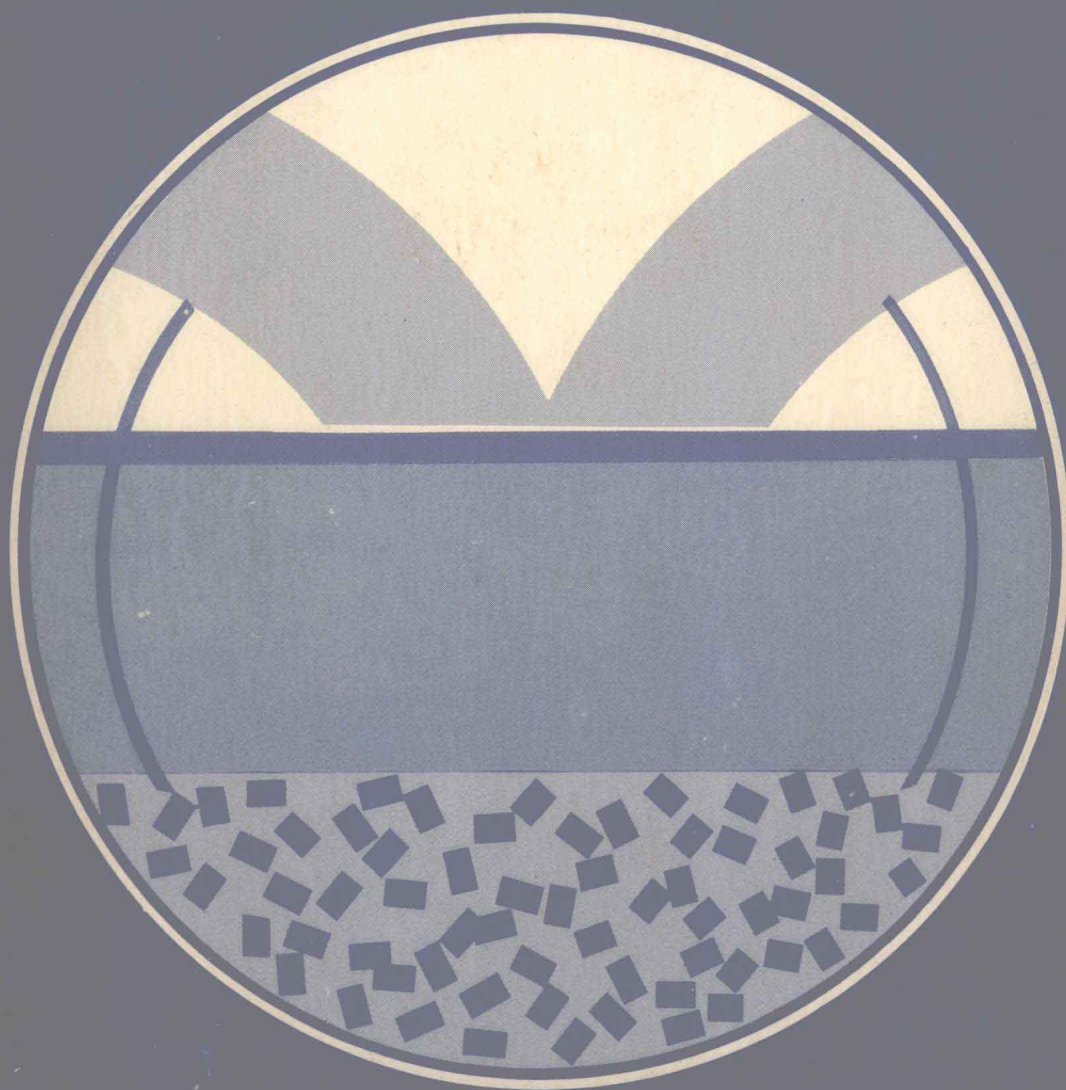


chemical cycles and the global environment

assessing human influences

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ACKNOWLEDGEMENTS

We are grateful to numerous students and colleagues for criticisms and suggestions, many of which have been incorporated in this text.

We thank Jean Kartchner, Leslie Yukuno, Bruce Mitchell and Cheril Cheverton for the illustrations. The devil in Fig. 43 is courtesy of John T. Stark.

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ISBN 0-913232-29-7

PREFACE

Numerous natural substances are important to the chemistry and biology of the earth--to the earth's "metabolism." There is a natural circulation of these materials through the earth's atmosphere, to the land and thence through soils into streams, and from streams and rivers to the oceans. In the oceans some of the material sinks and becomes part of the sediments of the ocean floor, and some of it is returned to the atmosphere.

This circulation of materials is known as the exogenic cycle. It has continued for millions of years at a roughly constant pace. Over the centuries, mankind's population and influences on the environment, and hence on the exogenic cycle, have been growing.

Everyone is aware of the kinds of local environmental problems caused by many human activities: pollution from automobiles, factories, agriculture. But few are acquainted with the "everyday geochemistry" that provides a way for us to assess the ways in which natural environmental processes and chemical cycles respond to the polluting effects that are a perhaps inevitable consequence of growing human populations.

This book grew out of an undergraduate course that we developed to provide perspective on the innumerable environmental issues that are raised, chiefly by local problems. Our idea was to examine the natural circulation of materials and then to try to assess man's impact on these cycles. We wanted to see whether or not particular pollutants are having irreversible or reversible effects on the environment. A major objective was to discover

those activities that may have irreversible effects and those whose effects, if controlled, may be transitory.

The book reflects the results of our efforts to fulfill these objectives and to provide an introduction to the chemistry of the natural environment. It has been developed and modified over a period of four years as a result of experiences in our own courses at Northwestern University and the University of Hawaii. It has also been influenced by helpful suggestions from teachers at other universities who have used earlier versions of our syllabus.

The present version is organized as follows: After several chapters on the general circulation of materials at the earth's surface and the characteristics of various environments, global cycles of particular substances that are important in the chemistry and biology of the earth are presented in detail. An attempt is made to assess the degree of interference with each cycle resulting from human activities and to determine whether the effects of human additions are short or long-term, trivial or important.

In most examples cited, the earth's surface environment is subdivided into four great reservoirs: the land surface, the atmosphere, the oceans, and the sedimentary rocks. The sizes of these reservoirs and the annual rates of transfer of selected substances among them are estimated. We believe that local and regional pollution problems must be fitted into the global framework. Many polluting substances are high local concentrations, resulting from human activities, of elements or compounds that have been migrating through the major earth reservoirs for hundreds of millions of years.

These substances have natural sources and sinks, and there are feed-back systems that regulate the earth's natural metabolism and that must be considered in investigations of local situations.

We believe this book can be used as a text for environmental courses in almost any science or engineering department. It is also designed to be sufficiently self-contained to be assigned as collateral reading or for independent study by the layman interested in human influences on the world ecosystem. The material has been taught successfully to students ranging from college freshmen with essentially no science or mathematics background to juniors and seniors majoring in chemistry, biology, engineering, earth sciences, physics, or oceanography. The first eleven chapters are appropriate for anyone who has had high school chemistry and algebra. The final chapter may pose some difficulties for students with these minimum requirements but not for students who have an interest in and aptitude for any of the sciences. We regard Chapter 12 as optional. The book is complete without it, but it has been successful in showing students the directions of present-day research and in giving them a feeling for the validity of the data we have used and the kinds of information that are urgently needed to solve many of the problems posed.

Most of the chapters are followed by study questions. Some of the questions contain information not included in the text. Answers to questions are given at the end of the book, rather than with the questions, because students found it tempting to read the answers before thinking about the questions if the two were juxtaposed.

The answers often are our interpretations; we have commonly found student disagreement with them, and they have therefore been useful in stimulating discussion.

In Appendix I, information is presented on the compositions of rocks and minerals; Appendix II contains some convenient conversion factors.

The selected bibliography provides suggested additional reading and includes some of our sources of data. It seemed impractical for student use to document all sources of data used in development of each cycle. The data on which the various cycles are based are being modified and added to daily.

One reason for the book's present format is to permit frequent updating. We are grateful to the publisher for his cooperation in making an experimental edition available. We invite readers to send us their constructive criticisms which might be incorporated into future editions.

Evanston, Illinois
June, 1975

Robert M. Garrels
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Chapter 1

GLOBAL FRAMEWORK

Analogy commonly is made between the earth's surface system and a giant chemical-engineering factory; material circulation in the natural system is driven by energy derived from the sun and by decay of radioactive elements in the earth's interior. In another sense, the earth has a natural metabolism; materials have circulated about the earth's surface for millions of years. Weathering and erosion of rocks moves materials in and out of the atmosphere, to the oceans via streams, from the atmosphere to the biota and back again, and to the continents by uplift. Each element follows a path through the natural system determined by its physical-chemical properties; each element has its natural chemical cycle. Man's activities have contributed materials to these cycles at an increasing rate; some of these materials are the same chemical species that have circulated for millions of years; others are synthetic compounds, foreign to the natural environment.

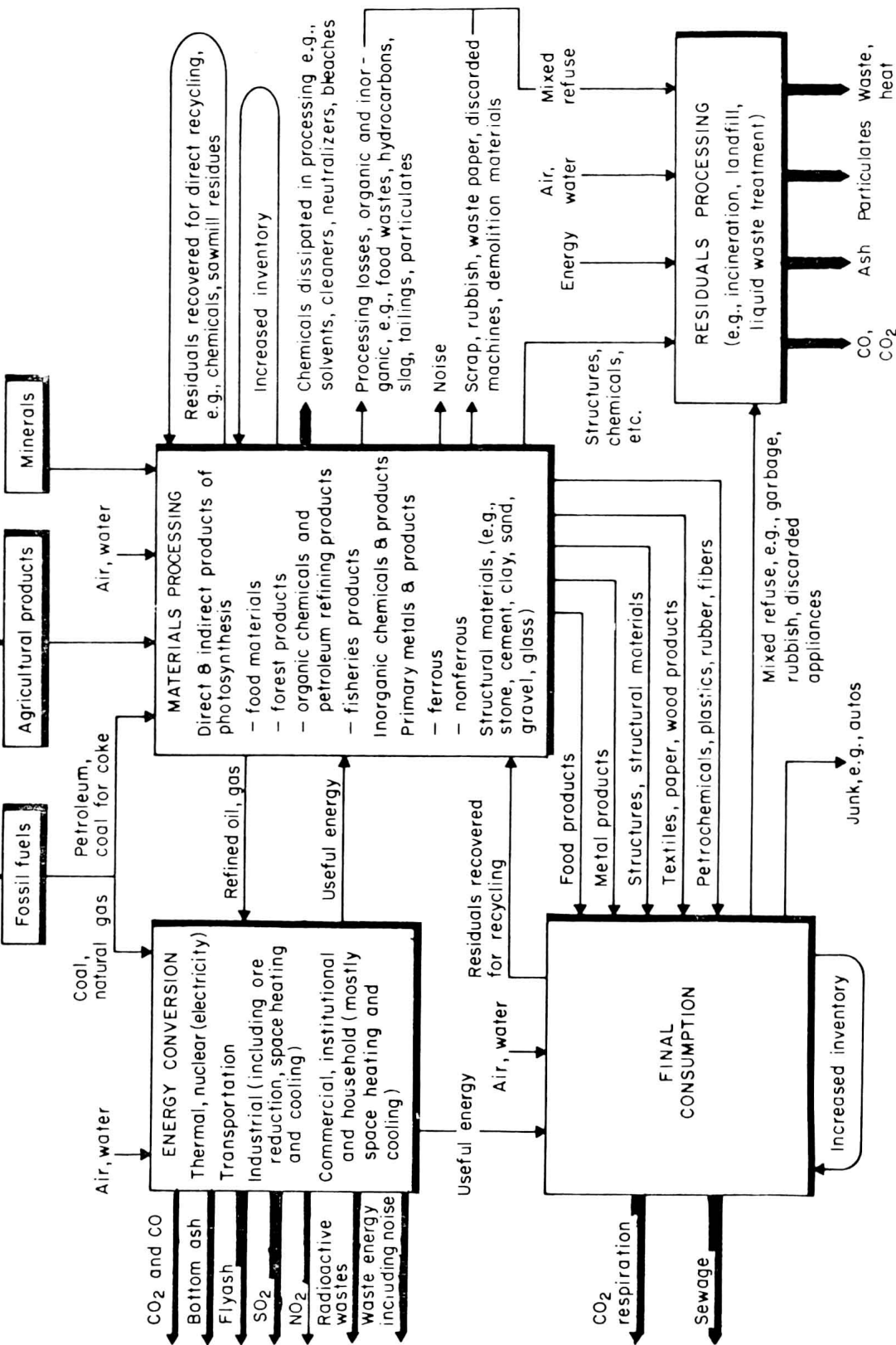
As background for discussion of man's additions to and the consequent effects on natural chemical cycles in subsequent chapters, we consider briefly some of the reasons for growing concern with environmental degradation and interference with these cycles.

Pollution arises from fluxes of materials such as metals, fuels and food-stuffs through the environment. Figure 1 is a schematic diagram portraying material pathways and factors involved in the flow of materials. Although constructed for a specific environment (urban), the diagram illustrates the complex interrelationships between factors involved in the flow of materials and environmental quality. A complete diagram would include flows of materials through the agricultural and rural environments and the interrelations of these with the urban environment.

Consumption of most basic materials such as metals, plastics, quarry stone, and so forth, in the U.S. has been rising steadily; for example, consumption of iron rose 30% between 1950 and 1971. Figure 2 illustrates consumption and production trends for some raw materials. Increased consumption is accompanied

FIGURE 1

Factors Involved in the Flow of Materials.



Source: Robert U. Ayres and Allen V. Kneese, "Pollution and Environmental Quality," *Quality of the Urban Environment*, Harvey S. Perloff, Ed., Resources for the Future, Inc., Washington, D.C., p. 37.

by increased use of fossil fuels and minerals used in energy conversion and materials processing. The residual materials (wastes) of consumption and materials processing include those discarded directly to the physical environment (witness the mountains of 'junked' automobiles), and others that may be incinerated, used in landfill projects, or treated in waste treatment plants. Whatever the case, energy conversion, materials and residuals processing, and consumption result in wastes being added to the physical environment as particulate and gaseous emissions, radioactive wastes and chemicals, sewage, and a variety of other solids and liquids. These wastes may eventually reach the ocean via the atmosphere or streams, or in some instances (e.g., petroleum) may be added directly to the oceans. In Figure 1 these wastes, commonly termed pollutants, are represented by the heavy, black arrows. The production and flow of agricultural products also produce wastes that enter the physical environment; e.g., application of DDT to crops results in escape of DDT to the atmosphere and its dispersion throughout the environment; use of nitrogen- and phosphorus-containing fertilizers results in release of these elements to stream systems. It is these types of wastes and their effect on the global environment with which we will be most concerned.

In general, a nation's wastes are proportional to its level of economic activity, or as an approximation of this activity, gross national product (GNP, expressed in the U.S. as total value in dollars of products produced). Economic growth rates of several nations are shown in Figure 3A. Notice that economic growth of the more industrialized nations has progressed, at least until recently, at a faster rate than for less industrialized nations. In other words, the gap between rich and poor has been widening.

A rough correlation exists between per capita GNP (dollars per capita) and consumption of energy, or BTU or kilocalories per year per capita (Fig. 3B). High energy consumption has been a prerequisite for high output of goods and services. Between 1962 and 1968, U.S. GNP/capita and energy consumption both increased 50%, accompanied by a commensurate increase in emissions. In contrast, population growth was less than 2% over this same period, and recently appears to have leveled out.

The rise in GNP/capita and energy consumption is well illustrated by the situation arising from the burning of fossil fuels. Carbon dioxide, as well as other materials, is released to the atmosphere when coal, oil and gas are burned.