The Handbook of Environmental Chemistry

Volume 1 Part B

The Natural Environment and the Biogeochemical Cycles

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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

Volume 2, Part B: **Reactions and Processes**

Volume 3, Part B: **Anthropogenic Compounds**

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Basic Concepts of Ecology

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Ecology: Some Definitions

The Science of Ecology

The world in which we live consists of living organisms and non-living structures. Often, relationships between organisms or between organisms and non-living structures are clearly visible. The science of ecology in its pure form studies the relationships of organisms with their environment. "Organisms" means all living entities; this definition excludes relationships between non-living entities as a possible object of study for ecology. The term "environment" is meant in the sense of "the surrounding world," i.e., all entities, living or not, which surround a living entity. Thus for a grazing rabbit the environment includes for example other rabbits, grass, soil and weather.

Ecology is a study of relationships. These can be very complex or hardly recognizable. Therefore often studies are done on the relationship of one kind or organism, a species, with its environment. This type of ecology is called autecology. Even then reality mostly appears to be incredibly complex, as parts of the organism (organs or even cells) react differently to environmental influences. Hence ecophysiology has gained more and more importance, particularly in the last few decades.

The study of the relationships between groups of organisms and between so-called "communities" and the non-living (abiotic) environment is called synecology. On this level of complexity autecological issues are often neglected as these would render any understanding at the community level almost impossible.

Another division within the science of ecology can be made by discerning structural and functional aspects. In studying the structural relationships (e.g. the occurrence of various plant and animal species in a particular non-living environment), description of pattern and process is prevalent. In studying the functional aspects (e.g. the flow of energy from the sun through plants, herbivores and carnivores), measuring of flows and input-output relations is relevant. Often structural ecology is rather descriptive, while functional ecology tends to be experimental.

Man is an organism. As such, his relationships with the environment are objects of study to the science of ecology. However, because of the importance of cultural aspects in the existence of *Homo sapiens*, human ecology is often seen as a separate discipline. This does not imply that some basic concepts (as dealt with in later Sections) would not be applicable to our species.

In human ecology, the division into biotic ecology and social ecology is often used. Biotic ecology studies the reaction of human beings on environmental influences, particularly toxic substances, noise, radiation etc. Social ecology is concerned with the pattern and process of human communities in relation to their environments, e.g. the use of communication systems like roads or the residential circumstances in a town as a result of structural processes. Basically human ecology can be viewed as a kind of autecology, be it that cultural aspects play a relatively important role. As human ecology makes use of theories and concepts from the social sciences while ecology requires contributions from physics, chemistry and earth sciences, the basic concepts of ecology can be regarded as the link between the natural and the social sciences [38].

Organization Levels of Ecological Systems

A system can be defined as an assembly of objects displaying some form of regular interaction or interdependence. Systems approach basically is a way of thinking about reality in which a collection of objects (or a series of events) in considered to be a single entity. In ecology the systems approach is applicable because organisms always interact with other organisms and with the non-living environment.

Ecological systems are always *open*, i.e. there is an exchange (or input-output relation) of energy and matter with neighboring systems. The delimitation of ecological systems is thus often arbitrary: one could easily speak of sub- or supersystems, depending on the degree of complexity and the number of entities included.

Collier et al. distinguished four levels of organization in ecological systems, depending on the degree of complexity [5].

1. The Level of the Organism. On this level, ecological studies focus mainly at the relationship of the individual with its environment in the morphological, physiological or behavioral sense.

2. The Level of Populations. A population is a group of organisms of *one* species, living within a certain area. Such groups show group characteristics (e.g. density, distribution, age structure, rates of natality and mortality) which cannot be explained at the organism level. Next, populations interact with other populations and with the abiotic environment.

3. The Level of (Biotic) Communities. A community is the assembly of different populations within a certain area. This combination of populations can be unique in space and time (or in pattern and process). Interactions between populations are very important for the composition of the community.

4. The Level of Ecosystems. An ecosystem is the system in which communities (including various populations) interact with the abiotic environment. At this level systems approach is most frequently used.

For each level of organization of ecological systems environmental abiotic factors are crucial. To a large extent they determine the possibilities for any life-form to survive. Many influences like solar radiation, wind and rainfall exert their influence over several ecosystems. This stresses the open character of these systems, which is also revealed by migration of organisms. Sometimes one abiotic factor is dominant (e.g. solar radiation in the arctic regions), but often a specific local combination of abiotic factors, particularly soil and nutrients, allows for the existence of particular organisms, populations or communities. Therefore knowledge of abiotic factors is extremely important for the understanding of structure and function of ecological systems.

The definition of an ecosystem allows for considering the earth one ecosystem. This would, however, lead to a purely theoretical approach of properties of such a system. Therefore it is convenient to limit the extent of ecosystems to more easily recognizable units like a forest, a lake, or an estuary. Assemblies of such ecosystems can be called ecological *formations* or major ecosystems. An easy division is the following:

1. Terrestrial ecological formations or *biomes*. These formations are largely defined according to climatic conditions. Examples are deserts, grasslands and forests, all existing in various forms on the continents.
2. Oceans and seas, both aquatic saline environments in which physical factors dominate (waves, tides, currents, temperature etc.).
3. Estuaries and seashores which are not only transition zones between land and water but also combine nutrient and energy inputs from both sides, thus displaying a rich variety of abiotic and biotic factors.
4. Freshwater formations, formed by inland water bodies. Examples are streams, rivers and lakes, again showing resemblances and differences from continent to continent.

These ecological formations do not represent a fifth level of organization. In some cases physical conditions can be the same for a spatial assembly of ecosystems but their relationships mostly take a general input-output form. Many formations are only recognized because structure and function of the ecosystems enclosed is roughly comparable (e.g. boreal forests).

The following four Sections are devoted to the description of properties of the organismal, the population, the community and the ecosystem level of organization. Section 6 deals with changes in ecological systems in time and space, while Sect. 7 is devoted to a brief description of the major ecosystems of the world. Finally, Sect. 8 deals with the influence of mankind on ecological systems.

This introduction into ecology only deals very condensedly with some basic concepts. It must be stressed that any reader interested in a particular subject should obtain more detailed information from one of the existing textbooks of ecology, e.g. E P. Odum (1971) [37]; Krebs (1972) [22]; Boughey (1973) [2]; Colinvaux (1973) [4], Collier et al. (1973) [5]; McNaughton and Wolf (1973) [29]; Ricklefs (1973) [45]; Poole (1974) [43]; Whittaker (1975) [58]; Odum (1976) [38]; Ehrlich et al. (1977) [11] and Ricklefs (1978) [46].

Species and Individuals

The Abiotic Environment

Energy

Energy is a main source of life, together with nutrients. The most important energy source for life on earth is, of course, the sun, but other energy inputs are cosmic radiation, the moon (tides) and forces from the earth itself such as gravity and heat. Secondary sources of energy which are available to ecosystems are currents, waves, streams and wind. Ecological systems tend to use high-grade energy and to dissipate low-grade energy (heat), thus keeping the entropy within the system low and also operating under the laws of thermodynamics.

Green plants are able to combine CO_2 and H_2O into carbohydrates by absorbing light in pigment cells (containing *chlorophyll*):

$$\underset{\text{(from air)}}{6\,CO_2} + 12\,H_2O \xrightarrow[\text{chlorophyll etc.}]{2.8\ \text{MJ}} C_6H_{12}O_6 + \underset{\text{(to air)}}{6\,O_2} + 6\,H_2O\,.$$

These carbohydrates, in one or another form, constitute the living tissue or *biomass* of plants. However, not all energy fixed this way is retained. Plants also need energy for maintenance activities. This energy consumption is called respiration and can be generally represented as follows:

$$C_6H_{12}O_6 + \underset{\text{(from air)}}{6\,O_2} \xrightarrow[\text{enzymes}]{\text{metabolic}} \underset{\text{(to air)}}{6\,CO_2} + 6\,H_2O + \text{energy}\,.$$

Thus accumulation of biomass in green plants (or net primary production) = energy fixed in photosynthesis − energy lost by respiration.

In bacterial photosynthesis, oxygen is not released. The reductant may be an inorganic compound (like H_2S) or an organic compound. This type of photosynthesis particularly occurs in conditions unfavorable for green plants like tidal mudflats and H_2S-rich stagnant lakes. Most green plants have a CO_2 fixation via a C_3 pentose phosphate cycle. However, in some plants (notably grasses) a C_4 dicarboxylic acid cycle operates. C_3 plants have their optimum in photosynthesis at moderate temperatures and light intensities, while C_4 plants are favored by high temperatures and light intensities. C_4 plants also need a smaller amount of water to produce the same biomass. Accordingly they dominate communities (deserts, grasslands) in the subtropics.

Carbon dioxide and oxygen also limit photosynthetic processes. CO_2 occurs in low concentrations (about 0.03 vol.-%) in the atmosphere. Increase of CO_2 concentration causes increase in photosynthesis. High O_2 concentrations inhibit the fixation of CO_2 because most plants continue respiration in the light. This does not hold for C_4 plants.

Animals cannot fix solar energy into living tissue. They are depending on already existing biomass and are therefore called *heterotrophs*, contrary to green plants which are called *autotrophs*. The biomass ingested consists of other organisms or particulate organic matter; this is converted to available nutrients by enzymes. Animals too, lose energy by respiration for maintenance activities. Endo-