about 60% of the total. In particular, the report by UNESCO [21] specifies that "water supply of such European cities as Budapest, Copenhagen, Hamburg, Munich, Rome and Vienna is completely or almost completely based on groundwater, and for Amsterdam, Brussels and other cities it provides for more than half of the total water demand".

It is thus clear how crucial is the protection of groundwater against misuse and degradation and its future role in this framework, being largely the main freshwater resource for vital needs at a global level. To reinforce this concept, it is important to note what Shiklomanov [17] says, "all water resources estimates are optimistic because no account is taken of the qualitative depletion of water resources through the ever increasing pollution of natural waters. This problem is very acute in the industrially developed and densely populated regions where no efficient waste water purification takes place. The major sources of intensive pollution of waterways and water bodies are contaminated industrial and municipal waste water as well as water returning from irrigated areas". And also, "Every cubic metre of contaminated waste water discharged into water bodies and water courses spoils up

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to 8–10 m³ of pure water". This means that the reliable availability of water does not depend only on climate-induced or men-induced scarcity, but it's also deeply influenced by the hazards to the quality of water, which potentially reduce the portion of the safely usable resource. The combination of the factors stated above stresses the importance of safeguarding water resources as a whole, implying that the particular role and the peculiarities of groundwater deserve a special attention.

Safeguarding groundwater necessarily includes the analysis and proactive prevention of the threats to the quality and availability of the resource. In fact, the characterisation of aquifer systems shall comprise the assessment of its quantitative characteristics, its eventual trends of depletion and the risks of deterioration in its quality (e.g. salinisation, industrial pollution, chemicals from agricultural activities, intrusion of urban wastewater, etc.). The assessment of such vulnerabilities is a key point in the frame of a strategic management of groundwater reservoirs, and it represents also a highly multidisciplinary exercise.

There are known threats of overexploitation and pollution of groundwater resources, particularly dealing with their very valuable renewable portion, in addition to the exploitation of non-renewable and even fossil water (as defined in [23]). As a consequence, there is evidence of the extreme importance to monitor, protect against pollution and manage the underground water storage in an optimal way. It is thus clear how effective inputs to decision-making come from the availability of data, assessment methods, monitoring technologies, models and the entire scientific and technological framework contributing to mitigate the exposure of groundwater resources to the known risks, in terms of quality and quantity. In addition, the assessment of a complete scenario involves the proper evaluation of the water footprints associated with the involved stakeholders [24], as it comes to an effective decision-making. Under this point of view, the wide interdisciplinary approach that is required to deal with the assessment and protection of the aquifer systems can also contribute to reduce the conflicts within stakeholders.

Prevention starts by knowing the main threats to the resource and its whole surrounding ecosystem; in particular, the protection of groundwater resources is connected with the action of controlling the entire encompassing environment, including the direct monitoring of the aquifer system, but not limited to it. In fact, there is a widespread consciousness nowadays that the scope of investigations and monitoring activities cannot be limited to the mere performing of direct measurements of the quality of water. The potential of new technological possibilities for investigating and modelling the whole environmental context and its background conditions is nowadays well perceived. In addition to that, only an overall vision that goes further merely technological viewpoints can potentially allow scientists, stakeholders and decision-makers to individuate and address the most relevant risks in an efficient way and determine effective countermeasures.

Chapters of this book focus on the scientific and technological aspects regarding the assessment and surveillance of groundwater resources, with the idea of providing a description of relevant issues and the possibilities to investigate them. Readers coming from diverse backgrounds can read across the contribution of multiple

disciplines with the option of going deeper through the suggested specialised literature. For this reason, the book is organised in order to bring the reader through various viewpoints, according to the diverse disciplines involved, without certainly being exhaustive, but with the aim of picking up emblematic topics for the relevance of their subjects in the context of groundwater protection and control.

The first chapter (by Doveri et al. [25]) introduces the concept of protection area of a groundwater source for human consumption, focusing on the regulations and the related scientific-technical approaches. This is a fundamental aspect to be brought to the readers' attention, before investigating pollution mechanisms and analysing possible sources of contamination. The concept of vulnerability, the assessment of the risks associated with local activities and the study of the hydrogeological background represent a common framework to all the possible kinds of contamination. In particular, the definition of protection zones is essential for safeguarding groundwater withdrawals for human consumption.

The following chapter (by Thomas et al. [26]) investigates the potential impact on groundwater quality resulting from geologic carbon sequestration, which is a practice introduced in the last decades in order to reduce the emissions of greenhouse gases to the atmosphere. Risks for freshwater resources can arise from low pH values and the subsequent dissolution of minerals, which may cause high concentrations in trace elements that are potentially dangerous for the human health. This aspect makes the threats to the quality of groundwater associated with the sequestration of geologic carbon clearly compelling. Ascending saline intrusion into shallower freshwater aquifers is an additional important risk discussed by the authors, which is also illustrated and discussed in the chapter.

Contamination sources can be either of natural origin or connected with human activities. The chapter by Biddau and Cidu [27] presents exemplary situations in which the geogenic degradation and the anthropogenic contamination mechanisms can be discriminated, in terms of natural water/rock interactions or as a consequence of mining activities. The chapter is focused on the assessment of contamination by heavy metals in the groundwater of Sardinia Island and has a general applicability in terms of understanding the background processes and the role played by the natural baseline of contaminants in such discriminations.

In particular, for what regards water pollution by arsenic (As), the variety of sources and the relevant concentrations found in Greece make this country a peculiar territory in order to generalise and better understand the methodology for the assessment of contamination from As. The review work by Gamaletsos et al. [28] analyses the geological sources of arsenic in the environment of Greece, which are demonstrated to affect underground, surface, and marine aquatic environments. Anthropogenic and natural sources are discussed also in this chapter, and the different degrees of exposure of the populations are considered, as a function of the geographic location, of the kind of source and of the transport mechanisms of As.

A complete assessment of groundwater quality implies the quantification of the total recharge and the identification of the various sources involved, in order to keep track of the origin and fate of chemical compounds, including eventual pollutants.