Environmental Toxicology and Chemistry

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DONALD G. CROSBY
Department of Environmental Toxicology
University of California, Davis

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About the Cover. Topographic projection of acetylcholine receptors obtained by cryoelectron microscopy of crystals grown from postsynaptic membranes of the electric ray, *Torpedo marmorata* [see N. Unwin, C. Toyoshima, and E. Kubalek, *J. Cell Biol.* **107,** 1123–38 (1988)]. Each rosette is about 90 Å across and consists of a fluid-filled pore surrounded by five rod-like glycoprotein macromolecules, two of which reversibly bind the acetylcholine. A bulky molecule of highly toxic nicotine alkaloid can bind to the receptor in place of acetylcholine, blocking the pore to the diffusion of the Na^+ and K^+ required for nervous system function. Thus, a familiar neurotoxic response to tobacco is seen to be a matter of chemistry (see Section 9.1).

TOPICS IN ENVIRONMENTAL CHEMISTRY

A SERIES OF ADVANCED TEXTBOOKS AND MONOGRAPHS

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To my students,
here and abroad, this book is
dedicated
with
affection and respect.

Preface

Environmental toxicology and environmental chemistry are inseparable, two sides of the same coin. I have tried to pursuade students of this fact for over 30 years, usually with success. When I started teaching environmental toxicology at the University of California in 1964, the only toxicology text available was the medically oriented *Textbook of Toxicology* by DuBois and Geiling, and there was no single text on environmental chemistry. Over the years, my colleagues and I grumbled about the lack of a book suited to our style of coursework, produced large volumes of lecture handouts, and directed students to reference works such as Casarett and Doull's *Toxicology: The Basic Science of Poisons* and Schwarzenbach's *Environmental Organic Chemistry*. A bit late, I am offering a text that seeks to combine what often are seen as two separate subjects.

The subjects are based on principles often poorly understood, or misunderstood, even by some of those who must apply them. Almost daily, news media describe some problem caused by toxic chemicals, but they seldom provide the necessary basic background. The people who are, or will be, responsible for uncovering, clarifying, and solving such problems deserve to share a common base of fundamentals and their applications. That is what this book is intended to provide.

In addition to the third- and fourth-year undergraduates and first-year graduate students for whom this book is primarily intended, it will also be appropriate for the growing range of professionals who require a refresher in environmental toxicology and/or environmental chemistry. I find that many toxicologists, chemists, ecologists, engineers, attorneys, journalists, educators, and government officials never had an opportunity to view toxicology and chemistry in a connected way. This treatment makes no attempt to be exhaustive, and so the references most often cite books and articles that review and expand the subject. It assumes that the reader has an acquaintance with general biology and chemistry but requires no previous knowledge of toxicology or environmental science.

The book is divided into three roughly equal parts: After an introductory chapter comes a review of principles that govern the occurrence of chemicals in the environment, then some principles of toxicology applied to those chemicals, and finally application of the principles to specific examples of environmental chemicals. Each chapter is expanded by a special topic of particular current interest, and most are further supplemented by appendices of pertinent data. Some important terms are indicated in bold type and collected in a glossary at the end, but the subject's scope and nontraditional presentation may require readers to use the index to locate all the places their favorite subject is to be found. The writing is intended only as a framework upon which the instructor or interested individual can impose additions and interpretations; no problem sets or questions are included.

No book comes into existence in isolation. I gratefully acknowledge the help and thoughtful suggestions of Mike Denison, Deanna Dowdy, Lynn Jaeger, Scott Mabury, Glenn Miller, Marion Miller, Randy Magdalena, Ken Ngim, Mike Stimman, and Ron Tjeerdema. Figure 9.1 is reproduced from Adrian Albert's *Selective Toxicity* (p. 29) by permission of Chapman and Hall, London. I am especially indebted to Jan Chambers of Mississippi State University, Richard Lee of the Skidaway Institute of Oceanography, and Scott Mabury of the University of Toronto for reviewing separately the entire manuscript and providing important suggestions. However, I alone bear responsibility for the interpretation, coverage, and accuracy of the topics presented. Special thanks go to editor Bob Rogers for his guidance, and to my wife, Nancy, for continual encouragement and moral support.

D.G.C.

Davis, California
February, 1997

Environmental
Toxicology
and
Chemistry

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CHAPTER 1

Environmental Toxicology and Chemistry

1.1 POISONS

Toxic means poisonous. People today are surrounded by, and often dependent on, a wide array of poisonous chemicals that require understanding and control if one is to live in safety. The purpose of this chapter is to introduce a few of those problem chemicals, outline their environmental toxicology and chemistry, and offer a preview of the rest of the book.

Popularly known as "toxics," toxic substances make news almost daily, often leaving the impression that they are something novel and manmade. Our ancestors, too, were confronted daily and often fatally by poisonous microorganisms, plants, animals, and minerals; poisoning is nothing new. Primitive people used poisons in hunting and warfare, and the term *toxic* comes from the ancient Greek word *toxikon* referring to a bow (poisoned arrows). Toxic chemicals also helped to catch fish, protect against diseases, and fight off insects. The poisons were all natural, of course, but there is no toxicological distinction between natural and synthetic chemicals.

People have always been fascinated by poisons. The Ebers papyrus of 1550 B.C. described common poisons such as hemlock *(Conium maculatum)*, the poison used over 1000 years later to execute the Greek philosopher Socrates and still killing the unwary today. Poisons continued to be employed over the centuries for social and political purposes, and the names Borgia and de'Medici from medieval Europe are still associated with poisoning. In seventeenth-century France, Catherine Deshay's victims were said to have included over 2000 unwanted babies, and an Italian woman named Toffana made her living and reputation by selling arsenic-laced *Aqua Toffana* to wives who longed to become widows. Interesting and entertaining accounts of historical poisonings are provided by Thompson (1931) and Casarett (1975).

Nature employs toxic chemicals as well. Plants, microorganisms, and wild animals use poisons for defense or to expand their living space. Microorganisms produce

TABLE 1.1
Causes of Human Death in the United States[a]

Cause	1970	1975	1980	1985	1990
Motor vehicles	54,633	45,853	53,272	45,901	46,814
Falls	16,926	14,896	13,294	12,001	12,313
Fire	6,718	6,071	5,822	4,938	4,175
Guns	2,406	2,380	1,955	1,649	1,416
Poisons, accidental	5,299	6,271	4,331	5,170	5,803
Poisons, suicide	6,584	6,426	5,453	5,704	5,424
Total poisons[b]	**11,883**	**12,697**	**9,784**	**10,874**	**11,227**

[a] USDC, 1993.
[b] Excludes homicide, adverse therapy, alcoholism, and venomous animals.

antibiotics, many plants release allelochemicals that prevent other plants from growing near them, and invertebrate animals often resort to toxic defense substances, as anyone who has been bitten by a fire ant or stung by a jellyfish can attest. The human tendency to get in the way of these natural battles sometimes has disastrous results, as in 994 A.D. when over 40,000 Europeans died from eating food contaminated with the toxic ergot fungus *Claviceps purpurea.* James Cook's eighteenth-century voyages in the South Pacific were stalked by death and illness from fish tainted with Ciguatera toxin, and members of Abe Lincoln's family, including his mother, died by drinking milk from cows that had eaten white snakeroot *(Eupatorium urticaefolium).* See Chapter 12 for more about toxic plants.

Poisons still present problems. In a typical year, thousands of people die from accidents, suicide, or homicide due to poisoning (Table 1.1), and many others are killed by tobacco and alcohol (Section 1.4.2), which, too, are poisons. Although the exact numbers vary among sources, human death by poison appears to be on the upswing, the government's Statistical Abstract listing a U.S. total of 9784 in 1980 and 11,227 a decade later (USDC, 1993). However, as only a small percentage of poisoning incidents are fatal, the total of toxic exposures is actually much greater. Reports to U.S. poison control centers exceeded 715,000 in 1992 (Litovitz et al., 1993), and worldwide, pesticides alone cause over 3 million poisonings annually (WHO, 1990). Accidental poisoning is widespread among both wild and domestic animals (Sections 1.4.3 and 1.4.4), and toxic chemicals are used intentionally and widely against undesirable weeds, rodents, and insects. The growing interest in environmental toxicology is well deserved.

1.2 ENVIRONMENTAL TOXICOLOGY

Toxicology is the science of poisons. It deals with the adverse effects of chemical agents on biological systems. The American Heritage Dictionary defines poison as "a substance that causes illness, injury, or death . . . by chemical means." In their 1959 textbook, DuBois and Geiling further define toxicology as dealing with the occurrence, physical and chemical properties, effects, and detection of poisons. Note that these definitions do not restrict toxicology to studies in animals. Scientific toxicology started during the historic period of 1810–1850, when great advances in chemistry, physics, and biology also were being made. The name appears to have been coined by M. J. B. Orfila (1787–1853), the Spanish "father of toxicology."

Subdivision of any field of knowledge is tempting. Zakrzewski (1991) describes only three branches of toxicology—clinical, forensic (legal), and environmental—but Ballantyne et al. (1995) suggest eight more, including veterinary, occupational, and regulatory. Although each has advanced rapidly in recent years, ***environmental toxicology,*** so named in the early 1960s, currently receives the major share of public attention.

From these definitions, it follows that environmental toxicology is the branch of science concerned with the nature, properties, effects, and detection of toxic substances in the environment and in *any* environmentally exposed species, including humans. The key word is ***environment,*** according to the dictionary "the complex of physical, chemical, and biotic factors that act upon an organism and ultimately determine its form and survival" which certainly includes poisons. The subject does not have rigid boundaries, and it merges with occupational toxicology in the work environment, clinical toxicology in the home environment, and so on.

However, the principal realm of environmental toxicology remains out of doors. The emphasis is on (1) the occurrence, availability, and form of toxic chemicals, (2) exposure to such chemicals and the accompanying dangers, and (3) comparative effects and mechanisms of action in the broad range of exposed species, again including but not focused on humans. The toxic chemicals of concern often are manmade ***xenobiotics,*** that is, substances foreign to living organisms, but natural poisons also are included, as are toxic levels of normal body constituents such as vitamins and hormones. While sometimes equated with "wildlife toxicology" or "pollution toxicology," environmental toxicology obviously represents much more.

Where traditional toxicology usually deals with relatively large, measured doses of known chemicals such as drugs, environmental toxicology usually must consider variable low levels of dispersed and often unidentified substances. This is where environmental chemistry comes in.

1.3 ENVIRONMENTAL CHEMISTRY

Toxicity is based on chemistry. Although often treated as separate subjects by college courses, professional organizations, and even many practitioners, toxicology and chemistry actually are inseparable. Poisons are chemicals (Chapter 2), exposure is governed by chemical forces (Chapter 10), and both the action of poisons (Chapter 9) and an organism's ability to protect itself (Chapter 6) are largely a matter of chemistry. Such practical problems as predicting what happens to toxic chemicals (Chapter 16) and remediating toxic wastes (Special Topic 15) require a knowledge and use of chemical principles.

Environmental chemistry is concerned with the sources, identity, levels, reactions, transport, and fate of chemical species in water, soil, and air environments (Manahan, 1994). It applies the principles of inorganic, organic, analytical, and physical chemistry to environmental chemicals and processes. Much of its current emphasis is placed on manmade pollutants, but as with toxicology, natural chemicals originating from animals, plants, or minerals must be included. As the environmental chemistry focus frequently involves the harmful effects of a substance, environmental toxicology and chemistry form a continuum.

From toxicology's viewpoint, perhaps the most important function of environmental chemistry is to provide the exposure information necessary for evaluation of toxicity and risk. This includes identification of toxic chemicals, reactions that reduce their availability or convert them into more toxic or less toxic forms, and quantitative measurement of both their environmental and available concentrations. As soon as any chemical enters air, soil, water, or a living organism, it starts to move and change (Chapters 3 to 6). Take smog, for example. Petroleum hydrocarbons volatilize from the earth's surface into the atmosphere, become dispersed, and are photooxidized by sunlight into products very different from, and toxicologically more interesting than, the original alkanes and alkenes. Structure, reactivity, availability, and exposure form the basis of intoxication.

1.4 TOXICITY

1.4.1. Intoxication

Intoxication is the scientific term for poisoning. It results from the interaction of a chemical "poison" with some biochemical entity or process that sustains life (Chapter 9). Like other chemical processes, intoxication is mass driven; that is, it is dependent on the degree of ***exposure*** or ***dose,*** and this ***dose–response relationship*** is perhaps the most significant feature of toxicity. The degree of subsequent harm is also controlled by the organism's ability to absorb, degrade, and eliminate the ***toxicants,*** as well as its particular biochemistry and physiology (Chapter 7). The balance of exposure to and removal of the chemical from the organism determines the toxic outcome. As the saying goes, **"The dose makes the poison."**

These characteristics also set the stage for ***selective toxicity,*** where one species can be affected by a poison while another seemingly is not. Selectivity is a necessary feature of most medicines and pesticides, and many weed killers, for example, are almost nontoxic to mammals because they kill plants by such nonanimal processes as photosynthesis. Nonetheless, intoxication is common to all living organisms, from people to bacteria, as illustrated in the next sections.