Environmental Inorganic Chemistry

Edited by
Kurt J. Irgolic and Arthur E. Martell

ENVIRONMENTAL INORGANIC CHEMISTRY

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Kurt J. Irgolic
and
Arthur E. Martell

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Kurt J. Irgolic
Associate Director
Center for Energy and Mineral Resources
Texas A&M University
College Station, Texas 77843

Arthur E. Martell
Distinguished Professor
Department of Chemistry
Texas A&M University
College Station, Texas 77843

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PREFACE

The U.S.-Italy Joint Seminar and Workshop on Environmental Inorganic Chemistry was held at the University Conference Center in the town of San Miniato al Monte thirty miles west of Florence.

The Workshop was attended by forty invited participants from China, England, Italy, Switzerland, Sweden, Wales, and the United States, and provided a much needed forum for the assessment of the major research trends, the current state-of-the-art, and the major concerns in environmental inorganic chemistry from the viewpoint of the inorganic chemists coming from the participating countries. The information presented during the workshop and the contacts made among the participants will lead to international cooperative efforts in environmental inorganic chemistry that will help promote rapid transfer of research results, joint use of specialized instrumentation and facilities, exchange of scientists, interchange of ideas, and the development of research priorities. Such scientific cooperation between countries will maximize the results of environmental research by planned exchange of results and by eliminating unnecessary duplication of effort.

Italy, surrounded by the Mediterranean Sea, is vitally interested in alleviating, preventing, and monitoring pollution in ocean waters. Concern about the Mediterranean Sea led to the establishment of the "Long-Term Program for Pollution Monitoring and Research (Med-Pol-Phase II)" of the Mediterranean Action Plan administered by the United Nations Environment Program. Other countries such as Sweden, England, Switzerland, and China are also concerned about environmental problems, and their scientists have contributed to the literature in this area. China, with one quarter of the World's population, is now moving toward large-scale industrialization. China's environmental pollution problems are expected to grow rapidly in the next decade. The Chinese delegation to this workshop made contact with environmental scientists from other countries. Technical information presented at the workshop, useful for the assessment and control of the environmental hazards that might develop in China, is now available to Chinese environmental scientists. Such exchange of information avoids duplication of work that has already been carried out in laboratories of the western countries.

Inorganic and organometallic compounds of main-group and transition elements are part of the environment and exert their beneficial or detrimental effects on biological systems through specific, but largely unknown chemical or physicochemical interactions with molecules essential for life. Biological processes are known to transform inorganic compounds through ligand-exchange, carbon-element bond formation, and redox reactions, to increase the variety of substances present in the environment, and to greatly enhance the complexity of the interactions that occur. Generally, environmental problems can be completely understood and solved in the most expeditious manner, or prevented before they occur, only when their chemical foundations have been elucidated and the nature of the metal compounds involved has been determined. To obtain the necessary knowledge, investigations of the toxic or beneficial effects of elements and determinations of total element concentrations in organisms and their biological compartments must be followed by studies identifying the various compounds, their transformations in biological systems, and their interactions with biomolecules. These principles apply to inorganic compounds in land, air, sea, and groundwaters, and surface waters.

The workshop addressed ongoing and planned future activities in the area of "molecular" environmental inorganic chemistry, examined the present state of knowledge, provided information on the reactions of inorganic and organometallic compounds on the molecular level, and evaluated hypotheses that have been advanced to explain the observed reactions. Many chemical disciplines are involved in this search for a fundamental understanding of the impact of inorganic and organometallic compounds on the environment: analytical chemists must provide the sensitive and compound-specific methods, without which advances will be almost impossible; chemists specializing in synthesis must make available sufficient quantities of important model compounds for detailed study; physical chemists must elucidate reaction mechanisms, determine formation constants, establish the nature of compounds in solution and ascertain molecular structures. This workshop brought together not only delegates from several countries to establish international cooperation, but also representatives of various chemical disciplines to assure an interdisciplinary approach to environmental inorganic chemistry.

A number of basic interdisciplinary issues emerged during the workshop that provide challenging research topics to the inorganic chemist. The influence of this workshop will make itself felt as ideas generated during the workshop lead to research projects, that explore the relationship between inorganic and organometallic compounds and biota, and - in a cyclic fashion - refine the list of priority research topics of fundamental significance to inorganic chemistry and the environmental sciences.

Environmental scientists and personnel in regulatory agencies have traditionally relied on a limited data base obtained from organic chemistry and geochemistry to estimate the scope, reactivity, bioavailability, and control strategies for both essential and toxic metals and metalloids. This workshop with its interdisciplinary emphasis on the role of inorganic chemisty in the environment emphasizes the importance of revitalizing and reassessing approaches to world-wide needs of industrial and developing countries for biotechnological controls and health measures associated with inorganic and organometallic compounds.

The proceedings of the San Miniato Workshop consist of the Workshop Summary and thirty five papers. The Workshop Summary is based on the presentations and discussions at San Miniato. After the plenary sessions and general discussions, at which the participants presented their insights and concerns, six groups were formed to probe in detail important topics in environmental inorganic chemistry. The topics of these group discussions were

- the role of inorganic processes in the environment,
- species, functions, and toxicities of metals,
- environmental biochemistry and toxicology,
- radionuclides in the environment,
- seawater, and
- analytical aspects of environmental inorganic chemistry.

The reports and recommendations that emerged from these groups were organized and edited. The edited Workshop Summary was reviewed by all workshop participants. Corrections and changes recommended during this review were incorporated into the final version. The Workshop Summary consists of six sections: coordination compounds, organometallic and organometalloidal compounds, radionuclides, inorganic compounds as therapeutic agents, environmental biochemistry of inorganic and organometallic compounds, and analytical aspects of environmental inorganic chemistry.

Each section sketches current knowledge, highlights important problems, recommends areas of research, and provides a bibliography. Roman numerals in brackets refer to pertinent papers collected in the second part of the proceedings.

The papers delivered at the workshop provide information about the general state of development of environmental inorganic chemistry and report recent, significant advances in this area. All papers were reviewed by the participants' peers and thoroughly edited. Although the workshop was held from June 5 - June 10, 1983, the articles were updated and the latest references added during the review and editing process. Each paper contains a liberal number of references (including 1984 references and references to papers in press) that may serve as a convenient entry to the literature on environmental inorganic chemistry.

This workshop on environmental inorganic chemistry was a beginning. Additional international workshops with participants from disciplines not represented in San Miniato (organic chemistry, industry, agriculture, medicine, atmospheric sciences, regulatory agencies) should be organized and held annually. The proceedings of these workshops will provide guidelines for the proper development of environmental inorganic chemistry, serve as a source of information for funding agencies, regulatory agencies and political bodies, and facilitate the entry into this field by interested scientists.

A. E. Martell
Chairman, U.S. Committee

Ugo Croatto
Co-Chairman
Italian Committee

P. A. Vigato
Co-Chairman
Italian Committee

Kurt J. Irgolic
Editor

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Kurt J. Irgolic

A. E. Martell

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ENVIRONMENTAL INORGANIC CHEMISTRY
WORKSHOP SUMMARY

K. J. Irgolic*, A. E. Martell* and Workshop Participants

*Department of Chemistry, Texas A&M University
College Station, Texas 77843 USA

Environmental Inorganic Chemistry addresses the beneficial and inimical interactions of inorganic, organometallic, and organometalloidal compounds with living organisms. To properly describe these interactions and identify their effects, detailed knowledge about the interacting entities and their transformations on a molecular basis is indispensable.

The space accessible to life is only a very small fraction of the total volume of earth and her atmosphere. Most of the planet consists of inorganic substances that supply the raw materials for the biotic domain. Biota need certain essential elements to carry out their life functions such as growth, maintenance, and reproduction, but would probably function better in the absence of the other, nonessential elements. Figure 1 identifies the essential

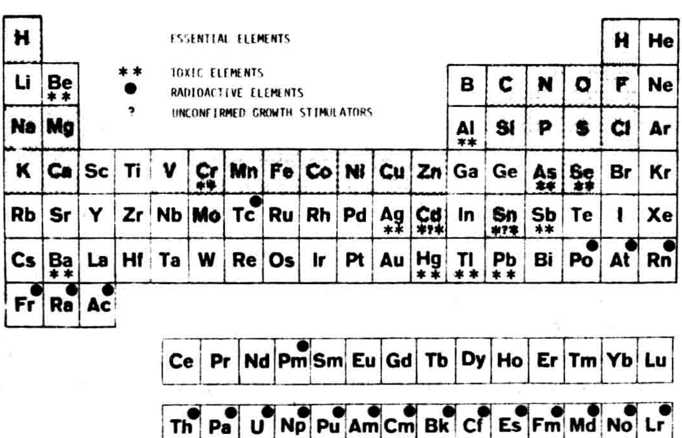

Figure 1. *Radioactive elements, and essential and toxic elements in the environment.*

elements and the toxic elements. Essentiality and toxicity are not exclusive properties of an element or its compounds. Which of these two properties manifests itself is determined both by the concentration of the element [XXIX] and its specific molecular form [III, IX].

Elements are cycled in nature (Fig. 2). Most of the

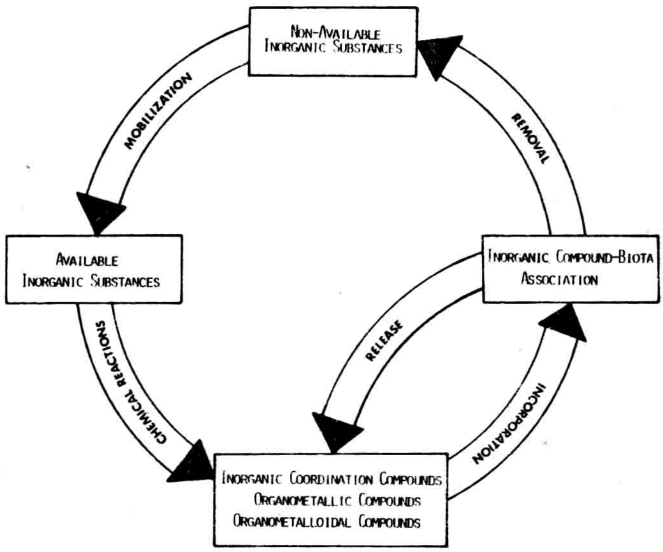

Figure 2. *Schematic representation of the cycling of inorganic, organometallic and organometalloidal compounds in the environment.*

elements are locked up in the form of insoluble inorganic compounds in rocks and sediments. These nonavailable inorganic substances must be mobilized and made soluble before biota can use them. This mobilization is effected by weathering processes involving abiotic chemical reactions and biologically mediated reactions. Metal ions can be released from sediments, for instance, as a consequence of the degradation of organic material and of redox changes [V, VII]. Among the biologically mediated reactions are those initiated by metal-tolerant bacteria and by man [IX, X]. Human activities release many substances into the environment in chemical forms capable of interacting with biota. After mobilization, which generally transforms insoluble substances to soluble substances, the primary products are changed by chemical reactions to inorganic coordination compounds, organometallic compounds and organometalloidal compounds. Which types of compounds are formed is determined by the nature of the metal and by the reactants present in the environmental compartment considered. These "inorganic compounds" - a term which shall refer to organometallic, organometalloidal and purely inorganic compounds - may now interact with biota. Such interactions - inimical or beneficial - may proceed on the outer surfaces of cells or may require transport of compounds through membranes into cells [XXIX]. The biochemical apparatus operating on these "inorganic compounds" may produce new chemical species, which can be released through excretion into the environment and made available to other biota. Alternately, the "inorganic compounds" associated with cellular materials may be removed from circulation upon the death of the organism, for instance, by deposition in sediments. There, these compounds may join the pool of nonavailable substances awaiting mobilization.

Such a brief, general summary of the cycling of "inorganic compounds" cannot cover the many important details of the various steps within the cycles. However, the complexities of the systems, which are the domain of environmental inorganic chemistry, become apparent upon inspection of the major components of such systems.

- Eighty-six naturally occurring elements - among them approximately 20 essential trace elements and ten toxic elements - provide the building blocks for a large variety of compounds. Most of the elements are classified as metals. These metallic elements form, upon mobilization, simple ionic compounds and more complex coordination compounds [III]. A few of the metallic elements (Co, Pd, Pt, Au, Hg, Ge, Sn, Pb, Sb, Bi, Po) and all the metalloids form element-carbon bonds, which are sufficiently stable toward hydrolysis to survive in largely aqueous media [IX-XI].

- Man-made radioactive elements (isotopes of naturally existing elements and synthetic elements) add compounds, which - in addition to their potential chemical toxicity - emit damaging radiation [XIV-XVII].

- Aqueous solutions of various compositions provide media in which chemical and biochemical reactions proceed under the influence and control of other dissolved substances [II-IV, VII-XI].

- Solid matter - suspended in water or deposited in sediments - offers adsorption sites for dissolved substances and provides catalytically active surfaces to influence the rates of reactions [VII, XIX]. Solid matter may also serve as a buffer system for their constituent ions in water [VIII].

- Biota with their variability in size, function, and biochemistry assure, that a multitude of interactions with "inorganic compounds" occur.

Environmental processes are a complex mixture of biological and abiotic reactions. Environmental inorganic chemistry is far from a detailed understanding of these interdependent and perhaps synergistic interactions. To improve our understanding of environmental processes and assist us in predicting their directions and effects, appropriate experimental systems serving as models for environmental compartments must be studied in the laboratory under well-controlled conditions. The results of such studies will contribute to the data base, which must be available to successfully interpret observations made on "real" environmental samples.

Traditionally, studies of the transformations and fate of chemicals in the environment dealt almost exclusively with organic compounds. The true role of metals and metalloids in biogeochemical cycles has only recently begun to receive well-deserved attention of inorganic chemists. Not unexpectedly, many compounds of metals and metalloids have been found in the environment. It is reasonable to assume that many more new compounds will be identified and reaction pathways unique to environmental processes uncovered. In this manner the new field of "ENVIRONMENTAL INORGANIC CHEMISTRY" is created.

COORDINATION COMPOUNDS

Eighty-two percent of the 108 known elements are metals. The problem of determining the nature of the coordination compounds formed by metal ions in the environment is enormous, even when only the thirty most important metallic elements are considered. These metal ions compete for a large number of ligands [III].

Approximately 100,000 different organic chemicals are produced and used throughout the world. Production and use are concentrated in the industrialized countries. These chemicals and an even larger number of byproducts of their manufacture find their way into the environment. Whereas only a fraction of these organic chemicals have functional groups, which allow them to act as ligands toward metal ions, most of these compounds may be modified in the environment by biological, chemical, or photochemical processes such as hydrolysis and oxidation, and converted to metal-binding agents. The number of organic substances and potential ligands increases annually by approximately two percent through development of new products.

The thirty essential and toxic elements might join with the available ligands to produce several million coordination compounds. A metal ion may form several complexes in solution and on surfaces with the same ligand and a much larger number of mixed-ligand complexes with several different ligands. Thus, the existence of five to ten million metal complexes in the environment is a possibility although only a small fraction of the possible complexes are expected to form. Their formation is governed by their thermodynamic stabilities and kinetic limitations under prevailing environmental conditions [III, IV, XIII].

The Problem of Species Distribution

It is important to know which complexes are actually present in the environment, because the toxicity of a metal is highly dependent on the nature of the ligand with which it is combined. Toxicity data are available for only a few complexes. The experimental determination of the nature of all potentially existing complexes and of their toxicities is physically and financially impossible. The determination of reliable toxicity data for a new compound costs approximately $100,000.

The problem of speciation plaguing environmentalists and inorganic chemists alike is largely unresolved for "inorganic compounds" in natural systems. Although progress has been made during the past few years in identifying "inorganic compounds" in environmental samples and laboratory systems mimicking environmental conditions, much more, well-targeted activity is urgently needed to identify "inorganic compounds" in the environment, determine their concentrations, and study model systems under well-defined