The Handbook of Environmental Chemistry

Volume 3 Part B

Anthropogenic Compounds

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With Contributions by
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With 38 Figures

Springer-Verlag Berlin Heidelberg New York 1982

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ISBN 3-540-11108-5 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-11108-5 Springer-Verlag New York Heidelberg Berlin

Library of Congress Cataloging in Publication Data
Main entry under title: Anthropogenic compounds. (The Handbook of environmental chemistry; v. 3, pt. A.–B.)
Includes bibliographies and index.
1. Pollution – Environmental aspects. 2. Pollution – Toxicology. 3. Environmental chemistry.
I. Butler, Gordon Cecil, 1913–. II. Bock, K. J. III. Series: Handbook of environmental chemistry; v. 3, pt. A.–B.
QD31.H335 vol. 3, pt. A, etc. 574.5′222s 80-16609
[QH545.A1] [574.5′222] AACR1
ISBN 0-387-09690-6 (U.S.: v. 1)

Printed in Germany

Typesetting, printing, and binding: Brühlsche Universitätsdruckerei, Giessen
2152/3140-543210

Preface

Environmental Chemistry is a relatively young science. Interest in this subject, however, is growing very rapidly and, although no agreement has been reached as yet about the exact content and limits of this interdisciplinary discipline, there appears to be increasing interest in seeing environmental topics which are based on chemistry embodied in this subject. One of the first objectives of Environmental Chemistry must be the study of the environment and of natural chemical processes which occur in the environment. A major purpose of this series on Environmental Chemistry, therefore, is to present a reasonably uniform view of various aspects of the chemistry of the environment and chemical reactions occurring in the environment.

The industrial activities of man have given a new dimension to Environmental Chemistry. We have now synthesized and described over five million chemical compounds and chemical industry produces about hundred and fifty million tons of synthetic chemicals annually. We ship billions of tons of oil per year and through mining operations and other geophysical modifications, large quantities of inorganic and organic materials are released from their natural deposits. Cities and metropolitan areas of up to 15 million inhabitants produce large quantities of waste in relatively small and confined areas. Much of the chemical products and waste products of modern society are released into the environment either during production, storage, transport, use or ultimate disposal. These released materials participate in natural cycles and reactions and frequently lead to interference and disturbance of natural systems.

Environmental Chemistry is concerned with *reactions in the environment*. It is about distribution and equilibria between environmental compartments. It is about reactions, pathways, thermodynamics and kinetics. An important purpose of this Handbook is to aid understanding of the basic distribution and chemical reaction processes which occur in the environment.

Laws regulating toxic substances in various countries are designed to assess and control risk of chemicals to man and his environment. Science can contribute in two areas to this assessment; firstly in the area of toxicology and secondly in the area of chemical exposure. The available concentration ("environmental exposure concentration") depends on the fate of chemical compounds in the environment and thus their distribution and reaction behaviour in the environment. One very important contribution of Environmental Chemistry to the above mentioned toxic substances laws is to develop laboratory test methods, or mathematical correlations and models that predict the environmental fate of new chemical compounds. The third purpose of this Handbook is to help in the basic understanding and development of such test methods and models.

The last explicit purpose of the Handbook is to present, in concise form, the most important properties relating to environmental chemistry and hazard assessment for the most important series of chemical compounds.

At the moment three volumes of the Handbook are planned. Volume 1 deals with the natural environment and the biogeochemical cycles therein, including some background information such as energetics and ecology. Volume 2 is concerned with reactions and processes in the environment and deals with physical factors such as transport and adsorption, and chemical, photochemical and biochemical reactions in the environment, as well as some aspects of pharmacokinetics and metabolism within organisms. Volume 3 deals with anthropogenic compounds, their chemical backgrounds, production methods and information about their use, their environmental behaviour, analytical methodology and some important aspects of their toxic effects. The material for volume 1, 2 and 3 was each more than could easily be fitted into a single volume, and for this reason, as well as for the purpose of rapid publication of available manuscripts, all three volumes were divided in the parts A and B. Publisher and editor hope to keep materials of the volumes one to three up to date and to extend coverage in the subject areas by publishing further parts in the future. Readers are encouraged to offer suggestions and advice as to future editions of "The Handbook of Environmental Chemistry".

Most chapters in the Handbook are written to a fairly advanced level and should be of interest to the graduate student and practising scientist. I also hope that the subject matter treated will be of interest to people outside chemistry and to scientists in industry as well as government and regulatory bodies. It would be very satisfying for me to see the books used as a basis for developing graduate courses on Environmental Chemistry.

Due to the breadth of the subject matter, it was not easy to edit this Handbook. Specialists had to be found in quite different areas of science who were willing to contribute a chapter within the prescribed schedule. It is with great satisfaction that I thank all 52 authors from 8 countries for their understanding and for devoting their time to this effort. Special thanks are due to Dr. F. Boschke of Springer for his advice and discussions throughout all stages of preparation of the Handbook. Mrs. A. Heinrich of Springer has significantly contributed to the technical development of the book through her conscientious and efficient work. Finally I like to thank my family, students and colleagues for being so patient with me during several critical phases of preparation for the Handbook, and to some colleagues and the secretaries for technical help.

I consider it a privilege to see my chosen subject grow. My interest in Environmental Chemistry dates back to my early college days in Vienna. I received significant impulses during my postdoctoral period at the University of California and my interest slowly developed during my time with the

National Research Council of Canada, before I could devote my full time to Environmental Chemistry, here in Amsterdam. I hope this Handbook may help deepen the interest of other scientists in this subject.

O. Hutzinger

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Lead

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Introduction

The quantity of published data available on the pollution chemistry of lead is staggering. Books and journal articles on lead are probably as numerous as those for any other pollutant. Because of the ease with which lead is mined and smelted, it was one of the first metals used by early man. Lead was used for glazing pottery, and making ornaments by the Egyptians in 7,000–5,000 BC. The Romans used lead pots for cooking, lead salts for sweeteners, and lead plumbing in their cities. There are even references to the discovery of the toxicological properties of lead by the Romans and the Greeks. High lead concentrations in the bones of Roman aristocrats have led some to believe that lead poisoning advanced the fall of the Roman Empire [50]. Since the technological revolution of the 18th and 19th centuries a more enlightened approach to public health problems has brought about extensive study of lead. It is hoped that this chapter will present some introduction to the many aspects of lead pollution.

Production, Use and Natural Occurrence

Production

Lead Mining

Lead occurs as a variety of ores, the most important of which is galena, with cerussite and anglestie being of secondary importance. Sphalerite (zinc), chalcopyrite (copper), and silver are common coproducts commercially mined with lead. Other minor constituents of lead ores are gold, bismuth, antimony, arsenic, cadmium, tin, gallium, thallium, indium, germanium, and tellurium [77].

In 1965, the world mine production of lead was 2.6 million Mg, with production increasing to 3.6 million Mg in 1975. The most important lead mining countries in 1975 were; the United States (16.0% total world output), the Soviet Union (14.5%), Australia (10.0%), Canada (9.6%), Peru (5.5%), Mexico (4.5%), China (3.8%), Yugoslavia (3.5%), and Bulgaria (3.0%). In addition, Ireland, Japan, the Democratic People's Republic of Korea, Morocco, Poland, Spain, and Sweden each had over 2% of the total world production of lead. The estimated proven lead reserves of the world are 93 million Mg by metal content.

Smelting and Refining

In the primary smelting and refining of lead, concentrated metallic minerals from the mine are formed into pellets, which are roasted. In the case of the primary lead ore, galena (PbS), the roasting process removes the S, creating a sinter that is fired along with coke to chemically reduce the Pb to its metallic form. The lead concentrate then undergoes a high-pressure aqueous oxidation to remove other metals that hinder the smelting process. The secondary smelting and refining of lead uses new process scrap that comes from manufacturing processes and old recycled scrap that comes from discarded lead-containing manufactured goods [45, 77].

Environmental Pollution from Production

Anthropogenic sources of lead in the environment from the production of lead can be associated with (a) the mining-milling operations, which include grinding, concentrating, and transportation of the ore, as well as disposal of the tailings and mine and mill wastewater and (b) the smelter-refininery process and problems associated with concentrate hauling, storage, sintering, refining, atmospheric discharges, and blowing dust [76].

In 1975, there was an estimated total of 19,225 Mg of lead emitted to the atmosphere from stationary sources. Of this total, 400 Mg were from primary lead smelting, and 755 Mg were from secondary lead smelting, representing 2.1 and 3.9%, respectively, of the total lead emissions from stationary sources. In 1975, 142,000 Mg of lead were emitted from mobil sources through the combustion of gasoline [73].

Use

Industry

Lead pigments are commonly used in paints, although less toxic pigments are presently used preferentially. Red lead (minimum) is used extensively in the painting of structural steel, and lead chromate is used as a yellow pigment (see Table 1). At

Table 1. Percentage of total lead consumption in 1969 and 1974 for selected industries in major industrial countries

Industry	1969	1974
Chemical	10.9	12.0
Cable and sheathing	10.9	9.2
Storage batteries	35.9	44.0
Lead in fuels	12.0	12.0
Alloys	8.1	10.8
Semi-Manufacturers	16.5	12.0

Source: WHO, 1977 [77]

one time, lead arsenate was extensively used as an insecticide, although present consumption is considerably reduced. Litharge (PbO) dissolved in a sodium hydroxide solution is used to remove sulfur compounds from petroleum during the refining process [77].

Lead consumption in the cable industry has declined because of the introduction of plastic sheathing and insulation (see Table 1). However, the total amount of lead used in the industry is significant. Cadmium, tellurium, copper, antimony, and arsenic are trace contaminants in alloys used for cable sheathing [77].

The largest consumer of lead is the electric manufacturing industry storage battery (see Table 1). A lead-antimony alloy is used in the preparation of grids and lugs. Litharge, red lead, and grey oxide (PbO_2) are used in the preparation of pasted plates [45]. The percentage of total lead consumption accounted for by the battery industry is increasing (see Table 1), although the demand for lead batteries has decreased. This may be partially attributed to the increased use of long-life batteries. About 80% of the lead in storage batteries is recovered at secondary smelters, making the battery industry the source for secondary lead production [77].

Lead additives are used in gasoline to increase the octane rating. The emission of these additives through the exhaust of internal combustion engines is the largest source of lead in the atmosphere [73]. The additives are almost exclusively tetramethyllead and tetraethyllead. World consumption of refined lead for the manufacture of lead additives reached a maximum of 380,000 Mg in 1973, with consumption declining 30% by 1975 [33, 77]. This decrease in consumption can be attributed to increased use of catalytic converters on motor vehicles, requiring the use of lead-free gasoline.

The production of manufactured lead components is responsible for an important part of total lead consumption. Lead surfaces oxidize readily, leaving the surface resistant to corrosion. Lead is used in construction when corrosion resistance is desired. Roofing, flashing, wall cladding, and sound insulation are all instances where lead is used. Alloys of lead are used in solder, ball bearings, brasses, typesetting metal, collapsible tubes, and radiation shielding. The manufacture of ammunition is also a major consumer of lead. There are many additional uses of lead components, but these account for a small portion of total lead consumption [77].