The Handbook of Environmental Chemistry

Volume 3 Part A

Anthropogenic Compounds

Anthropogenic Compounds

With Contributions by R. Anliker, G.C. Butler, E.A. Clarke, U. Förstner, W. Funke, C. Hyslop, G. Kaiser, C. Rappe, J. Russow, G. Tölg, M. Zander, V. Zitko

With 61 Figures



Professor Dr. Otto Hutzinger

Laboratory of Environmental and Toxicological Chemistry
University of Amsterdam, Nieuwe Achtergracht 166
Amsterdam, The Netherlands

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At the moment three volumes of the Handbook are planned, Volumed.

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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 contries 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 processess 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. Part A of all three volumes is now being published and the second part of each of these volumes should appear about six months thereafter. 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. Plans also exist for volumes dealing with different subject matter such as analysis, chemical technology and toxicology, and 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 in 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 contries 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.

Preface

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.

Amsterdam, May 1980

O. Hutzinger

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The Hydrosphere. J. Westall and W. Stumm
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List of Contributors

Dr. R. Anliker ETAD Clarastr. 4–6 CH - 4005 Basel 5 Switzerland

Dr. G. C. Butler Div. of Biological Sciences National Research Council of Canada Ottawa, Canada K1A OR6

Dr. E. A. Clarke ETAD Clarastr. 4–6 CH - 4005 Basel 5 Switzerland

Prof. U. Förstner Institut für Sedimentforschung Universität Heidelberg D - 6900 Heidelberg Federal Republic of Germany

Prof. W. Funke
II. Institut für Technische Chemie
Universität Stuttgart
D - 7000 Stuttgart 80
Federal Republic of Germany

Dr. Colleen Hyslop Div. of Biological Sciences National Research Council of Canada Ottawa, Canada K1A OR6 G. Kaiser Max-Planck-Institut für Metallforschung D - 7070 Schwäbisch Gmünd Federal Republic of Germany

Prof. C. Rappe Dept. of Organic Chemistry University of Umea S - 901 87 Umea Sweden

Dr. J. Russow Hoechst AG D - 6230 Frankfurt/M. 80 Federal Republic of Germany

Prof. G. Tölg Max-Planck-Institut für Metallforschung D - 7070 Schwäbisch Gmünd Federal Republic of Germany

Prof. M. Zander Rütgerswerke AG D - 4620 Castrop-Rauxel Federal Republic of Germany

Dr. V. Zitko
Fisheries and Environmental
Sciences
Fisheries and Oceans
Biological Station
St. Andrews, N. B.
Canada EOG 2XO

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G. Kaiser, G. Tölg

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, Laboratorium für Reinststoffe D-7070 Schwäbisch Gmünd, Federal Republic of Germany

Historical Background

The story of mercury can be traced back to prehistoric times. A precise dating is, however, impossible because reliable written records are lacking [1]. The first evidences of the use of mercury originate from the ancient Chinese, who used the metal and its principal ore cinnabar as a medicine to prolong life [2] and cinnabar for the preparation of red ink [3]. Often the Hindus [4], the Egyptians [5, 6], the Hettities [7], and the Assyrians [8] were credited with the use of mercury. Positive proofs for this assumption are, however, still lacking [9, 10]. The metal is said to have been known very early in Persia [9, 11] but a chronological assignment is impossible [12]. The Phoenicians exploited cinnabar in Spain from the 8th century B.C. but there is no direct evidence of their involvement with the metal [14]. In the 5th century B.C. cinnabar was used as a pigment by the Greeks [13, 15] but Aristotle is reputed to be the first in Europe who mentioned the metal itself [16].

By the first century B.C. the preparation of mercury by roasting cinnabar and distilling off the metal was well known [17]. Roman writers describe for the first time the process of amalgamation [18] for the recovery of gold from garments [19]. The first recorded mention of an amalgamation process being worked on a large scale appeared in the 12th century in Egypt [9] and was technologically applied in Mexico and South-America to process silver in the 16th century [20]. About one and a half pounds of mercury were used to produce one pound of silver. The life expectance of the native miners was about 6 months [21]. Already in about 1567 Paracelsus described a therapy for mercurial diseases of miners [22].

Throughout the Middle Ages mercury was used as an intermediate to produce gold and silver from base metals [23-26] and for the treatment of various diseases [5, 10, 27-29]. The endeavour to cure syphilis with Hg and its compounds persisted till the 19th century [30] although the toxic nature of mercury was already reported by ancient authors [31] and the danger of mercury vapour had been demonstrated adequately in 1493 [22].

During the 18th century as chemistry slowly evolved from alchemy into a science, the physical and chemical properties of mercury were investigated [32–35], entraining a growing use of the metal and its compounds [36, 37].

The first anthropogenic release of mercury into the environment began with the industrial revolution. The steam engine was invented in 1705 entailing an increased consumption of fossil fuels, and in 1892 a new technique for the production of chlorine and caustic soda by electrolysis using a mercury cathode. Moreover in 1900 organo-mercury compounds ("chlorophenol-quecksilber") were introduced as fungicides to treat seed and from about 1950 as slimicides [21]. The quantities discharged into the environment remained unnoticed and were disregarded until serious hazards that occurred in the 1950s in Japan and Sweden were brought to light.

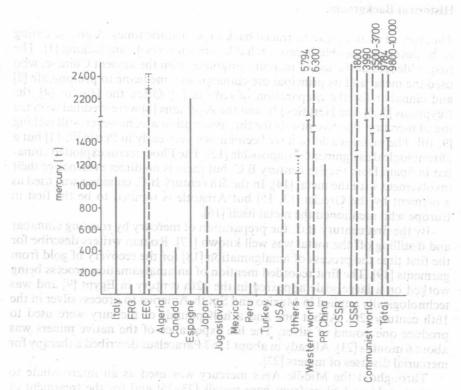


Fig. 1. Production and consumption of mercury in 1973 [68, 54]

production; ---- consumption; EEC: European Economic Community

Production-, Use-, Shipment-, and Release Data

Occurrence. Mercury is commonly found in nature as the red sulfide (cinnabar) and in lesser amounts as the black sulfide (metacinnabar), the formula of which may be assumed as (Hg,Zn,Fe)(S,Se) [38–42]. It is also found in a number of minerals in which it is not an essential constituent, and in which it substitutes for other elements [38, 41]. It is often combined with pyrite, quartz, calcite, dolomite, stignite and others. Major deposits of cinnabar are in Spain, Italy, Yugoslavia, USSR, USA, China, Mexico [29, 40–42]. The Hg content in ore ranges from 0.3–2% [39, 43–45]. About 80% of the world supply of the last years came from these countries [46] (Fig. 1).

The deposits of mercury were formed when hydrothermal solutions from hot springs or volcanic activity penetrated unstable geological formations to replace porous sandstone or limestone formation with mineral solution containing mercury [39, 40].

Preparation. Mercury is still prepared, in principle, as described in the 16th century [47–49]. The mined ore is crushed, ground and concentrated by flotation before being roasted in a kiln [50, 51] at 500–600 °C in the presence of air, and sometimes with added iron and calcined lime to remove sulfur. The liberated mercury passes over with the combustion gases and is condensed in water-cooled condensers. The recovery is $\geq 95\%$. Mechanical impurities can be removed by passing the metal through a perforated paper or leather. Contaminating heavy metals can be dissolved from mercury by pouring it in a thin jet through diluted nitric acid. The purity of the metal is $\geq 99\%$. The metal is further purified by either threefold distillation or by electrolysis [52] and is commercially offered normally in 3 purity categories (I technically pure 99.995%, II chemically pure 99.9999%, III analytically pure 99.9995%), but also 99.999995% [53] and 99.9999999% [110] qualities are available.

Production. Quantities for the global production in 1973 are reported between 8,747 t [46] and 9,784 t [54]. It is assumed that the amount of the produced Hg kept nearly constant at about 10,000 t (Table 1) up to 1978.

Consumption. Data in Table 1 and Fig. 1 indicate declining rather than increasing global use of mercury. Precise data from eastern bloc countries are lacking. Most of the requirements of these countries are supplied by imports [54]. In 1973 the use of mercury in the USSR amounted to 1,800 t [55]. The production in Red China largely supplies its own requirements.

Anthropogenic Discharged Mercury

Specific Uses and Discharges. Table 1 shows the use of mercury by final use. Data up to 1976 are available only from the USA and the FRG [54, 56]. The table does not show the potential capacity to pollute the environment by the manufacture of the corresponding compounds by the chemical industry. An indication of the size of pollution problems posed by the use of mercury is given by the following examples valid for the USA:

Table 1. Consumption of mercury classified by use [54, 56] mornal decomposition of mercury clastic classified by the mercury classified by the mercury classif

Industrial division (Consum	Consumption [t] at Laurel Vianamiera et via 2001/1 was a 2000					
	EEC	USA		FRG	eFRG modes reason at bo		
	(1973) ^a	1973	1975	1973	1975 b	1976 b	
Electrolysis net cons. invest.	730	451	520	372	siyaksoyu	226	
Electrotechnique and instruments				60.1			
	70	262	250	18.7	5.6	12.4	
Catalysis	60	23	25	17 17 17 17 17 17 17 17 17 17 17 17 17 1	12	16	
Agriculture '	95	63	30		31.9		
Dental use	135	92	60	31	25	26	
Pharmaceutical products				bonner of l			
Laboratory products	170	23	ота in 15 i beb	40	61.3	78.1	
Others and stock	690	35	160	190	44.2	46.7	
Total	2,570	1,873	1,770	808	377.6	514.6	

^a In 1969 the total amount was 2,830 [84] loss up to the class and all the contract of the c

^b If exportation and increase in stock are considered the consumption amounts to about 330 t [56] EEC: European Economic Community

1. Mercury losses in industry are assumed to amount to 10,850 t over a period 1944–1959 [57].

2. Up to 1974 recycled mercury accounts for less than 20% of the total consumption [58]. (About 500 t from 2,900 t total consumption.)

3. It is estimated that in 1968 the chloralkali industry used 590 t only to maintain inventory [58].

Electrolysis. The chloralkali industry is usually the biggest consumer (Table 1) and has been one of the biggest polluters. In recent years this industry made every effort to reduce the emissions [59] as can be seen from the consumed and the emitted mercury quantities (Table 2), which have been evaluated in the FRG [56].

Although the mercury cell capacity might be replaced by the diaphragm process by which less mercury is released to the environment, there is a trend to the former on economical grounds.

Electrical Apparatus and Control Instruments. Mercury finds widespread use in fluorescent, and discharge lamps, in industrial power rectifiers, and to a great extent in mercury-cell batteries. The most part thereof is assumed to be lost, e.g., by breakage of thermometers [60], waste of fluorescent lamps