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Emerging and Priority Pollutants in Rivers

Bringing Science into River Management Plans

Springer

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Volume 19

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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; geo-ecology; 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 "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*

Volume Preface

The enduring changes in the aquatic environment and the increasing input of contaminants require research on novel conceptual and methodological approaches in relating chemical pollution and ecological alterations in ecosystems. Improving environmental risk assessment based on the analysis of priority pollutants or other preselected contaminants and extending the risk evaluation to new pollutants are essential for a better understanding of the causes of ecological quality loss and the cause–effect relationships of pollution.

At the same time, a great effort has been undertaken by European Member States to implement the Water Framework Directive. The ultimate goal of this Directive is the achievement of the "good quality status" of water bodies in EU river basins by 2015, it being understood as the combination of both "good ecological and chemical status." Whereas the connection between these two dimensions of water quality is accepted as one of the underlying premises of the WFD, there is still a lot to know on how it is produced. But in any case, there is little doubt that it has practical consequences for a proper river basin management. Therefore, it is of great interest to bring the increasing pool of scientific knowledge to water managers, providing a link between the scientific research and management practices aiming to evaluate the effects of emerging and priority pollutants in river ecosystems. With this aim, the Marie Curie Research Training Network KEYBIOEFFECTS organized the workshop "Emerging and Priority Pollutants: Bringing science into River Basin Management Plans" (Girona, Spain, 2010).

This book provides an overview of the main outcomes of the KEYBIOEFFECTS project as they were reflected in the aforementioned workshop. It includes scientific advances concerning the sampling, analyses, occurrence, bioavailability, and effects caused by emerging and priority pollutants in European rivers, the current status of the River Management Plans in Europe, and the applicability of the newly developed techniques for water monitoring purposes. These scientific advances are presented in the context of the Water Framework Directive evaluating their missing gaps and providing the basics for filling them.

A special attention is dedicated to report the occurrence and elimination of emerging pollutants such as pharmaceuticals during conventional wastewater treatment. Assessing the bioavailability of organic contaminants is also presented, highlighting the difficulties for regulation, more specially in the case of emerging contaminants. The book presents an extensive set of newly developed methods to assess ecological integrity in multistressed rivers. Different ecological perspectives: heterotrophic, phototrophic, and macroinvertebrate community indicators, laboratory and field investigations, as well as multibiomarker approaches are reviewed providing, in each case, the pros of cons for their application. Finally, a specific case study of river quality status assessment performed by a river basin water authority following the principles of the Water Framework Directive is presented.

It is not always evident how science returns its value to society. We hope that the results presented in this book will serve as a good example of how scientific research is able to provide support to issues of public concern, as it is the management of the water cycle and hence contributing to the preservation of ecosystems health and human welfare.

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Contents

Occurrence and Elimination of Pharmaceuticals During Conventional Wastewater Treatment

Aleksandra Jelić, Meritxell Gros, Mira Petrović, Antoni Ginebreda, and Damià Barceló

Abstract Pharmaceuticals have an important role in the treatment and prevention of disease in both humans and animals. Since they are designed either to be highly active or interact with receptors in humans and animals or to be toxic for many infectious organisms, they may also have unintended effects on animals and microorganisms in the environment. Therefore, the occurrence of pharmaceutical compounds in the environment and their potential effects on human and environmental health has become an active subject matter of actual research.

There are several possible sources and routes for pharmaceuticals to reach the environment, but wastewater treatment plants have been identified as the main point of their collection and subsequent release into the environment, via both effluent wastewater and sludge. Conventional systems that use an activated sludge process are still widely employed for wastewater treatment, mostly because they produce effluents that meet required quality standards (suitable for disposal or recycling purposes), at reasonable operating and maintenance costs. However,

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this type of treatment has been shown to have limited capability of removing pharmaceuticals from wastewater. The following chapter reviews the literature data on the occurrence of these microcontaminants in wastewater influent, effluent, and sludge, and on their removal during conventional wastewater treatment.

Keywords Pharmaceuticals • Removal • Sludge • Wastewater

Contents

Abbreviations

HRT	Hydraulic retention time
NSAIDs	Nonsteroidal anti-inflammatory drugs
SRT	Solid retention time
WWTP	Wastewater treatment plant

1 Introduction

Pharmaceuticals are a large and diverse group of compounds designed to prevent, cure, and treat disease, and improve health. Hundreds of tons of pharmaceuticals are dispensed and consumed annually worldwide. The usage and consumption are increasing consistently due to the discoveries of new drugs, the expanding population, and the inverting age structure in the general population, as well as due to expiration of patents with resulting availability of less expensive generics [1]. After intake, these pharmaceutically active compounds undergo metabolic processes in organisms. Significant fractions of the parent compound are excreted in unmetabolized form or as metabolites (active or inactive) into raw sewage and wastewater treatment systems. Municipal sewage treatment plant effluents are discharged to water bodies or reused for irrigation, and biosolids produced are reused in agriculture as soil amendment or disposed to landfill. Thus body metabolization and excretion followed by wastewater treatment are considered to be the primary pathway of pharmaceuticals to the environment. Disposal of drug leftovers to sewage and trash is another source of entry, but its relative significance is unknown with respect to the overall levels of pharmaceuticals in the environment [2].

Continual improvements in analytical equipment and methodologies enable the determination of pharmaceuticals at lower concentration levels in different environmental matrices. Pharmaceuticals and their metabolites in surface water and aquatic sediment were subject of numerous studies concerning pharmaceuticals in the environment [3–5]. Several studies investigated the occurrence and distribution of pharmaceuticals in soil irrigated with reclaimed water [6–8] and soil that received biosolids from urban sewage treatment plants [9, 10]. These studies indicated that the applied wastewater treatments are not efficient enough to remove these micropollutants from wastewater and sludge, and as a result they find their way into the environment (Fig. 1). Once they enter the environment, pharmaceutically active compounds can produce subtle effects on aquatic and terrestrial organisms, especially on the former since they are exposed to long-term continuous influx of wastewater effluents. Several studies investigated and reported on it [11–13]. No evidence exists linking the presence of pharmaceuticals in the environment to human health risks; still complex mixtures may have long-term unseen effects, especially on tissues other than those on which the pharmaceuticals were designed to act.

Therefore, the occurrence of pharmaceutical compounds in the environment and their potential effects on human and environmental health, as well as the extent to which they can be eliminated during wastewater treatment, have become active subject matter of actual research. Since the concern about the discharge of pharmaceuticals (and other emerging contaminants, as well) into wastewater is relatively recent, it is not strange that they are not yet covered by the currently existing regulation.

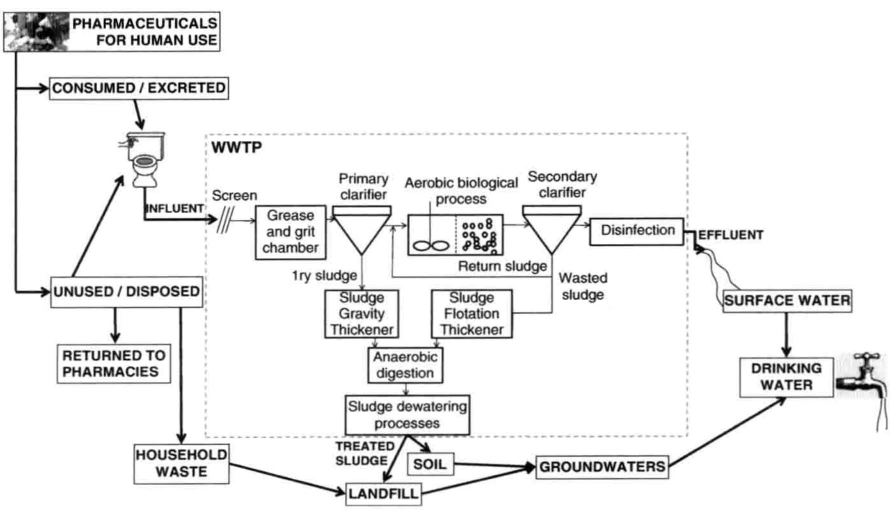

Fig. 1 Routes of release of pharmaceuticals for human use to the environment with a schematic diagram of a conventional WWTP

2 Activated Sludge Process for Treatment of Wastewater

Wastewater treatment systems that use activated sludge processes have been employed extensively throughout the world, mostly because they produce effluents that meet required quality standards (suitable for disposal or recycling purposes), at reasonable operating and maintenance costs. Figure 1 shows a schematic diagram of a conventional wastewater treatment. All design processes include preliminary treatment consisting of bar screen, grit chamber, and oil and grease removal unit [14], typically followed by primary gravity settling tank, in all but some of the smaller treatment facilities. The primary-treated wastewater enters into a biological treatment process—usually an aerobic suspended growth process—where mixed liquor (i.e., microorganisms responsible for the treatment, along with biodegradable and nonbiodegradable suspended, colloidal, and soluble organic and inorganic matter) is maintained in liquid suspension by appropriate mixing methods. During the aeration period, adsorption, flocculation, and oxidation of organic matter occur. After enough time for appropriate biochemical reactions, mixed liquor is transferred to a settling reactor (clarifier) to allow gravity separation of the suspended solids (in form of floc particles) from the treated wastewater. Settled solids are then returned to the biological reactor (i.e., return activated sludge) to maintain a concentrated biomass for wastewater treatment. Microorganisms are continuously synthesized in the process; thus some of suspended solids must be wasted from the system in order to maintain a selected biomass concentration in the system. Wasting is performed by diverting a portion of the solids from the biological reactor to solid-handling processes. The most common practice is to waste sludge from the return sludge line because return activated sludge is more concentrated and requires smaller waste sludge pumps. The waste sludge can be discharged to the primary sedimentation tanks for co-thickening, to thickening tanks, or to other sludge-thickening facilities, in order to increase the solid content of sludge by removing a portion of the liquid fraction. Through the subsequent processes such as digestion, dewatering, drying, and combustion, the water and organic content is considerably reduced, and the processed solids are suitable for reuse or final disposal. To achieve better effluent water quality, further treatment steps - tertiary treatment - can be added to the above outlined generla process, e.g. activated carbon adsorption, additioanl nutrient removal etc.

3 Occurrence of Pharmaceuticals During Conventional Wastewater Treatment

3.1 Occurrence of Pharmaceuticals in Wastewater Influent and Effluent

More than 10,000 prescription and over-the-counter pharmaceuticals are registered and approved for usage today, with around 1,300 unique active ingredients (Orange book, FDA). This is a versatile group of compounds that differ in the mode of action, chemical structure, physicochemical properties, and metabolism. They are typically classified using the Anatomical Therapeutic Chemical Classification System (ATC system) according to their therapeutic application and chemical structure. Because of the volume of prescription, the toxicity, and the evidence for presence in the environment, nonsteroidal anti-inflammatory drugs (NSAIDs), antibiotics, beta-blockers, antiepileptics, blood lipid-lowering agents, antidepressants, hormones, and antihistamines were the most studied pharmaceutical groups [15].

Even though a number of research publications have been focused on the occurrence, fate, and effects of pharmaceuticals in the environment, we have data on the occurrence of only 10% of the registered active compounds, and very little information on their effects in the environment. There is even less information regarding the occurrence and fate of the transformation/degradation products (active or not) of pharmaceuticals. Both the qualitative and the quantitative analysis of pharmaceuticals in the environmental matrices are definitely a starting point for the establishment of new regulations for the environmental risk assessment of pharmaceutical products.

The pharmaceuticals find their way to the environment primarily via the discharge of raw and treated sewage from residential users or medical facilities. Through the excretion via urine and feces, extensively metabolized drugs are released into the environment. But the topically applied pharmaceuticals (when washed off) along with the expired and unused ones (when disposed directly to trash or sewage) pose a direct risk to the environment because they enter sewage in their unmetabolized and powerful form [2]. Even though the production of drugs is governed by rigorous regulations, pharmaceutically active substances are frequently released with the waste from drug manufacturing plants [16–18].

The occurrence of the pharmaceutical compounds in wastewater treatment plants has been investigated in several countries around the world (Austria, Canada, England, Germany, Greece, Spain, Switzerland, USA, etc). More than 150 pharmaceuticals belonging to different therapeutic groups have been detected in concentration ranging up to the μg/L level in sewage water. Their environmental occurrence naturally depends on the rate of production, the dosage and frequency of administration and usage, the metabolism and environmental persistence, as well as the removal efficiency of wastewater treatment plants (WWTPs). Figures 2 and 3 show the occurrence of the selected, most investigated pharmaceuticals in wastewater influent and effluent, as found in the literature.

NSAIDs are the most used class of drugs for the treatment of acute pain and inflammation. They are administered both orally and topically and available as prescription and over-the-counter (nonprescription) drugs. High consumption and way of administration of NSAIDs result in elevated concentration reported in the effluent from WWTPs. Among the most studied NSAIDs during wastewater treatments are ibuprofen, diclofenac, naproxen, ketoprofen, and mefenamic acid [19]. The compounds usually detected in the highest concentrations in the influent of WWTPs are ibuprofen, naproxen, and ketoprofen (in range of some μg/L)