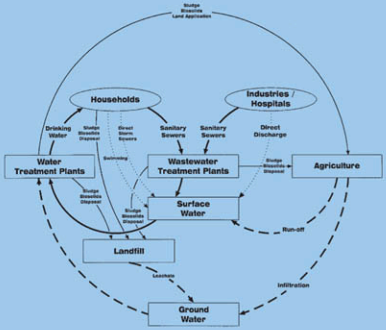
Contaminants

of Emerging Environmental Concern



Edited by

Alok Bhandari, Rao Y. Surampalli, Craig D. Adams, Pascale Champagne, Say Kee Ong, R. D. Tyagi, and Tian C. Zhang

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of the American Society of Civil Engineers

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Preface

The 21st century has unfolded the widespread occurrence of a new category of contaminants which have attracted the attention of citizens, scientists and engineers, researchers, state and federal agencies, environmental groups, industrial and commodity groups, and regulators. These contaminants are predominantly unregulated anthropogenic chemicals that occur in air, soil, water, food, and, human/animal tissues in trace concentrations, are persistent in the environment, and are capable of perturbing the physiology of target receptors. These chemicals are considered to be contaminants of emerging environmental concern (CoEECs).

The ASCE's Technical Committee on Hazardous, Toxic, and Radioactive Waste Management identified the need to collect and present the latest information on the occurrence and fate of CoEECs in natural and engineered systems. The committee envisioned to prepare an easy-to-read book that would serve as a reference for practicing professionals and be equally effective as a text in undergraduate or graduate courses.

This book report is organized by types of commonly occurring and widely studied CoEECs. Chapter 1 introduces the topic of the book report and presents the need to understand the characteristics and environmental occurrence of these chemicals. Chapter 2 discusses analytical chemistry methods for sampling, separation, purification, identification and quantification of CoEECs in environmental samples. Chapter 3 discusses pharmaceuticals, while Chapter 4 talks about personal care products. Chapters 5 and 6 present information about antibiotics and hormones, respectively. Chapter 7 discusses the occurrence and fate of phthalate plasticizers and their degradation products in natural and engineered systems. Chapters 8 and 9 focus on surfactants and their derivatives, and fire retardants. Chapter 10 discusses pesticides, several of which are considered to be CoEECs at trace concentrations. Chapter 11 focuses on nanomaterials, a category of CoEECs whose health and environmental implications are just beginning to be evaluated. Finally, Chapter 12 talks about organisms capable of degrading CoEECs and the molecular biology tools used to study these organisms.

The editors acknowledge the hard work and patience of all authors who have contributed to this book.

- AB, RYS, CDA, PC, SKO, RDT, TCZ

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CHAPTER 1

Introduction

Alok Bhandari

1.1 Background

Over the past century our industries have produced thousands of chemicals to enhance our overall quality of life. These compounds have allowed us to increase agricultural productivity, improve animal health, and boost human longevity. The improper use and disposal of some of these chemicals, however, has also resulted in adverse human health impacts and environmental problems. The societal need to ensure the quality of soil and water environments was first recognized in the mid-20th century. Soon thereafter, we began regulating our coastal waters and surface streams for sediments and oxygen-consuming organic material. Then came Rachel Carson's *Silent Spring* which introduced the public to the environmental and human health impacts of a wide array of persistent and toxic anthropogenic chemicals. Regulations were reinforced and maximum contaminant levels (MCLs) were established to minimize human exposure to chemicals characterized as acutely toxic or carcinogenic. The National Pollutant Discharge Elimination System (NPDES) ensured that these contaminants were not discharged into surface water from point-sources such as industries and municipal wastewater treatment plants (WWTPs).

The late 20th century produced great advancements in trace chemical analysis including separation and identification methods such as solid phase extraction, gas-chromatography/mass-spectrometry (GC/MS), and liquid-chromatography/mass-spectrometry (LC/MS). These technologies allowed scientists to separate compounds from environmental media and identify them at unprecedented levels of parts per trillion (ppt or ng/L) and lower. Suddenly, a broad range of previously undetected micropollutants became apparent in media as diverse as food, tissue, breast milk, and water samples collected from rivers, lakes, aquifers, municipal water treatment plants and WWTPs. Thus, the dawn of the 21st century has brought with it the knowledge of widespread, trace-level environmental occurrence of a generally unregulated group of chemicals that have been variously termed as 'emerging chemicals of concern', 'contaminants of concern', 'contaminants of emerging concern', 'micro-constituents', 'unregulated contaminants', 'persistent organic pollutants', 'pharmaceuticals and

personal care products', or 'contaminants of emerging environmental concern (CoEECs)'.

CoEECs are usually unregulated, but persistent anthropogenic chemicals that are discharged into the environment or generated therein at low concentrations. These are potentially harmful compounds whose effects on ecology and human health are poorly understood because of their recent discovery in the environment. CoEECs enter the environment through a variety of domestic, industrial and agricultural activities. Some CoEECs are used by humans as pharmaceuticals or personal care products and enter the hydrological cycle through discharges from municipal wastewater treatment plants or on-site septic systems. Others are used in the animal agriculture for growth promotion or disease control and enter the environment when animal waste is applied on agricultural fields. Still others are used in industrial surfactants, plasticizers, or flame retardants and released via industrial discharges. These compounds are mobile and persistent in the environment and occur in air, water, sediments, and tissues of ecological receptors at concentrations of ppt to low parts-per-billion (ppb, μg/L).

Scientists from the U.S. Geological Survey (USGS) were among the first to report a widespread occurrence of CoEECs at targeted sites in streams across the United States (Kolpin et al., 2002). USGS's Toxic Substances Hydrology Program has since conducted other nation-wide field investigations and have recently reported on the presence of these compounds in groundwater and sources of municipal drinking water (Barnes et al. 2008; Focazio et al., 2008). The most frequently detected compounds in groundwater in human and animal waste sources included N,N-diethyltoluamide, (DEET, insect repellent), bisphenol-A (plasticizer), tri(2-chlroethyl)phosphate (flame retardant), sulfamethoxazole (antibiotic) and 4-octylphenol monoethoxylate (surfactant metabolite). When untreated sources of municipal drinking water were tested, the five most frequently detected CoEECs in surface water included cholesterol, metolachlor (herbicide), cotinine (nicotine metabolite), β-sitosterol (natural plant sterol), and 1,7-dimethylxanthine (caffeine metabolite).

Robust data on ecological and human health effects of exposure to CoEECs at environmentally relevant concentrations is still lacking. However, extensive research is being conducted on this topic and early results appear to suggest some ecological concern. Frogs exposed to the anti-bacterial agent, triclosan, have been found to show reduced activity and startle response (Fraker and Smith, 2004). Residues of the anti-inflammatory, diclofenac, have been implicated with declines in vulture populations in South Asia (Oaks et al., 2004). Fish collected downstream from municipal wastewater treatment plants discharging effluent containing a variety of estrogenic chemicals have revealed signs of altered sex ratios, reduced gonad size, gonadal intersex, disrupted ovarian and testicular histopathology and vitellogenin induction, that are typical of exposure to estrogenic chemicals (Vajda et al., 2008). Intersex gonads and high vitellogenin concentrations were recently reported in male fish

collected from four river basins of the Southeastern United States indicating exposure to EDCs and estrogenic chemicals (Hinck et al., 2008).

The antiepileptic drug, carbamazepine, has been shown to impact the survivability of the non-biting midge *Chironomus riparius* but it had no effects on other organisms such as the oligochaete *Lumbriculus variegates* and the freshwater snail *Potamopyrgus antipodarum* (Oetken et al., 2005). Other researchers have found little or no ecological impact of some CoEECs. No adverse impact of exposure of the antidepressant, fluoxetine, was observed on zooplankton at environmentally relevant concentrations (Laird et al., 2007). The antibiotic, tylosin, was shown to pose little or no risk for aquatic macrophytes (Brain et al., 2005). Exposure to the surfactant derivative, 4-nonylphenol, at or above the EPA toxicity-based chronic exposure level produced no changes in morphological endpoints such as the gonadosomatic and hepatosomatic indices, secondary sexual characteristics and histopathology in male fathead minnows (Schoenfuss et al., 2008).

1.2 Types of CoEECs

Several classes of anthropogenic compounds can be classified as CoEECs. In its national reconnaissance studies of US streams, groundwater and raw drinking water, the USGS has focused on the subset of CoEECs summarized in Table 1.1 (USGS, 2008). These include human and veterinary antibiotics, sex and steroidal hormones, household and industrial chemicals and other human pharmaceuticals. The latter category includes lifestyle medicines analgesics, anti-inflammatories, stimulants, antacids, antidepressants, antihypertensives, antidiabetics, anticoagulants, antianxiety, antiasthmatics, antihyperlipidimics, and antianginals. This book report includes specific chapters focusing on pharmaceuticals (chapter 3), personal care products (chapter 4), antibiotics (chapter 5), hormones (chapter 6), plasticizers (chapter 7), surfactants (chapter 8), fire retardants (chapter 9), pesticides (chapter 10), and nanomaterials (chapter 11). Also discussed are analytical methods used for the separation, clean-up, and identification of CoEECs in environmental samples (chapter 2) and molecular biology techniques for CoEEC degrading organisms (chapter 12).

1.3 Future Challenges

Modern analytical tools and techniques have allowed detection of CoEECs at minute concentrations. Continued development and refinement of techniques for separation and quantitation of trace level CoEECs in complex environmental matrices is necessary to improve our understanding of factors affecting the fate and transport of these contaminants. This knowledge will lead to the development of models that can accurately predict the behavior of these contaminants in the soil and water environment.