Marine Environmental Quality

Suggested Research Programs for Understanding Man's Effect on the Oceans

NATIONAL ACADEMY OF SCIENCES

GC
1085
.N38
1971

AUTHENTICATED
U.S. GOVERNMENT
INFORMATION
GPO

The workshop leading to the preparation and distribution of this report was sponsored by the National Science Foundation Office of the International Decade of Ocean Exploration.

U.S. DEPARTMENT OF COMMERCE NOAA
COASTAL SERVICES CENTER
2234 SOUTH HOBSON AVENUE
CHARLESTON, SC 29405-2413

Marine Environmental Quality

Suggested Research Programs for Understanding Man's Effect on the Oceans

The report of a special study
held under the auspices of the
Ocean Science Committee of the
NAS-NRC Ocean Affairs Board
August 9-13, 1971

Property of CSC Library

GC 1085 .N38 1971
34248603
MAR 10 1997

NATIONAL ACADEMY OF SCIENCES
Washington, D.C.

SECOND PRINTING

NOTICE: The study reported herein was undertaken under the aegis of the National Research Council with the express approval of the Governing Board of the NRC. Such approval indicated that the Board considered that the problem is of national significance; that elucidation of the problem required scientific or technical competence and that the resources of the NRC were particularly suitable to the conduct of the project. The institutional responsibilities of the NRC were then discharged in the following manner:

The members of the study committee were selected for their individual scholarly competence and judgment with due consideration for the balance and breadth of disciplines. Responsibility for all aspects of this report rests with the study committee, to whom we express our sincere appreciation.

Although the reports of our study committees are not submitted for approval to the Academy membership nor to the Council, each report is reviewed by a second group of scientists according to procedures established and monitored by the Academy's Report Review Committee. Such reviews are intended to determine, *inter alia*, whether the major questions and relevant points of view have been addressed and whether the reported findings, conclusions, and recommendations arose from the available data and information. Distribution of the report is permitted only after satisfactory completion of this review process.

NRC Library

OCEAN SCIENCE COMMITTEE

JOHN A. KNAUSS, Graduate School of Oceanography, University of Rhode Island
WALLACE S. BROECKER, Lamont-Doherty Geological Observatory of Columbia University
JOHN D. COSTLOW, JR., Duke University Marine Laboratory
RICHARD C. DUGDALE, Department of Oceanography, University of Washington
KENNETH O. EMERY, Woods Hole Oceanographic Institution
EDWARD D. GOLDBERG, Scripps Institution of Oceanography, University of California, San Diego
JOHN W. KANWISHER, Woods Hole Oceanographic Institution
HENRY W. MENARD, Scripps Institution of Oceanography, University of California, San Diego
OWEN M. PHILLIPS, Department of Earth and Planetary Sciences, The Johns Hopkins University
MAURICE RATTRAY, JR., Department of Oceanography, University of Washington
HENRY M. STOMMEL, Department of Meteorology, Massachusetts Institute of Technology
MANIK TALWANI, Lamont-Doherty Geological Observatory of Columbia University

LIST OF PARTICIPANTS

RICHARD T. BARBER, Duke University Marine Laboratory, Beaufort, North Carolina

IZADORE BARRETT, Fishery-Oceanography Center, National Marine Fisheries Service, La Jolla, California

DONALD BAUMGARTNER, Environmental Protection Agency, Corvallis, Oregon

JOHN BLAXTER, Marine Research Laboratory, Oban, Scotland

JOHN BUNT, Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, Florida

ROY CARPENTER, Chemistry Department, University of Washington, Seattle, Washington

JAMES CHOW, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California

NORMAN CUTSHALL, Oceanography Department, Oregon State University, Corvallis, Oregon

REZNEAT DARNELL, Department of Oceanography, Texas A & M University, College Station, Texas

ROBERT DUCE, Graduate School of Oceanography, University of Rhode Island, Kingston, Rhode Island

WILLIAM O. FORSTER, Puerto Rican Nuclear Center, Mayaguez, Puerto Rico

WILLIAM GARRETT, Naval Research Laboratory, Washington, D. C.

EDWARD D. GOLDBERG, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California

LIST OF PARTICIPANTS

GEORGE GRICE, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

DONALD HANSEN, Atlantic Oceanographic Laboratory, National Oceanic and Atmospheric Administration, Miami, Florida

DONALD W. HOOD, Institute of Marine Science, University of Alaska, College, Alaska

HOLGER W. JANNASCH, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

FEENAN D. JENNINGS, National Science Foundation, Washington, D. C.

ARNE B. JERNELOV, Swedish Institute of Water and Air Pollution Research, Stockholm, Sweden

GALEN JONES, Estuarine Laboratory, University of New Hampshire, Durham, New Hampshire

BOSTWICK KETCHUM, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

JOHN A. KNAUSS, Graduate School of Oceanography, University of Rhode Island, Kingston, Rhode Island

VICTOR LINNENBOM, Ocean Sciences Division, Naval Research Laboratory, Washington, D. C.

JOHN A. MCGOWAN, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California

DAVID W. MENZEL, Skidaway Institute of Oceanography, Savannah, Georgia

THEODORE METCALF, Department of Microbiology, University of New Hampshire, Durham, New Hampshire

JOHN NOAKES, Geo-Chronology Laboratory, University of Georgia, Athens, Georgia

PATRICK L. PARKER, Marine Sciences Institute, University of Texas, Port Aransas, Texas

TIMOTHY R. PARSONS, Institute of Oceanography, University of British Columbia, Vancouver, Canada

RICHARD PERKINS, Radiological Chemistry Section, Battelle Northwest Laboratory, Richland, Washington

DAVID PETERSON, United States Geological Survey, Menlo Park, California

LAWRENCE POMEROY, Department of Zoology, University of Georgia, Athens, Georgia

ALAN PRESTON, Ministry of Agriculture, Fisheries, and Food, Fisheries Radiobiological Laboratory, Lowestoft, Great Britain

DONALD W. PRITCHARD, Chesapeake Bay Institute, Johns Hopkins University, Baltimore, Maryland

LUIGI PROVASOLI, Haskins Laboratory, New Haven, Connecticut

JAMES G. QUINN, Graduate School of Oceanography, University of Rhode Island, Kingston, Rhode Island

JOSEPH L. REID, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California

JOHN H. RYTHER, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

WILLIAM SACKETT, Department of Oceanography, Texas A & M University, College Station, Texas

MARSTON C. SARGENT, California Cooperative Oceanic Fisheries Investigations, La Jolla, California

KARL SZEKIELDA, College of Marine Science, University of Delaware, Newark, Delaware

KARL TUREKIAN, Department of Geology, Yale University, New Haven, Connecticut

JUN UI, Urban Engineering, University of Tokyo, Tokyo, Japan

RICHARD C. VETTER, Ocean Affairs Board, National Academy of Sciences, Washington, D. C.

MICHAEL WALDICHUK, Pacific Environment Institute, Fisheries Research Board of Canada, West Vancouver, Canada

JOHN W. WINCHESTER, Department of Oceanography, Florida State University, Tallahassee, Florida

HERBERT L. WINDOM, Skidaway Institute of Oceanography, Savannah, Georgia

PREFACE

In the spring of 1971, the International Decade of Ocean Exploration Office of the National Science Foundation requested that the Ocean Science Committee of the Ocean Affairs Board conduct a workshop to examine, in detail, the scientific problems related to its marine environmental quality program. Five major problem areas were selected: 1) the identification of major recognized and unrecognized pollutants, their sources and rates of input; 2) delineation of processes affecting the dispersal of these pollutants; 3) understanding the geochemical and biological transfer of critical elements or compounds in the ocean; 4) establishing the effects of pollutants on organisms including man; and 5) identification of the sites of final deposition of specific elements and compounds in the ocean environment.

An ad hoc steering committee, chaired by David W. Menzel (Skidaway Institute of Oceanography), was formed to organize a workshop to study these areas. Based on recommendations from many ocean scientists, approximately 50 scientists, selected to include specified areas of expertise rather than representation by geographical location, government agency, or private laboratory, were invited to participate. Task groups were formed to study each of the five problem areas, chaired respectively by Edward D. Goldberg (Scripps Institution of Oceanography), John W. Winchester (Florida State University), John S. Bunt (University of Miami),

Richard Barber (Duke University), and Donald W. Hood (University of Alaska). The workshop was held at the New England Center for Continuing Education, Durham, New Hampshire, August 9-13, 1971.

This report aims to highlight areas of investigation that the group believed were important for further study. There was no attempt to be either exhaustive or encyclopedic. In this field, in which the hard data are sparse, changes in emphasis can be expected as new information becomes available. A continuing examination of the scientific problems involved in understanding man's effect on the quality of the marine environment will be necessary in order to further plan and develop research programs. While this report is necessarily incomplete and fragmentary, we hope it will be of use to scientists and administrators both nationally and internationally who are concerned with problems of marine environmental quality.

The preparation of this report was carried out as a special study under the auspices of the Ocean Science Committee of the Ocean Affairs Board. The funds for the study were provided by the National Science Foundation.

We gratefully acknowledge the invaluable assistance with local arrangements given to us by Dr. Galen Jones (University of New Hampshire). We extend appreciation to the six University of New Hampshire graduate students (Edward R. Gonye, Jr., Richard Fralick, Kenneth Turgeon, Barry Hutchinson, Edward Washburn, and Judith E. McDowell) who assisted the participants in their work, to Deena Wallace of the National Science Foundation IDOE staff and Ruth Jeralds of the Jackson Estuarine Laboratory for their secretarial assistance, and especially to Susan H. Anderson, Administrative Assistant to the Ocean Affairs Board, for assuming the detailed conference management responsibilities and for the final editing and preparation of this report.

Richard C. Vetter

CONTENTS

1 INTRODUCTION 1

2 FLUXES OF MATERIALS TO THE MARINE ENVIRONMENT 5

Introduction, 5
Petroleum, 6
Nitrogen and phosphorus, 8
Pulp-mill effluents, 10
Heavy metals, 11
Synthetic organic chemicals, 16
Microbiological pollution of coastal waters, 21
Radioactivity, 24
Summary and general conclusions, 26
Specific recommendations, 27

3 DISPERSAL AND TRANSPORT OF POLLUTANTS IN THE MARINE ENVIRONMENT 29

Introduction, 29
Transport processes of pollutants, 30
Factors affecting transport, 36
General recommendations, 43
Specific recommendations, 45

4 BIOLOGICAL EXCHANGE PROCESSES IN RELATION TO MARINE ENVIRONMENTAL QUALITY 49

Introduction, 49
Pollutants, 50

Mechanisms, 52
Field studies, 54
Laboratory studies, 56
Development of models, 58
General recommendations, 58
Specific recommendations and summary, 59

5 THE EFFECTS ON MARINE ORGANISMS 63

Introduction, 63
Inadequacy of acute toxicity tests, 65
Selecting organisms and systems for study, 66
Importance of a conceptual framework, 67
Implementation of the framework, 69
General recommendations, 80

6 THE ULTIMATE FATE OF SUBSTANCES THAT RELATE TO THE QUALITY OF THE MARINE ENVIRONMENT 83

General introduction, 83
Pollutants, 85
Recommendations, 98

REFERENCES 101

MARINE
ENVIRONMENTAL
QUALITY

JOHN W. WINCHESTER

CHAPTER I

INTRODUCTION

The addition of chemical pollutants to the marine environment may be a serious threat to man and to the marine ecosystem with which he is involved. The following study, based on this premise, reviews the current status of our knowledge of ocean pollution, identifies areas requiring additional research, and establishes priorities for research efforts.

Marine pollution problems arise from what has happened or is now happening in the environment. These problems differ from those in the basic sciences of biology, chemistry, and physics, which involve universal properties of matter and for which a scientific method of verification of hypotheses through experimentation is well suited. Environmental problems involve phenomena that vary with time and that are the result of combinations of conditions that may never be exactly repeated. A scientific method of research under such conditions must be a combination of experimentation and observation that enables us to confirm hypotheses with sufficient certainty that we can make policy decisions relating to the control of our environment.

To design the most effective scientific method for research in marine pollution was the most important task confronting the study participants and one that will be frequently discussed together with more specific technical questions. It is to our advantage that we develop a satisfactory method for this research soon.

In recent years, we have become aware of the spread of lead, mercury, and other heavy metals and of chlorinated hydrocarbon insecticides and industrial chemicals into remote regions of the world ocean. Few scientists had foreseen that this could happen, and few are confident that they fully understand how it did happen. Many study participants agreed that high priority should be given now to research on the pathways for these specific pollutants and on their impact on man and the marine ecosystem. The results of this research may help us to control the leakage of these substances into the oceans and may enable us to predict more effectively the entry of additional equally serious pollutants before we are surprised by a disaster.

In order to solve marine pollution problems, which are truly complex, scientists from differing disciplines should study, simultaneously, the interacting components of the marine ecosystem. To overcome technical language or other communications barriers, scientists should compare results from different scientific groups by means of frequent study workshops. The primary scientific effort should be directed toward research on specific problems of marine pollution that leads us most directly to the knowledge required for making wise environmental-control decisions and that captures the imagination of the best scientists to conduct an inspired multi-disciplinary research program. Marine pollution is a global problem, and the effort to curb it requires the scientific resources of all countries.

The study participants, working in five task groups of six to ten members each, considered in depth the links in a chain from introduction of pollutants to final disposition of pollution in the oceans and the effects of pollution on life. The following questions were asked of task groups 1 through 5 respectively:

1) *What quantity of pollutants is now entering the oceans, and what are the points and modes of entry?*

2) *By what physical and chemical processes are these pollutants dispersed or transported from their entry points into the ocean?*

3) *How are pollutants taken up by marine organisms?*

4) *What are the effects of pollution on marine life and man?*

5) *What is the final disposition or resting place, if any, of pollutants in the ocean?*

Each task group attempted to examine its question in detail from a technical standpoint and to recommend research priorities. Some general recommendations that emerged during the plenary sessions included the following:

+ *Similar study workshops should be held regularly to review technical progress in the study of marine pollution and to update our priorities for research. Young as well as established scientists should be encouraged to participate.*

+ *Scientists from related disciplines should be encouraged to learn about and to work on problems of marine environmental pollution.*

+ *The sea surface and its overlying atmosphere should be given special attention as an entry point and accumulation zone for some important pollutants in the oceans.*

+ *The chemical and biological processes that take place in the continental coastal zones and estuaries should be thoroughly investigated for those pollutants carried to the oceans by flowing water.*

+ *Biochemical transformation and biological concentration of specific pollutants should be investigated in detail so that we may better predict their active transport through the marine environment and their toxic impact on man and the ecosystem. For example, research should be conducted on the microbiological conversion of mercury to methyl mercury and on the biological concentration of DDT in the food chain.*

+ *We should determine whether there is a final resting place of pollutants (e.g., on the*

sea floor, so that the oceans are self-cleaning) or whether the oceans or atmosphere and their biota are stable reservoirs for pollutants.

For each of these recommendations, it is important to understand that marine pollution can not be successfully studied if arbitrary limits are set on the subject (e.g., salt water only) or geography (e.g., only far from land). In the following report, the 50 scientists who participated in this study have tried to contribute comprehensive and constructive suggestions for the control of marine pollution.

EDWARD D. GOLDBERG
ROY CARPENTER
JAMES CHOW
ROBERT DUCE
JOHN NOAKES
ALAN PRESTON
JUN UI
DAVID PETERSON
KARL SZEKIELDA
THEODORE METCALF

CHAPTER II

FLUXES OF MATERIALS TO THE MARINE ENVIRONMENT

INTRODUCTION

The mobilization of matter from the continents to the marine environment by man is quantitatively rivaling the movements of materials by weathering processes. Man's impact alters the levels of constituents already present (e.g., lead or mercury) or introduces substances alien to the surroundings (e.g., DDT or artifically produced radioactivities such as cesium-137).

Matter is normally transported to the oceans by the rivers, winds, or glaciers. Society has created two additional paths: ships and waste outfalls.

The most evident changes brought about by man have occurred in the coastal and estuarine areas. From studies in such regions, more meaningful investigations can be mounted on the open ocean zone, where the influence of man can be less distinct and perhaps more subtle.

Knowledge of the fluxes of substances is necessary to evaluate effects on the organisms and on the character of the marine environment. Such knowledge is often especially difficult to obtain, and estimates made from tenuous data and assumptions must be used.

The site of injection, chemical form, and state are parameters of importance in ascertaining the subsequent fates of the substances in question.

Two other concerns, evident during our deliberations, were that the reliability of assay methods can be of crucial importance in interpreting or evaluating the existing data, and that exposure standards for public health considerations are one prerequisite to sensible surveillance operations.

PETROLEUM

The annual world production of petroleum is estimated at 1820 million tons. Of this amount, 1180 million tons/yr passes through the world's shipping lanes as 60 percent crude oil and 40 percent refined products (SCEP, 1970). The proximity of processing and storage facilities to the marine environment, offshore wells, and ship transportation have resulted in substantial inputs of petroleum products into the world ocean.

Natural and man-induced injections of petroleum into the marine environment have been estimated and are given in Table 1. Offshore oil-well production constitutes 17 percent of the total world production, with over 8,000 offshore wells in the Gulf of Mexico alone. This amount is expected to grow to 30 percent of the world production by 1980. Worldwide seepage from these offshore wells is estimated at near 0.1 million tons/yr. The episodic loss from the Santa Barbara blowout is estimated at .003 to .011 million tons. The loss of oil to the sea from ships because of poor operating procedure or accidents is about 1.2 million tons/yr. The Torrey Canyon incident alone released 0.1 million tons, and larger accidental injections can be expected as tankers continue to increase in size. The deliberate dumping at sea constitutes one of the larger sources of direct release, estimated at 0.5 million tons/yr. As port facilities and tankers become better equipped with oil-skimming equipment we can expect to make the effect of dumping minimal. Natural oil seepage from geologic formations has been estimated to be less than 0.1 million tons/yr. A total budget covering the four

modes of direct injection into the ocean can be estimated at 1.9 million tons/yr.

TABLE 1 The Involvement of Petroleum with the Marine Environment[a]

	million tons/yr
World oil production (1969)	1820.
Oil transport by tanker (1969)	1180.
Injections into marine environment through man's activities	2.6
Offshore oil production (seepage from wells)	0.5
Tanker operations	0.5
Other ship operation	0.5
Accidental spills	0.2
Deliberate dumping	0.5
Refinery operations	0.35
Industrial & automotive wastes	0.45
Torry Canyon discharge	0.117
Santa Barbara blowout	0.003-0.011
Atmospheric input from continents through vaporization of petroleum products	90.
Natural seepage into marine environment	< 0.1

[a]Data from SCEP (1970).

Land-based operations release petroleum products to the oceans through river discharge or through the atmosphere. Refinery operations releases have been estimated at approximately 0.35 million tons/yr. Industrial and automotive wastes are near 0.45 million tons/yr. Vaporization of a wide range of petroleum products such as gasoline

and other volatiles yields a variety of degraded petroleum products approaching 90 million tons/yr. A total yearly budget for direct and indirect contributions of petroleum products to the marine environment shows a flux that may reach 100 million tons/yr, over 95 percent of which is air-borne.

NITROGEN AND PHOSPHORUS

The photosynthesis of plankton populations in the ocean is commonly limited by a lack of nitrogen and phosphorus. Growing plants frequently exhaust these elements from water almost simultaneously. When these elements are present in excess, secondary pollution effects result in the formation of dense growths of phytoplankton. These plants, if not utilized by grazing organisms, may cause oxygen depletion and esthetic degradation of localized areas. Chemical species containing nitrogen and phosphorus are added to the ocean in river discharges and from the atmosphere as a result of natural weathering processes. Their rate of input is increased by domestic sewage and agricultural runoff.

Bowen (1966), Emery *et al.* (1955), Tsunogai and Ikeuchi (1968), and Holland (unpublished data) have estimated the quantities of phosphorus and nitrogen contributed to the ocean in river discharges. These estimates differ by almost an order of magnitude (Table 2). The contribution of combined nitrogen to the ocean from the atmosphere has been estimated at 59 million tons/yr (Emery *et al.*, 1955), 10 million tons/yr (Holland, unpublished data), and 210 million tons/yr (Tsunogai and Ikeuchi, 1968). Tsunogai and Ikeuchi estimate this input to be equal to the transfer of nitrogen gas back to the atmosphere. The input of phosphorus from the atmosphere has been estimated to be zero (Emery *et al.*, 1955), although this bears further investigation.

Because of the wide range of input values reported in the literature, it is difficult to assess realistically the influence that man exerts on total input to the oceans. However, the time

TABLE 2 Nutrients Added to the Oceans in River Discharge and Through the Atmosphere (million tons/yr)

Estimated by	N		P	
	River	Air	River	Air
Emery *et al.* (1955)	19	59	2.	0
Bowen (1966)	78.5	--	0.18	--
Holland (unpublished data)	10	10	0.8	--
Tsunogai and Ikeuchi (1968)	7	210	--	--
Total ocean reserve[a]	920,000		80,000	

[a]From Holland (unpublished data).

required to double the entire ocean's reserve of all inputs is probably at least 10,000 years. We can estimate the amounts of nitrogen and phosphorus contributed by domestic sewage as follows. In the United States, 60 percent of the population lives in the coastal zone, and it can be assumed that 50 percent of this population is serviced by sewers that discharge directly into the rivers, estuaries, or coastal zones. On the basis of the composition of Los Angeles' sewage (NAS-NAE, 1970), and the above assumptions, the US population contributes 0.1 million tons of phosphorus and 0.5 million tons of nitrogen per year.

The maximum acceptable concentrations of these elements in a confined body of water are extremely difficult to estimate, because they depend on flushing and dilution rates and the type of organisms that results from the enrichment of the water. If these organisms are utilized by higher trophic levels of the food chain, increased yields of commercial fish or shellfish result. This is termed enrichment. If, on the other hand, noxious species accumulate, decompose, and are not utilized by higher trophic organisms, the secondary pollution effects may become serious.

In many of the estuaries in developed nations, the concentration of nutrient elements in the water

is excessive. It can be estimated, for example, that the amounts added to the Hudson estuary are five to ten times greater than the capacity of the estuary to assimilate and recycle them (Ketchum, 1969). In metropolitan New York, much of the sewage is discharged without treatment, and it appears certain that secondary treatment alone would not adequately solve the problems of nutrient addition. In the long run, sewage treatment that reclaims these elements essential for plant growth and makes it possible to recycle them on land for agricultural purposes is desirable.

PULP-MILL EFFLUENTS

Pulp-mill effluents directly introduced into coastal waters are significant sources of pollution in areas such as Puget Sound, the Strait of Georgia, the Pacific coast of Washington, and the Atlantic coasts of Georgia, South Carolina, Maine, Canadian Maritime Provinces, Sweden, and the USSR.

The effluent solids in suspension increase the turbidity of the receiving waters, limiting light penetration and productivity. The wood chips and fibers settle out over the bottom and may smother benthic life. The bacterial degradation of organic materials uses up oxygen in the bottom sediments and may release gases such as methane and ethylane. The liquid components also put a significant oxygen demand on the receiving waters. Both organic and inorganic toxic components of the liquid wastes are relatively well known, with the constituents varying with wood species, dryness of wood, finish, and with variations in processing. The amounts and nature of the toxic effluents vary considerably depending on whether the mill uses sulfate or sulfite liquor, on the cation involved, and on the age of the mill. In general, spent sulfite liquor leads to more oxygen depression in the receiving waters, whereas the sulfate wastes are relatively more toxic.

The total amounts of sulfur and wood used in pulp mills are not a meaningful indicator of

quantities of pulp-mill effluents. Direct estimates of the volumes of wastes discharged could not be ascertained. The trend of the industry has been toward smaller water volumes and toward more recycling and recovery. The US consumption of sulfur in the pulp and paper industry in 1968 is given in US Bureau of Mines Bulletin 650 (US Department of Interior, 1970a) as 0.54-1.1 million tons, about one fourth of the world consumption. The estimated worldwide uses of sulfur, 2-4 million tons/yr, represent an upper limit for discharges to the marine environment. When this estimate is compared with the 3.4 million tons of sulfur released from fossil fuels (Bertine and Goldberg, 1971) and with the 140 million tons of sulfur mobilized as the result of natural weathering, the effluents from the pulp mills are expected to be significant only locally. In estuaries these discharges may have serious impact on coastal fisheries that are dependent on estuaries as nurseries for early life stages and sources of food organisms.

The environmental problems associated with pulp mills have been known for decades. Industrial technology is available to affect large reductions in the effluents; it remains for the mills to be persuaded or required to invest in appropriate control facilities.

HEAVY METALS

Many toxic or potentially toxic heavy metals are being released to the ocean environment at increasing rates. The present scale of man-introduced heavy metals can be put into perspective by comparing man's input to the ocean with the natural input.

Table 3 lists the annual world heavy metal production and estimates of man's inputs. The estimate of heavy metal input from atmospheric washout (Table 3, column 4) is described in the example given below for mercury. Both mercury and lead are identifiable heavy metal pollutants in the ocean and are discussed in some detail below.

TABLE 3 World Heavy Metal Production and Potential Ocean Inputs

Substance	Mining Production[a] (million tons/yr)	Transport by rivers to oceans[b] (million tons/yr)	Atmospheric Washout[c] (million tons/yr)
Pb	3	0.1	0.3
Cu	6	0.25	0.2
V	0.02	0.03	0.02
Ni	0.5	0.01	0.03
Cr	2	0.04	0.02
Sn	0.2	0.002	0.03
Cd	0.01	0.0005	0.01
As	0.06	0.07	
Hg	0.009	0.003	0.08[d]
Zn	5	0.7	
Se	0.002	0.007	
Ag	0.01	0.01	
Mo		0.03	
Sb	0.07	0.01	

[a]US Department of Interior, (1970 a and b).

[b]Bertine and Goldberg, (1971).

[c]Estimated from aerosol data of Egorov *et al.*, (1970) and Hoffman, (1971).

[d]Goldberg, unpublished data.

MERCURY

The increase in recent years of the mercury contents in snows deposited on the Greenland Glacier is one indication that substantial quantities of mercury are being mobilized over large expanses of the earth by the activities of man (Weiss *et al.*, 1971). This mercury was presumably removed from the atmosphere in precipitation at levels ranging from 30 to 75 nanograms/kilogram of water (average 60) during the period 800 BC to 1952 and from 87 to 230 nanograms/kilogram of water (average 152) between 1952 and 1965. If this increase

is man-caused, how did he bring it about? An examination of environmental mercury fluxes (Table 4)

TABLE 4 Environmental Mercury Fluxes[a]

	tons/yr
NATURAL FLOWS	
Continents to atmosphere (by degassing of the earth's crust)	
based on precipitation with rain	8.4×10^4
based on atmospheric content	$15. \times 10^4$
based on content in Greenland Glacier	2.5×10^4
River transport to oceans	$< 3.8 \times 10^3$
FLOWS INVOLVING MAN	
World production (1968)	8.8×10^3
Entry to atmosphere from fossil fuel combustion	1.6×10^3
Entry to atmosphere during cement manufacture	$1. \times 10^2$
Losses in industrial and agricultural usage	$4. \times 10^3$

[a]Weiss *et al.* (1971).

suggests that the mercury burden of the atmosphere results from the degassing of the earth's crust and that, if there is an impact by man, it must be through an enhancement of this degassing process.

A survey of industrial activities has not revealed any mercury releases to the atmosphere that rival that of the natural degassing rate (Table 4). Landscape alterations that result in disturbances to surface solids, agriculture, mining, and construction can allow more mercury vapor and more gaseous mercury compounds to enter the atmosphere.

The flow of mercury from the continents to the atmosphere is calculated to be about 2.5 to 15 x 10^4 tons/yr (Table 4). The mercury content in unpolluted airs ranges from 1 to 10 nanograms/m^3 with a conservative average around 1 nanograms/m^3, which yields a total atmospheric burden of 4 x 10^3 tons. Rain effectively washes the mercury out of the air. Taking an average time between rains of 10 days, the annual flux of mercury is 15 x 10^4 tons. A complementary calculation in rain water averages 0.2 parts per billion. An annual world precipitation of 4.2 x 10^{17} liters gives a flux of 8.4 x 10^4 tons/yr. Using the pre-1952 glacier waters as representative of typical fallout, a flux of 2.5 x 10^4 tons/yr is calculated.

The principle transfer of mercury from the continents to the oceans most probably takes place through the atmosphere. The mercury carried by the rivers to the oceans appears at least to be one order of magnitude less than the amount volatilized from the earth to the atmosphere (Table 4).

LEAD

Lead, like mercury, is being introduced to the marine environment through man's activities in amounts that begin to rival those brought in by the rivers (Table 5). The primary source of lead from

TABLE 5 Annual Lead Budget[a]

	million tons/yr
World lead production (1966)	3.5
Northern hemisphere production	3.1
Lead burned as alkyls	0.31
River input of soluble lead to marine environment	0.24
River input of particulate lead to marine environment	0.50

[a]Murozumi *et al.* (1969).

society is its emission from internal combustion engines where it is used as an antiknock additive in the fuel. Fourteen percent of the lead consumed in the United States is released in this way.

Measurable amounts of lead have been dispersed by man to his surroundings for at least several millenia. The concentrations of lead that precipitate from the atmosphere are recorded in the annual layers of permanent snowfields. Murozumi *et al.* (1969) found lead increasing in a north Greenland glacier 25-fold from 800BC to 1750 as a result of smelting operations. By 1940 the lead levels were 175 times greater than the prehistoric values. In 1966 they were 500 times greater. Up to 1940, the increases are attributed to smelting, and subsequently to the combustion of lead tetraethyl. The lead emitted from internal combustion engines, in the micron and submicron ranges, is removed primarily by precipitation from the atmosphere after a residence time of several weeks (Patterson, 1965; Patterson, 1971).

Surface ocean concentrations of lead have dramatically increased as a consequence of the "rainout" of man introduced lead from the atmosphere. Contents in surface waters of the northern hemisphere today are about 0.07 micrograms of Pb/kg of sea water compared with estimated prehistoric values of 0.01 to 0.02 micrograms/kg (Chow and Patterson, 1966).

Probably most of the lead burned in internal combustion engines eventually enters the marine environment. The lead that rains down on the continents can be transferred to the ocean by the rivers. The effect of this increased lead on surface marine organisms is, at present, unknown. If the use of lead in gasoline is curtailed, the concentration in surface waters will probably revert to much lower values within a decade, because the residence time of this element in surface waters seems to be of the order of several years.

SYNTHETIC ORGANIC CHEMICALS

Because the number of synthetic organic chemicals is large, emphasis will be given to those groups of compounds that have the following characteristics: relatively large production; persistence, or a tendency to accumulate in the environment; or toxic or harmful effects on organisms. The following chemicals are not meant to be an exhaustive compilation of harmful materials but are illustrative and useful as guidelines for further investigation and research: chlorinated hydrocarbons for agricultural and public health use; chlorinated hydrocarbons for industrial use; and volatile, low-boiling organic liquids and gases. A summary of data concerning them is given in Table 6.

Table 6 Estimated Production and Environmental Leakages of Some Synthetic Organic Chemicals

	Global Production		Estimated Leakage to Environment	
Chemical	Annual Million Tons	Total Million Tons	Annual Million Tons	Total Million Tons
DDT	0.1	2	0.25	1
Aldrin-toxaphene	0.1	1	0.25	0.5
BHC	0.1	0.5	0.05	0.25
PCB	0.1	1	0.025	0.25
1, 2 dichloroethane	5		0.5	
Freons	0.4-0.6		0.4-0.6	
Dry cleaning solvents	2		1-2	
Total synthetic light organic	20-30		2-3	
Total synthetic organic	100		?	

CHLORINATED HYDROCARBONS FOR AGRICULTURAL AND PUBLIC HEALTH USE

These chlorinated hydrocarbons include DDT, the aldrin-toxaphene group, and BHC (benzyl hexachloride) and their residues or degradation products.

+ DDT: The global production of DDT is estimated at 0.1 million tons/yr (NAS, 1971a). At least 25 percent or 0.025 million tons/yr reaches the sea, apparently almost entirely via the atmosphere (NAS, 1971a; Lloyd-Jones, 1971).

+ Aldrin-toxaphene group: The global production rate of the aldrin-toxaphene group is also estimated at 0.1 million tons/yr (NAS, 1971a). Its properties are similar to those of DDT. It is estimated that at least 25 percent or 0.025 million tons/yr of these chlorinated hydrocarbons work their way to the sea, primarily via the atmosphere.

+ BHC: The global production rate of BHC is estimated at 0.1 million tons/yr on the basis of the Japanese production rate of 0.04 million tons/yr (Kanazawa *et al.*, 1971). It is estimated that, with a higher vapor pressure than DDT or aldrin-toxaphene, well over 50 percent of the BHC produced will reach the ocean via the atmosphere.

In the atmosphere DDT, aldrin-toxaphene, and BHC are either present as gases or absorbed on particulate matter. They are removed from the atmosphere by rain, dry fallout, and possibly direct uptake on sea surface films. Measurements for these substances should be made in the atmosphere (in the gaseous phase and on particulates), in sea surface films, in sediments, and in primary producers and primary consumers. Monitoring should take place primarily in coastal and estuarine regions. In addition, there should be a monitoring program in remote areas of the world, because these pollutants are distributed globally.

The impact of the compounds in this group on the ecosystem on land has been better investigated

than that of the other two groups, but little is known concerning their behavior in the marine environment. Their distribution may be significantly modified by the existence of surface films of oil and other materials such as natural slicks (Seba and Corcoran, 1969).

CHLORINATED HYDROCARBONS FOR INDUSTRIAL USE

The chlorinated hydrocarbons used in industries consist of chlorinated hydrocarbons exemplified by the polychlorinated biphenyls (PCB), which are used as an insulator in capacitors, as transformer oil, as heat exchangers, as plasticizers, and in a variety of other ways. Global production figures for PCB are very difficult to obtain, primarily because the manufacturers do not make their production data available publicly. Based upon Japanese production figures of 0.0165 million tons/yr, the global production of PCB is estimated at 0.05-0.1 million tons/yr, with the total production of PCB estimated at approximately 1 million tons (Isono, unpublished data). It is estimated that approximately 25 percent of the PCB produced leaks to the environment, 20 percent to the atmosphere for subsequent long range transport in the global wind system, and about 5 percent directly into sewers and rivers. The resulting annual rate of transport to the oceans is approximately 0.025 million tons/yr. Concern about PCB is relatively recent, and considerable study must be made of the fate and distribution of this substance in nature.

For an understanding of the impact of PCB on human health, more thorough investigations of accidental exposure, such as the Kanemi Rice Oil Case in Japan in 1968 where more than 5 deaths occurred (Ui, unpublished data), are urgently needed. PCB use is so variable (it is believed that there are more than 100 different uses) that it is difficult to point out specific areas of discharge. PCB concentrations of 100 parts per billion in samples from the open ocean biomass (Harvey *et al.*, 1971) and 100 parts per million in samples from the fresh water and coastal biomass in Japan (Isono, unpublished data) suggest that PCB pollution is a

global as well as local problem. Many of the substances that have been used as substitutes for PCB (e.g., diphenyl, triphenyl, diphenyl ether, and alkylnapthaleins) are also highly toxic.

VOLATILE, LOW-BOILING ORGANIC LIQUIDS AND GASES

Volatile, low-boiling organic liquids and gases have easy access into the atmosphere and can subsequently be transported great distances. Three examples of this type of chemical are 1, 2 dichloroethane, freon, (e.g., trichlorofluoromethane and dichloro-difluoro methane), and dry cleaning solvents.

+ 1, 2 dichloroethane is a volatile liquid used largely in the production of vinyl chloride, as an additive to gasoline, a cleaning solvent, and industrial additive. The production in the United States in 1968 was 2.2 million tons (US Tariff Commission, 1970) and the global production rate is estimated at 5 million tons/yr.

+ Freons are used in propellants, aerosol cans, and in the production of plastics as refrigerants. The production of trichlorofluoromethane and dichloro-difluoro methane in the United States in 1968 was 0.3 million tons (US Tariff Commission, 1970) and the global production rate is estimated at 0.4-0.6 million tons/yr. Nearly all of this goes into the atmosphere from the primary use as a propellant, for long range transport by the wind system. Lovelock (1971) has detected trichlorofluoromethane in the atmosphere over southwestern Ireland. He found values ranging from 1×10^{-11} volume per volume of air in winds from 45°-135° to 20×10^{-11} in winds from 225°-315°. Using the lower value of 1×10^{-11} volume per volume and an atmospheric mass of 5.14×10^{15} tons (SCEP, 1970) results in a total atmospheric burden of 0.24 million tons. The annual global production of CI_2F_2C is

approximately half the total freon production, or ~0.25 million tons/yr indicating an atmospheric residence time of approximately one year.

+ Dry-cleaning solvents: The United States produces approximately 1 million tons/yr of these chemicals (Isono, unpublished data); global production is estimated at 2 million tons/yr. It is estimated that 50-80 percent or 1-1.6 million tons/yr evaporates into the atmosphere (Goldberg, unpublished data), with lesser amounts discharged into sewers. Primary source areas are in population centers.

Other synthetic, low-boiling (< 100°C) organic compounds, such as vinyl chloride, carbon tetrachloride, aldehydes, ketones, and alcohols, are also released into the environment. Global production of these light synthetic organisms is estimated at 20-30 million tons/yr. The total worldwide production of synthetic organics is estimated at 100 million tons/yr (Goldberg, unpublished data) and includes, for example, polymers and detergents (FAO, 1971).

All the pollutants in this category will be found in the atmosphere either in the gas phase or on particle surfaces. Removal to the sea will be by precipitation, dry fallout, and direct gas phase dissolution. Many of these substances will be quite persistent in the environment and may be serious problems in some coastal and estuarine ecosystems. A program to sample for these substances in the atmosphere, in surface and subsurface water, and in the marine biota should be undertaken. Only some of the many examples of low boiling synthetic organics have been given here.

A detailed inventory should be made of production rates and environmental leakage factors for all synthetic organic chemicals. In addition, detailed research is needed on the effects of these various substances on different parts of coastal ecosystems. The systematic analysis of easily detectable compounds such as freon might give a picture of the distribution between various phases

and trophic stages. Intensive and comprehensive case studies of areas heavily polluted by known pollutants will give us important information on the mode of impact to human health and the marine environment.

MICROBIOLOGICAL POLLUTION OF COASTAL WATERS

Public health authorities recognize the dangers associated with the occurrence of bacterial and viral pathogens in raw sewage. Pathogens for which an oral-anal cyclic transmission route can be described are of special interest. Members of enteric bacteria and virus groups (organisms that occur in human or other animal intestinal tracts) are of primary importance in human infections caused by infectious agents transmitted through a human waste product route. Table 7 provides a listing of those enteric bacteria and viruses that most need to be considered.

Estuary waters receiving primary treated sewage effluents have been shown to contain bacterial pathogens (Brezenski, 1970; Geldreich and Donsel, 1970; Slanetz, Bartley, and Metcalf, 1964). Enteric viruses of human origin have been isolated not only from estuary waters but also from shellfish inhabiting these waters (Metcalf and Stiles, 1968). Counting enteroviruses and adenoviruses of human origin, reoviruses, and presently unclassified hepatitis virus, there are about 100 enteric viruses of public health concern in considerations of water quality. The injection of human pathogens into estuary waters can be expected until waste treatment practices are adopted that eliminate these pathogens. Seasonal fluxes occur in north temperate zones in which pathogen injection rises to a peak in late summer and early autumn months.

The number of enteric viruses in domestic raw sewage has been estimated at 500-700 units/100 ml.

About 1 unit/100 ml is estimated for polluted surface water (Clarke, *et al.*, 1964). The minimal oral infective dose for man has been estimated at one virus, provided contact with susceptible cells is established (Plotkin and Katz, 1967).

TABLE 7 Pollutants, Actual or Potential, of Microbiological Nature, Occurring in Coastal Waters As a Consequence of Contributions of Human or Animal Waste Products

Enteric Viruses		Enteric Bacteria
Human Origin	Animal Origin	Human or Animal Origin
Polioviruses	Simian	Salmonellae
Coxsackieviruses A	Porcine	Shigellae
Coxsackieviruses B	Bovine	Vibrio parahemolyticus
Echoviruses	Foot and Mouth	
Reoviruses	Vesicular Exanthema of Swine	
Adenoviruses		
Hepatitis viruses		

Methods for direct isolation of virus are expensive and time-consuming. Consequently indirect procedures indicating the possible presence of virus are used commonly in sanitary examinations of water at the present time. The fecal coliform index is one of these (Hosty *et al.*, 1970). Its acceptability as a measure of virus is subject to some question. One objection concerns a possible longer survival time for virus in water, leading to the continued presence of virus in the absence of *Escherichia coli*. Prolonged virus survival allows its dissemination from the original point of pollution. Isolation of virus several miles from

the nearest sewage outfall illustrates this point. Another objection to *E. coli* indices concerns a possible multiplication of *E. coli* in water that could lead to faulty interpretation of test results. Animal sources of *E. coli*, other than man, could also offer problems in the interpretation of test results.

Demonstration of bacterial pathogens in estuary waters and shellfish has some of the technical problems associated with viruses. Consequently, the *E. coli* index frequently is used in sanitary tests to indicate the possible presence of pathogens such as members of the Salmonella group.

The seriousness of viral hepatitis as a world problem has been documented by Mosley and Kindrick (1969). Transmission of infectious hepatitis as a consequence of sewage-polluted estuaries has occurred through consumption of virus-containing shellfish, either raw or improperly cooked. No direct evidence of a significant health problem arising from recreational use of sewage-contaminated seawater is available (British Medical Journal, 1968). Nine outbreaks of infectious hepatitis have been attributed to shellfish (Liv, 1970), while 50 episodes involved a direct water-borne transmission route (Mosely, 1967). Sewage polluted water leads to the closing of oyster beds to commercial harvesting, denying public use of a natural resource and causing economic repercussions in the shellfish industry. One editorial charges that one fifth of the US 10,000,000 acres of near-shore shellfish grounds have been closed because of pollution (Hacker, 1971).

There is an urgency to define the problems of the virus pollution of coastal waters. Reliable assay methods for measuring small numbers of virus in large volumes of water are needed. Expanded studies on virus isolation procedures are needed. Quantitative enumeration of virus is needed to answer questions such as the number of viruses occurring in sewage, water, or shellfish, or the effect of waste water treatment practices upon virus populations. A quantitative enumerative capability is needed before standard methods can be considered.

Preliminary findings suggest that virus in a marine environment survive for as long as a few days to about two weeks, with longer intervals possible in cold weather. However, at this time, there is no agreement about the causes of virus inactivation in marine waters.

Epidemiologic studies are needed to determine the incidence, duration, and number of virus types found in water. What human pathogens are found in what numbers, and how often? Are viruses from large or small animals occurring in water? Is there a chance for unnatural infections in man or animals caused by some of these viruses, which lead to oncolytic effects? What is the incidence of tumor causing viruses found in some species of fish, and how broad is the host specificity?

Comparative virology studies are needed in which the occurrence of or potential for virus carriage in marine hosts is determined.

R A D I O A C T I V I T Y

During the last three decades the principal source of artificial radionuclides in the marine environment has been nuclear weapon-testing (Table 8). The present content of the world oceans from this source, including tritium, is estimated as 10^9 curies (FAO, 1971). This type of contamination is widespread due to the diffuse nature of the source following dispersion in the atmosphere prior to entry to the ocean, and therefore, relatively speaking, is low and uniform in concentration. The bulk of the activity is still associated with surface waters and lies largely within the northern hemisphere. Assuming that the present rate of nuclear weapon testing continues, this distribution will become more uniform with time. This figure compares with 5×10^{11} curies of naturally occurring ^{40}P in the oceans. However, this simple comparison of curie quantities should not be construed as one of relative biological significance, because different radionuclides have

widely different toxicities, and their significance in a given situation will depend not only on this but also on the uses of the environment that will lead to human radiation exposure.

TABLE 8 Total Content of Artificial Radionuclides in the World Ocean

	Year 1970	Year 2000
Nuclear explosions		
Fission products (exclusive of Tritium)	2-6 x 10^8Ci	? x 10^8Ci[a]
Tritium	10^9Ci	? x 10^9Ci[a]
Reactors and Reprocessing of Fuel		
Fission and activation products (exclusive of Tritium)	3 x 10^5Ci	3 x 10^7Ci
Tritium	3 x 10^5Ci	? x 10^8Ci
Total	10^9Ci	10^9Ci

[a]Assumed that atmospheric nuclear testing will continue at about the rate of 1968-1970.

Nuclear power programs that involve power reactors, fuel fabrication, and reprocessing provide the second important source of artificial radioactivity. These installations, which utilize radioactive species, may be described as a series of point-sources, where rates of introduction vary from a few curies per year to 10^5 curies per year. The point-sources of principal significance to the marine environment will be liquid wastes flowing directly to coastal and estuarine waters via pipelines. Indirect introduction of liquid wastes via

rivers or introduction of solid radioactive material to the deep ocean in dumping operations will be smaller in scale and have less environmental significance.

Releases of radioactive gaseous species, other than those containing tritium, will be of little significance in a marine context because the magnitude of such releases will be small in relation to the direct growth discharge of radioactivity to the marine environment. Uncontrolled or accidental releases, other than nuclear explosions, are likely to be infrequent and of small magnitude in relation to the capacity of the world ocean and will probably cause local problems only.

Two problems will increase in scale over the next few decades. One is the introduction of tritium to the marine environment from reactor operation and fuel reprocessing. It is estimated that this will result in an oceanic inventory of the order of 10^8 curies by the end of the century. However tritium is of very low radiotoxicity, will not concentrate to any extent in biological materials, and does not present a significant problem in the contest of marine disposal. The second problem relates to the production of long-lived plutonium wastes and the need to insure their containment over periods of time of the order of 10^5 years. Such wastes will be produced in many countries throughout the world, not all of which will have the resources necessary to provide the required containment. The best means of dealing with this problem must be determined. These wastes might be deposited in the deep sea in ceramics of low leachability, and, where appropriate, international storage or containment facilities might be provided.

SUMMARY AND GENERAL CONCLUSIONS

Materials are carried to the oceans as a result of human activities at rates comparable to

those at which substances are introduced by weathering processes. The most important impacts occur within the coastal and estuarine areas. Studies of pollutants there will provide a basis for subsequent investigation in open ocean areas.

Although pollutants that pose threats not only to man but also to ecosystems and resources in the marine environment have been identified, a systematic study of leakages of man's wastes to his surroundings must still be made. Our knowledge seemed particularly inadequate in areas such as losses in mining operations and cement manufacture, and in hospital and feedlot discharges. An area of real concern that could not be effectively explored with available information was the dispersion of non-degradable solids to the marine environment. For example, of the 20 million tons of plastics made annually, a substantial amount may be introduced to the marine environment that have impact upon the health of marine communities or that destroy the natural beauty of the landscape.

The two groups of chemicals that appear to offer the greatest dangers through promiscuous release to the environment are the heavy metals and halogenated hydrocarbons. Although some baseline studies are being carried out on representatives from these groups, more extensive biological and water assays are needed. In addition, we feel that many other synthetic organic chemicals, as yet unlooked for, may be present in quantities that pose threats to the biosphere.

Finally, the problem of virus pollution of coastal waters appears to be grossly understudied. Problems such as the isolation, identification, and assay of viruses have not been attacked in even preliminary fashion.

SPECIFIC RECOMMENDATIONS

Highest priority is proposed for research involving the dispersion of the polychlorinated biphenyls to the environment. With the observations made by a number of laboratories that the PCB

levels now exceed those of DDT residues and with the recent mortalities and illness associated with the ingestion of PCBs by man, the public-health concern of these chemicals becomes evident.

The properties of petroleum films at the ocean-atmosphere interface in the uptake of atmosphere-borne pollutants and in their transfer to members of the marine biosphere should be developed in detail.

More analyses of metals such as cadmium, zinc, lead, mercury, and arsenic in food products of the marine environment are needed, both to alert us to any potential public-health problems and to identify the sources of leakages of such materials.

JOHN W. WINCHESTER
DONALD BAUMGARTNER
NORMAN CUTSHALL
WILLIAM GARRETT
DONALD HANSEN
ARNOLD B. JERNELOV
DONALD W. PRITCHARD
WILLIAM SACKETT

CHAPTER III

DISPERSAL AND TRANSPORT OF POLLUTANTS IN THE MARINE ENVIRONMENT

INTRODUCTION

Our task group focused on chemical, biochemical, and physical processes occurring in the zones through which pollutants enter the oceans. These processes are extremely important because they actually determine whether a pollutant reaches the ocean. They are complex, however, and require intensive study. In order to predict the behavior of a chemical pollutant, the relative importance of the dynamics of mass transport of water, the transformations of chemical form by biological processes, the transport of a pollutant contained in nektonic marine organisms, and the movement of sediment particles carrying adsorbed pollutants must be assessed. Each of these factors is considered in this report.

We believe that marine pollution is best controlled at its source. Pollutants with a few discrete sources may be controlled by closing valves, eliminating the problem from the study of oceanography. Many pollutants, however, come from many dispersed sources or from little known sources. For these we must predict whether they enter the oceans or are retained on land, in freshwater, or in the air. Acquiring this predictive capability seems to be of paramount importance, and learning how such pollutants subsequently move within the deep oceans seems, at present, to be of secondary concern.

In studies of the chemistry of the oceans, oceanographers have usually overlooked two areas through which pollutants enter the oceans: the coastal zone and the sea-air interface. Transition from fresh to salt water and from the land's edge across the continental shelf to the ocean basin occurs in the first zone. Here, water-borne contaminants may be carried by currents to the open sea, or they may be retained by sediments or materials of the biosphere, depending on their chemical and biochemical properties. In the second area, airborne contaminants may enter the sea and water droplets and dissolved vapors may be cycled back to the atmosphere. In order to evaluate the dispersal and transport processes that regulate the input of pollutants to the oceans, study of what occurs in these areas is of highest priority.

The weakness in our knowledge of chemical changes limited our understanding of coastal zone and sea-air transport processes. Dynamic theory cannot predict the transport of a non-conservative water contaminant (e.g., one that precipitates to the sediment), and we do not yet know whether most pollutants of interest in the two input zones tend to be absorbed on sediment particles, taken up by organisms, extracted by surface films, or modified otherwise by chemical or biochemical reactions. We cannot predict pollution transport by free-swimming fauna unless we know whether the fauna tend to concentrate pollutants.

The task group recommends that the study of significant pollution transfer processes in the coastal zone and at the sea-air interface include chemical measurements and theoretical principles of chemistry as a central feature. The chemical research necessary for this study must have full coordination with physical, biological, and geological oceanography.

TRANSPORT PROCESSES OF POLLUTANTS

Transport of pollutants in the marine environment is effected by mass movements of water,

atmosphere, and sediments, and by migration of organisms. Evaluation of the transport processes, therefore, requires knowledge of the mass movements of the media and the organisms and knowledge of the pollutant concentration within each. The transport of conservative substances is at least conceptually straightforward. However, many pollutants are highly reactive in the marine environment and need to be better understood.

In order to describe the concentration of pollutants (e.g., organic compounds, suspended particles) or water quality parameters (e.g., dissolved oxygen, clarity) at any given point or time, we must account for the transport of materials within a specified physical segment of the marine system, the transformation of materials within the system, and the transfer of materials into and out of the system along the boundaries. Transport within the system can be thought of as passive (e.g., materials carried by the water and, possibly, acted on by gravity) or active (e.g., fish migrations against the current or, on a more local scale, schooling of organisms).

WATER MOVEMENTS

Transport of pollutants by mass movements of water must be considered in determining marine environmental quality parameters. The ability to model flows appropriately is required for testing chemical and biological reactions within the water.

Pollutants originating from man's activities on land tend to pass through the coastal zone to the major ocean basins, with a progressive decrease in concentration and an increase of time and space scales for important changes. It is convenient to consider the transport of pollutants by tracing their movement through these paths.

ESTUARIES

Physical processes of advection and diffusion have been studied with increasing vigor for nearly 60 years. Considerable progress has been made in

classifying and understanding the mechanisms acting in estuaries and in modeling some physical behavior (Ward and Espey, 1971). In particular, the state of the art of modeling well-mixed estuaries is well advanced for some purposes. A major problem in utilizing these barotropic models is the determination of horizontal dispersion coefficients, which are usually empirically inferred from the distribution of some easily observed variable such as salt or dye. These coefficients are a composite effect of several identifiable physical processes and, therefore, are not necessarily valid for application to concentration distributions different than that from which the coefficient is inferred. Furthermore, the coefficients have limited utility in predicting response of the physical processes to major environmental modification.

The state of the art of modeling stratified estuaries is still poorly developed, although the major physical processes are qualitatively understood. The greatest difficulties are associated with *a priori* specification of turbulence and its effects in fjords and other estuaries having vertically restricted exchange with external waters.

Large time variations in fresh-water inflow and in other external factors, such as wind stress, significantly modify the flow patterns of many estuaries. Such estuaries seldom, if ever, approach steady-state conditions. Consequently, adequate predictions of the consequences of man's activities in such estuaries require the development of time dependent models for stratified estuaries. Further physical measurements in estuaries will be required primarily to test and quantify prediction models.

WATERS OVER THE CONTINENTAL SHELF

Where purely local influences are concerned, development of predictive or interpretive models for coastal circulation over the continental shelf is a conceptually straightforward extension of estuary modeling developments, although the shelf does not have lateral boundaries. Considerable difficulty may be encountered, however, because of

the relatively large influence of the deep ocean circulation and its variation on the movement of water over the continental shelves and the effect of local winds that may dominate other factors on the shelf. At present, detailed studies of the importance of these various processes in representative coastal regions are greatly needed.

DEEP OCEAN

We must consider the entire spectrum of ocean currents in research on global transports of pollutants. At very large scales, however, the nonconservative nature of contaminants becomes more important. We wish to emphasize only those aspects of ocean circulation that seem to have particular relevance to marine environmental quality. To ascertain the degree to which polluting activities comprise purely local versus more general problems man must evaluate the residence time or flushing characteristics of water in semi-isolated mediterranean seas. Other features that must be considered include exchanges with the surface mixed layer, vertical mixing in the water column in general, regions and rates of upwelling or downwelling, horizontal divergence, and convergence because of its tendency to concentrate surface contaminants.

THE INFLUENCES OF THE PHYSICAL FORM OF THE POLLUTANTS ON THEIR TRANSPORT AND DISPERSION

Within any region of the ocean, it is possible to make an evaluation of transport processes relating to the physical nature of the pollutant: dissolved, particulate, and in films.

DISSOLVED

Transport of pollutants is most easily described for dissolved constituents. However, the ability to describe the movements and mixing of water masses is not uniformly good for all geophysical regions of the marine environment, as

described for estuaries and in more extensive reviews (NAS-NAE, 1970). For example, the available techniques in calculating the concentration of dissolved organic compounds is subject to biochemical oxidation. The same techniques are basic to (but not sufficient for) the description of particulate pollutant transport. Unfortunately, we cannot exclusively depend on the simplest prediction techniques, because significant chemical and biological actions do occur in the marine environment causing dissolved pollutants to precipitate and react with particulates or liquid films.

PARTICULATES

Atmospheric transport of particulates may be a major route of entry for a number of important oceanic pollutants (NAS, 1971b). In spite of possible sporadic distribution of pollutants through this boundary transfer of material, we have little difficulty accounting for subsequent marine transport, although computational techniques may become cumbersome. Full evaluation of this problem depends on a better description of the type and distribution of major atmospheric pollutants.

Transport calculations for particulates within the water system (with the possible exception of neutrally buoyant particles) are more difficult to make than those for dissolved substances. At the very least, calculation of particle transport requires knowledge of the vertical eddy diffusivity and its variation with depth. Calculations of scour and periodic resuspension from bottom deposits require knowledge of both the boundary input parameters and the hydrodynamics of flows very near the bottom of estuaries, continental shelves, and oceanic basins. This knowledge is generally required in coastal shelf regions because of the possible oceanic contributions of particulates as well as the direct particulate contribution by rivers and by waste discharges to the area. Furthermore, the dearth of information on biological, chemical, and physical transportation of liquids to solids, and vice versa, and the physical factors influencing particle size agglomeration make transport calculations for particulates difficult.

Turbidity currents consisting of flows of finely divided particles can be described by methods developed for measuring stratified flow of fluids of different densities. Because, from a practical point of view, nothing substantive is known about the size, location, and occurrence of these flows, little can be said about their importance as mechanisms of seaward transport of pollutants.

IN FILMS

Films form on the sea surface from a variety of complex interactions in the environment and, also, from direct (sometimes accidental) discharges of industrial and municipal outfalls plus oil spills. In the long term, transport of films will be dominated by wind. Major ocean surface currents and wind patterns are relatively well known, at least near continental margins, and it is probable that, given a location for continued or catastrophic discharges and other necessary basic data, a fair picture of eventual transport could be drawn. Considerations of processes that depend on interactions such as volatilization, sediment and particle interchange, and sinking of oil globules are of greater importance. Present knowledge of such processes is inadequate. On the short term (and on smaller scales), it is not possible, at present, to predict whether films will break up and disperse and at what rate sinking and emulsification occurs due to the physical action of localized wind and wave patterns. However, under calm conditions, fairly good conceptual models exist to predict the thickness and spread of films.

ACTIVE TRANSPORT

Some pollutants are concentrated by marine organisms; thus, the movement of these organisms constitutes a transfer mechanism. As a consequence pollutants move to regions where their presence or their concentrations would not be predicted by passive transport with the water mass. Even

though the mass of pollutants incorporated in marine organisms may not be a large portion of the total mass of pollutants, it is necessary to account for transport by marine organisms because of the ecological significance of the result. Biological models of growth and transport are presumably needed. These will be discussed by other task groups.

FACTORS AFFECTING TRANSPORT

CHEMICAL

CHEMICAL SPECIES AND REACTIONS IN SOLUTION

The state of chemical combination of a pollutant determines its chemical behavior and pathway of transport through the marine environment. Ionic species, such as many heavy metals, tend to be held in solution or to establish solubility or ion exchange equilibria with sediments or suspended solids. Uncharged species, such as hydrocarbons, may be attracted to interfaces with the atmosphere or sediments, especially in association with organic films. Therefore, in order to predict transport routes of specific pollutants, it is essential to know chemical forms of pollutants as well as their concentrations or concentration gradients. We recommend the acquisition of baseline information that determines both the concentration and principal chemical form of pollutants in sea water.

Chemical pollutants may enter the oceans by flow through the coastal zone, where salinity may change from fresh to salt water. Although considerable deposition of pollutants has been observed in sediments near river mouths and considerable transport to the deep ocean also occurs, the chemical factors governing the efficiency of deposition and transport in solution are poorly understood. Many thermodynamic properties of pollutants are known to vary non-linearly with salinity, and it is likely that shifts in chemical potentials, which

may serve as driving forces for reactions, can result from estuarine mixing. Because both inorganic chemical reactions and biochemical and biological processes may be affected, these chemical driving forces must be better understood in order to assess the efficiency of transport of a pollutant through the coastal zone to the waters of the continental shelf and beyond. Therefore, baseline information should include both a review of chemical thermodynamic properties of pollutants in waters of variable salinity and an assessment of forces for chemical reactions associated with estuarine mixing.

Exchange of pollutants between sediments and water may depend critically on the oxygen content of the water, which may be controlled by decay of organic matter and is often increased by excessive phytoplankton growth as a result of nutrient pollution. As an example, in oxygenated water Mn may be held by sediments as MnO_2 and accumulate certain trace heavy metals, but in anoxic waters the MnO_2 may dissolve and release the heavy metals to solution. Also, in anoxic waters certain elements may be bound to sediments as sulfides. Moreover, organic reactions may be induced by a transition from high to low oxygen content of water. Consequently, research should be undertaken on the detailed shifts in chemical equilibria associated with anthropogenic transformation of bottom waters to anoxic condition.

ACCUMULATION OF ORGANIC POLLUTANTS AT INTERFACES

Surface-active organic compounds adsorb readily at phase boundaries such as the air-sea interface, the water-solid boundary of suspended particulate matter, or the oil-water interface of a petroleum spill. At the air-sea interface the organic molecules may undergo concentration by convergent forces until they form a coherent monomolecular film, commonly called a sea slick. These slicks are visible because of their ability to damp capillary waves and produce a light reflectance anomaly on the sea surface. In addition, surface-active organic species in petroleum products cause the chemical spreading of oil slicks and promote

the emulsification and dispersion of the spilled oil into the sea. These molecules derive their surface activity from a polarized chemical structure containing a hydrophilic functional group that anchors it to a phase boundary while its hydrophobic segment (hydrocarbon portion) is oriented away from the high energy interface.

In general, the polar fatty compounds, such as fatty acids, alcohols, and glyceride esters of fatty acids, are the most water-insoluble and persistent constituents of the sea surface. Although there has been no specific chemical identification of other classes of compounds in surface films, the existence of positive nitrogen and phosphorus tests suggests that small quantities of denatured proteinaceous fragments, phospholipids, and sterols are present.

In seawater, the organic pollutants (e.g., chlorinated hydrocarbons and organic forms of heavy metals) will be distributed preferentially into the less-water-soluble organic phases. These organic accumulators may be sea surface films (FAO, 1971; NAS, 1971a), adsorbed organic layers, or petroleum products. Thus, aggregates of natural or contaminant organic material will accumulate and concentrate other organic pollutants that are preferentially soluble in the relatively water-insoluble hydropholic matter. For example, the partition coefficient of DDT between sedimental river oils and water has been found to be 1.5×10^6 (Hartung and Klingler, 1970). DDT is almost wholly water insoluble, while it dissolves to the extent of 8-12 g/100 ml in vegetable oils, kerosene, and gasoline. Its solubility in benzene, an aromatic organic chemical, is 78 g/100 ml. Consequently, petroleum spills, natural sea slicks, and adsorbed water-insoluble organic matter should accumulate lipophilic pollutants, which can then be incorporated and further concentrated into the oceanic food chain by biological assimilation.

Organic surface films are often ephemeral and fragile at a dynamic air-sea interface. When dispersed by wind and waves, the slick constituents (along with the organic pollutants) will be driven to some site in the underlying water dictated by the nature of the disturbance. Upon the return of

calm conditions, the surface film can re-form by adsorption of film-forming material, again possibly containing oil-soluble pollutants. Atmospheric fallout and precipitation scavenging transport organic pollutants into natural surface films or oil spills at the air-sea interface. Conversely, bursting air bubbles and spray can reintroduce such pollutants into the atmosphere along with organisms that have assimilated them.

As mentioned previously, there is experimental evidence for the concentration of DDT in sea slicks. However, these data come from one research study, and considerable confirmatory evidence is required to determine the extent of this effect, not only for surface films but for organic aggregates, water-insoluble organic molecules at the sea surface (not in coherent films), and petroleum products at various sites in the sea. There is also the possibility that heavy metals may be accumulated in organics by solubility effects when the metals are organically combined or associated with the surface of organic aggregates.

Thus it is recommended that a research program be established to determine the organic pollutant levels in natural and contaminant (petroleum) surface films, organic aggregates, nonslicked sea surface, and particle-free seawater. Distribution coefficients of organic pollutants between various organic phases and seawater should also be determined. It is anticipated that these determinations will be most easily performed in organic-rich coastal water, although a few deep-sea samples would also be desirable. Samples from shipping lanes or ports where oily pollution is present would demonstrate possible concentration by petroleum products. Where suitable analytical methods are available, the amounts of heavy-metal organics, chlorinated hydrocarbons, and polycyclic aromatic hydrocarbons, (e.g., 3, 4-benzopyrene, a carcinogenic compound) should be determined.

We recommend a research program that includes controlled laboratory verification of this accumulation mechanism to substantiate and support the data from the sea sample analysis. Perhaps an artificial sea slick of nonpolluting, film-forming chemical, such as oleyl alcohol (Barger *et al.*,

1970), should be generated to determine its rate of pollutant uptake. This experiment might be performed in a tropical portion of the ocean under the influence of easterly winds that transport organic pesticides from North Africa toward Florida.

Two existing methods may be used to effect sea-surface sampling: a screen sampling technique (Garrett, 1965) and a rotating drum skimmer (Harvey, 1966). A discussion of the relative utility and validity of these sampling schemes is detailed in the FAO Fisheries Report (1971).

CHEMICAL EFFECTS OF SEDIMENT-WATER AND PARTICLE-WATER INTERFACES

The distribution of a pollutant between dissolved forms and forms associated with particles is an important factor in determining how the pollutant will be transported. This distinction is especially important in the coastal zone through which many pollutants are carried. Totally dissolved substances will generally follow water motion very closely, and their transport is relatively well understood. Substances associated with particles will tend to settle toward bottom where their transport can be less adequately predicted. In some estuaries, particle-borne pollutants may simply be accumulated. Particles passing through an estuary tend to settle on the continental shelf, although the very finest material may travel well away from its source in suspension.

Many pollutants entering estuaries will already be adsorbed. Changes in composition and ionic strength of the supporting solution will be encountered by particulates during transport from rivers into the sea. These changes may induce a redistribution between dissolved and particle-associated forms of a pollutant.

Release of adsorbed pollutants from particles may occur because of displacement by sea salt constituents or of changes in activity coefficients (Kharkar *et al.*, 1968; Johnson *et al.*, 1967). Estuarine zones may be the site of sorption or precipitation of other pollutants (Kautsky, 1966). The formation of hydrous oxide precipitates of Fe

and Mn and their flocculation along with other suspensoids may provide effective scavenging of pollutants entering the estuaries either from land or sea.

Most of the particles with adsorbed pollutants passing through an estuary are deposited relatively near shore on the continental shelf. Because of occluded organic material, these sediments become anaerobic almost immediately below the sediment-water interface. The subsequent reduction of various chemical species results in an immobilization of some species, such as sulfur, from dissolved sulfate to insoluble metal sulfides, as well as a mobilization into interstitial waters of iron, manganese, and other metals. These shelf sediments act both as a source and sink for various elemental and molecular species.

At the edge of a continental shelf in the vicinity of river outflow, deposition of sediment eventually produces an unstable structure that collapses, and the subsequent sediment-water suspension with its high density flows rapidly down slope, as a turbidity current, to the abyssal plain of an ocean basin. This suspension would include the interstitial water with its solublized-reduced forms. On the abyssal plain, reoxidation and immobilization through adsorption would occur. However, on the abyssal plain, the distribution of a pollutant between aqueous and solid species will be different than on the shelf because of the decreased pH of deep ocean water and the pressure effect on chemical equilibria.

A small fraction of the particles introduced on the shelf remains in suspension, is transported for long distances, and is deposited in the deep ocean. This fraction, apparently consisting of an association of small particles and water known as coacervates, forms a tongue of aluminosilicate material in the vicinity of the thermocline. This type of suspended material is about 20 percent of the total in the Gulf of Mexico and has an estimated settling rate of about 3 meters/day (Feely *et al.*, 1971). The other major components of suspended materials are particulate organic carbon, produced in the surface layer (especially in near shore and other highly productive areas), and a non-aluminosilicate

inorganic material consisting of the tests of foraminifera and diatoms and hydrated oxides of metals such as iron and aluminum. Each of the major types of suspended material should exhibit a different sorption of extraction medium for pollutants. Petroleum and chlorinated hydrocarbons should prefer particulate organic material over the others; trace metals should prefer the sorption sites on aluminosilicates.

The processes referred to in general terms above are not well enough understood to predict how a specific pollutant will be transported through an estuary, across the shelf, and into the deep sea. In the immediate future it will be necessary to determine the direct distribution of specific pollutants. Our ability to forecast the particle-solubility relationships for classes of pollutants should be improved, in part through acquiring descriptive knowledge of particular pollutants. In addition, fundamental research on the processes and mechanisms whereby pollutants are attached to and retained by particles, determination of thermodynamic changes in the solution-particle relationship under changing salinity, pressure, temperature, pH, and Eh, and understanding the kinetics with which new equilibrium conditions are approached will improve our forecasting ability.

BIOLOGICAL AND BIOCHEMICAL PROCESSES AFFECTING POLLUTANT TRANSPORT

Most pollutants as well as some naturally occurring substances are accumulated in organisms. The mechanisms for this accumulation vary from compound to compound and could be passive depending on fat solubility (chlorinated hydrocarbons) or tendency to form complexes with sulphur groups in proteins (heavy metals) or due to an active transport (arsenic oxides may proxy biochemically for phosphate).

The concentration figures obtained for a given pollutant might be very high, as for PCB's, with the result that the organisms' nerve tissues would contain a large proportion of the amount of the pollutant present in the ecosystem. The concentration of a pollutant in organisms will, of

course, be of importance for the transport pattern of the compound.

When a pollutant compound passes through an organism it is unlikely to come out in the same form as it entered. One extreme of the metabolism in this sense is total degradation, but, even in cases where complete breakdown does not occur, the properties of the pollutant are still likely to be changed. A typical example of such a change involves a decreased fat solubility and an increased water solubility. Often the secreted compound comes out in association with fecal pellets.

These changes in chemical properties and associations frequently cause the pollutant to move from one phase in the transport system to another. Often the general direction of metabolic change in properties of a pollutant passing through an organism is from fat to water soluble. However, several exceptions with a considerable ecological impact exist (e.g., the biological methylation of mercury) in which fat solubility is increased by metabolism.

In most cases, while the change of properties is known to be very important for the transport pattern, the metabolic fate of pollutants and the change of their properties from compound to metabolite are very poorly understood. These must be understood before predictions can be made of the route of transport for a pollutant.

Another effect of accumulations of a pollutant in organism tissues like fat might be a decreased rate of metabolism, which could allow the pollutant to be more widely spread. Such a protective accumulation may be most important for certain highly toxic substances with a low persistence, such as organic phosphate compounds used as pesticides or nerve gases. This field, however, is very poorly understood, and the possible role of this kind of process must be evaluated.

GENERAL RECOMMENDATIONS

In the coastal zone, the physical transport processes in stratified estuaries and over

continental shelves that affect conservative pollutants are still poorly understood. The driving forces for chemical reactions caused by mixing fresh water with sea water have not been evaluated for pollutant substances. We still lack good field data on sedimentary particles and chemical data on their pollution content in contaminated areas. In view of this and the specific recommendations below, the task group recommends coordinated physical, chemical, and sedimentological field investigations of selected coastal locations that make a serious attempt to account for the transport of pollutants into the marine environment.

The sea surface is both an entry zone for airborne pollutants and a location for accumulation and chemical weathering of crude oil spills and other contamination, yet we lack even rudimentary chemical data on sea slick composition. The task group feels that organic slicks, suspended aggregates, and particle coatings may be important sites for pollutant concentration and chemical change. Research on the chemistry of these materials should be given high priority.

The study of pollutant accumulation and transport by sediments is complex and does not lend itself to simple elegant approaches. Because the sea floor, particularly near land, is being seriously polluted in many areas, our control decisions must be based on sound knowledge of pollution behavior in sediments. We have no choice but to undertake the extensive and often painstaking research necessary to assess the damage already done and to avert further sea floor deterioration.

The task group suspects that it may be a rule rather than an exception that pollutant substances are altered in form by microbiological processes in the sea. Mercury is rendered more toxic by conversion to methyl mercury, and the same may be true of a number of other metallic contaminants. Biodegradation rates of organic pesticides in general have not been measured under complex marine conditions but may be different, perhaps slower, than they are where the pesticides are applied. Consequently, the task group recommends that the knowledge and skills of biochemists be ultilized to the greatest extent possible in marine pollution research.

S P E C I F I C R E C O M M E N D A T I O N S

PHYSICAL OCEANOGRAPHIC RESEARCH AREAS

+ Undertake quantitative descriptions of physical transport processes in stratified estuaries.
+ Develop time dependent solutions (analytical and/or numerical) for the dynamic and kinematic equations defining the transport and diffusion of natural constituents and of introduced pollutants in stratified estuaries.
+ Improve quantitative understanding of physical transport processes in continental shelf areas through intensive observational programs in representative regions.
+ Determine residence times of water in major ocean basins and mediterranean seas.
+ Develop methods to describe the physical distribution of particulates in all coastal regimes, coupled with programs to collect field data on particulate concentrations and on the occurrence of turbidity flows.

WATER AND SEA SURFACE CHEMISTRY RESEARCH AREAS

+ Acquire baseline information on pollutants in sea water, including both concentration measurements and the determination of principal chemical form.
+ As baseline information, review the chemical properties of pollutants in waters of variable salinity and assess the potentials for chemical reactions associated with estuarine mixing.
+ Undertake research on the shifts in chemical equilibria associated with anthropogenic transformation of bottom waters to anoxic condition.

+ Establish a research program to determine the organic pollutant levels in sea surface samples from natural surface films, contaminant films of man-made effluents (petroleum, etc.) and clean, nonslicked water. These pollutant levels should be determined in organic aggregates and particle-free sea water.

+ Determine distribution coefficients of organic pollutants between these organic phases and seawater. Determine decomposition rates and half-lives of organic pollutants in marine fats and oils and potential petroleum contaminants.

RESEARCH AREAS IN THE GEOCHEMISTRY OF SEDIMENTS AND SUSPENDED PARTICULATES

+ Determine the distribution of pollutants (e.g., heavy metals, petroleum compounds, pesticides) between dissolved forms and particulates such as mineral fragments, Fe and Mn oxides, and organic detritus when they enter the marine environment and after introduction.

+ Determine the relative importance of the physical, chemical and biological processes that lead to incorporation of pollutants into particulate phases or to release of pollutants from particles into solution.

+ Determine the rates at which changes in particulate-soluble distribution of metals and pesticides occur during passage through the coastal ocean. This may involve essentially unidirectional reactions induced by changes in equilibria and continuous dynamic processes approaching steady state.

+ Determine the rates and mechanisms for transport of minerals and organic detritus through estuaries, across and along the continental shelf, and into the deep sea.

+ Determine the character of spatial distribution and horizontal and vertical transport rates of natural suspensoids in the air and water in the vicinity of pollution centers.
+ Determine the effect of sea water on various pollutants on particles deposited in the ocean from the atmosphere.

BIOCHEMICAL RESEARCH AREAS

+ Study modifications of chemical form of trace elements and trace organic pollutants induced by metabolic processes, especially when transport routes in the marine ecosystem are affected.
+ Measure degradation rates of normally low persistence pesticides in the marine environment, especially when persistence may be increased under low temperature conditions or if the pesticides are accumulated in protective organic or inorganic phases.

JOHN BUNT
GALEN JONES
TIMOTHY R. PARSONS
JOHN H. RYTHER
REZNEAT DARNELL
HERBERT L. WINDOM

CHAPTER IV

BIOLOGICAL EXCHANGE PROCESS IN RELATION TO MARINE ENVIRONMENTAL QUALITY

INTRODUCTION

Living organisms may profoundly influence the movement, chemical states, and ultimate fates of polluting agents that enter the sea. In some instances, they may accumulate the pollutants in concentrations far exceeding those encountered in the water itself. In other cases, the organisms may pass the material along quickly to the water, sediments, or other organisms after modifying the chemical and physical states of the polluting agents. In either instance the organisms may directly or indirectly transport the materials over long distances and through a considerable range of depths. On the other hand, the pollutants may act as toxins or stress agents affecting a broad spectrum of marine organisms or only particular life history stages of selected species. Whether one focuses attention on the mechanisms by which marine organisms affect the pollutants or on the effects of the pollutants on organisms, it is clear that many marine species, including those useful to man, may in the long run be adversely influenced by the level of marine pollution. Because of the variety of potentially important polluting agents, the diversity of marine life and the complexity of its processes, as well as the great expanse of the world oceans, the assessment of the organism-pollutant problem is a task of considerable magnitude. Nevertheless, the variables may be sorted out,

rational analytic approaches may be devised, and priorities can be established for field and laboratory investigations that will provide the critical information necessary for understanding the relationships of pollutants to the living systems of the sea.

In order to understand the transfer, transport, and concentration activities of marine organisms that influence the movement, chemical states, and ultimate fates of polluting agents, the following steps are essential:

+ Identification of the specific polluting agents,
+ Identification of the biological mechanisms that may be involved in the transfer of pollutants,
+ Review of the present state of our knowledge of the pollutant-organism relationships in the sea,
+ Laboratory study of biological transfer mechanisms, and
+ Development of models capable of reliable prediction.

POLLUTANTS

Three major classes of pollutants need to be considered: nonsoluble particulates, water soluble materials, and fat-soluble materials, because these properties determine reactivity and fate. A fourth special class includes the microbial pathogens. It is useful to be aware that pollutants may be of natural origin, in most cases concentrated by man, or may exist entirely through human design. The fact that the number of individual pollutants is very large and that biological activity, specificity, and response is widely variable and often not known makes it difficult to recommend specific materials or agents for prior attention in relation to environmental quality. It must be recognized

that technologies and their by-products change. Furthermore, experience on the ecology of pollution is limited and is needed as much as the information on specific pollutants.

NATURAL POLLUTANTS

Crude oil and the constituents of crude oil are basic to the world's economy and the character of modern society. Locally, through sea-floor leaks or by accidental release and, for petroleum products at a wide variety of specific or dispersed entry points, these materials reach the marine environment in quantity and will continue to do so in the future. As a class, these materials present complex ecological problems. However, because of the chemical diversity of the components of oil, researchers should be expected to offer cogent reasons for giving major attention to individual compounds.

Heavy metals (such as mercury, copper, lead, cadmium, nickel, silver, chromium, and cobalt) are normal to the environment and some, at least, perform critical biological functions. As by-products of various industrial processes, however, these substances are likely to become associated with biological materials in toxic concentrations and to accumulate in species contributing to human food needs. The selection of specific elements for study should be based on known or suspected biological activity as well as on existing or potential environmental loading.

Most ecologists are concerned with major nutrient elements as factors limiting productivity. Local overloading, especially by nitrogen and phosphorus, is common and offers a number of alternatives for management that could demand considerable insight in view of likely factor interactions.

Pathogenic organisms create special problems as pollutants, both as agents of human disease carried passively by marine animals and, perhaps, because they could become important as parasites of aquatic organisms in culture at high density. The problems are likely to be confined to zones very close to shore, although it would not be difficult to visualize interference of a much more extensive kind.

Pathogens as well as micro- and macro-organisms with toxic properties can create dramatic situations with individuals or communities as victims. However, consideration of biological agents as pollutants should be held in careful perspective. Ectocrine substances (allelochemicals) may deserve more extensive investigation, although perhaps not in relation to programs addressed to environmental quality.

ARTIFICIAL SUBSTANCES

This remarkably diverse group of chemical compounds includes aromatic and halogenated hydrocarbons, metallo-organics, organic phosphates, detergents, enzymes, chelators and pharmaceuticals. A study of only a few of these materials in large scale is practical, although problems with individual compounds are always likely to arise requiring active research and management. With few exceptions, compounds should be singled out for study as representatives of pharmacological classes, especially those resistant to decomposition and irreplaceable in terms of agricultural practice or some other widespread and essential activity. Halogenated hydrocarbons almost certainly demand priority.

M E C H A N I S M S

The exchange of pollutants in the marine biosphere is governed in part by purely biological processes. These processes may be divided into transfers, involving either the exchange of substances between organisms, or between organisms, water, and detritus, including soluble organic material; and transport, involving the exchange of substances over considerable horizontal or vertical distances. Understanding the dynamics of how pollutants may be exchanged by these two biological processes requires investigation. Further elaboration of the processes involved follows.

BIOLOGICAL TRANSFERS

Biological transfer mechanisms are essentially energy dependent; for example, the uptake of an organic molecule, such as glucose, is an active process involving ATP. At times, however, the transfer of pollutants to some organisms in the biosphere may be facilitated or enhanced by purely physical/chemical processes, such as precipitation, dissolution, adsorption, complexation, and diffusion.

In the act of feeding, organisms transfer pollutants throughout the food web. An important aspect of this transfer is that, in the process of recycling organic material, the food web acts as a continuous extractor in which pollutants may become most concentrated in the oldest organisms of the highest trophic level. The mechanism of feeding may be broadly divided into filter feeding and raptorial feeding; the partition of a pollutant within a single community (e.g., the plankton) may differ, therefore, depending on the feeding process involved. Food secured by either process is not entirely retained by the animal; the initial transfer involves ingestion, which leads to a division of the food item into the portion that is assimilated into the animal's body and the portion that is voided as feces. Of the material that is assimilated into the animal's body, a portion is returned to the environment through excretion. Additional substances may be discarded by some animals, for example, exoskeletons from crustaceans and mucus from fish. Among phytoplankton and seaweeds, organic material formed through photosynthesis may be lost through exudation of soluble substances from living plants. Autolysis and microbial degradation of dead plant and animal tissues also result in the return of substances into the reservoir of detritus in the sea. Biological transfers may lead to a change in form of the original pollutant. Such changes might include detoxification mechanisms (e.g., glucuronide conjugation of phenols), decomposition, dissolution, and specific biochemical modifications (e.g., the methylation of Hg by certain microbes).

BIOLOGICAL TRANSPORT

The transport of pollutants over great distances in the oceans may be accomplished through animal migrations. Anadromous fish and sea birds, may carry pollutants to and from the land under natural conditions. The distances involved in these transport mechanisms may be as much as several thousand miles /yr. In addition, man's harvesting of marine resources results in the transport of marine organisms from the sea to the land. The quantity of biomass transported in this manner may amount to 60 million tons/yr.

Vertical transport in the water column ranges from several meters/day (the sinking rate of phytoplankton) to 1000 meters/day (the migration rate of certain deep sea fishes). Benthic animals transport material through considerably shorter horizontal and vertical distances than those through which pelagic animals transport materials. However, the benthic community reworks sediments, which results in partial return of material to the pelagic food web.

Marine biological processes have the capacity to transfer and transport pollutants more rapidly than most chemical and physical processes. The transfer of pollutants through the food web and their transport over great distances constitutes a rapid transit system in the sea that is comparable to and often exceeds the movement of ocean currents, sedimentation, and vertical mixing processes. It appears important therefore that the mechanisms of transfer and transport outlined above should be identified and quantified in any environment. From these data, and data on the partition coefficients of pollutants in different organisms, it may be possible to provide the information required for models of pollutant exchange discussed in Chapter III.

F I E L D S T U D I E S

To assess the impact of pollutants upon the marine environment, we must determine their

occurrence, distribution, and concentration in the various phases or compartments of the ocean ecosystem. These phases or compartments include the water, sediments, suspended particulate matter, dissolved organic matter, and living biota and, within the latter, the plankton, nekton, and benthos. Only fragmentary information of this kind is now available for some of the better known pollutants and for certain substances such as heavy metals that also occur naturally in the sea. The existing data are also scattered both in time and location and are not adequate to provide a complete budget of any single pollutant in any marine area. Obtaining such basic information is a prerequisite to understanding chemical and biological transfer of pollutants and their oceanic transport. For those pollutants that occur naturally in the ocean, baseline data are also needed from areas believed to be minimally exposed to wastes in order to closely approximate natural levels and distributions of such substances.

Assessment on a world ocean basis is obviously not possible, but assessment could reasonably be undertaken in selected areas. The area should be selected to include tropical, temperate, and polar environments and regions that are both heavily and minimally exposed to pollutants. Four to six such study areas might be a reasonable objective for an initial assessment program, at least half of which should include or traverse major commercial fishery areas. Some of the surveys should extend from the coast, including estuaries and embayments, across the continental shelf and into the abyss, with attention to each of the major depth zones.

Where possible, the selection of areas for pollution studies should take advantage of previous or continuing fisheries surveys or general ecological investigations that can provide pertinent data on standing stocks. The refinement of standing stock estimates should be emphasized only when the information is required as an integral part of ongoing programs of environmental quality.

Organisms should be carefully selected to represent the total biota, and random or opportunistic collections should be avoided. Selections should be based on criteria such as trophic levels,

feeding habits, size, habitat, geographic distribution, quantitative importance in the system, and commercial importance. In order to determine the total mass balance and flux of pollutants through the environment, both the concentration of a given pollutant in each compartment and the total mass of the various compartments must be known. Although the total mass is known for some of the compartments in some geographical areas with reasonable accuracy (e.g., phytoplankton, zooplankton, particulate matter, and dissolved organic matter), present technology limits our knowledge of other categories (e.g., pelagic fishes, benthos).

An understanding of the flux of pollutants through the various compartments of the marine ecosystem also requires knowledge of the routes or pathways of organic matter through food webs. The highly complex subject of food webs is understood only in very general terms in marine systems. However, existing knowledge and recent advances in both qualitative and quantitative aspects of food web dynamics can be used to advantage in the selection of both study areas and representative organisms for the field investigations. Food webs in marine systems should be studied only when they constitute an integral part of other environmental studies.

L A B O R A T O R Y S T U D I E S

Field studies should indicate possible routes of pollutants through marine biological systems and, therefore, suggest which transfer mechanisms are most important. The nature of these mechanisms can be elucidated through laboratory experimentation that permits detailed examination of interactions between cultures of organisms and pollutants under controlled conditions. Laboratory studies also permit the qualitative and quantitative investigation of mechanisms important in the transfer of pollutants from one organism to another within a representative food chain, as suggested by results of field investigations.

Laboratory studies of the biological exchange kinetics of pollutants should be designed to answer the following types of questions:

+ When in the growth cycle of an individual organism is the net uptake rate of the pollutant a maximum?
+ How does the concentration of a pollutant affect its biological exchange kinetics?
+ What effect do environmental factors such as temperature, pH, and oxygen concentration have on biological exchange kinetics?
+ How does the form in which a pollutant exists affect its biological exchange kinetics?
+ Do combinations of pollutants synergistically affect the biological exchange kinetics of the individual substances (e.g., ion exchange and competition for active sites)?

Information concerning organism-to-organism transfer of pollutants is needed. For example:

+ How does the concentration of a pollutant in one trophic level affect that in another?
+ What is the transfer of a pollutant during biological decomposition?

Laboratory studies to determine the basic physical, chemical, and biochemical nature of biological transfer mechanisms should be emphasized so that the information obtained from the artifical laboratory system can be more generally applied to the natural system. Examples of questions that require consideration are:

+ Is the concentration of a given pollutant by an organism due to active uptake or due to physical or chemical processes (e.g., adsorption)?
+ Where in various organisms are pollutants concentrated?
+ What is the biochemical association of a pollutant within a given organism (e.g., heavy metals associated with enzyme systems and porphyrins)?

DEVELOPMENT OF MODELS

Because it is not possible to analyze any one marine system in exhaustive detail or to analyze all marine systems even partially, it is necessary to develop general models for the behavior of pollutants in the marine systems. Such models should incorporate information from both field and laboratory studies and should simulate the behavior of different classes of pollutants in several types of marine situations.

Several types of models should be explored, such as flow diagrams, differential equations, and linear computer models. Models should incorporate information concerning transfer pathways, flow rates, residence times in various compartments, and overall budgets. By bringing together all the available information concerning a given type of pollutant within the context of a particular type of marine system, such models should provide understanding and predictive capability. Thus, it should eventually be possible to estimate the biological effects of various levels of initial pollutant concentration, even as the system is subjected to additional external perturbations (for example, weather or other pollutants).

GENERAL RECOMMENDATIONS

The following recommendations are made in order to establish a predictive capability based on a knowledge of transfer and transport mechanisms:

+ Studies that are likely to provide information on fundamental and widely applicable principles governing the transfer of pollutants should be emphasized.
+ Information on the effect of environmental factors on the transfer processes involved must be obtained.

+ A small number of well-coordinated multi-component field investigations should be chosen, based on their applicability to the control of pollution problems in the sea.

SPECIFIC RECOMMENDATIONS AND SUMMARY

Understanding the influence of community biological activities in distributing pollutants in the sea is especially difficult. Although we have a reasonably good and constantly improving conceptual understanding of ecological species webs, we lack really detailed information on the organization and dynamics of even healthy marine ecosystems. We cannot offer complete budgetary information for even single pollutants in a marine ecosystem, an essential first step in understanding biological control of pollutant transfer. We know little of the effect of pollutants at the ecosystem level or how, once polluted, ecosystems behave in terms of pollutant exchange.

Action on the pollution problem cannot be put aside while scientists unravel the complexities of ecosystem integration. We must take whatever steps are possible with the knowledge currently at our disposal. At the same time, it would be dangerously short-sighted to neglect studies of what may be termed the healthy ecological state.

While there are many reasons for looking into pollutant transfer in entire ecosystems as well as within individual components or segments of the food web, this task group recognized that research along these lines could easily become diffuse and ineffectual. It follows that investigations at the ecosystem level should be expected to have very well-defined objectives and limits. There are a number of options available to assure that researchers effectively manage their activities. Those concerned with the direction of research

effort have a special responsibility in this regard but should not neglect the potential of the innovative individual or small group of investigators in favor of larger frames of control, however important coordinated action may be.

The task group was convinced that progress in marine environmental research will require funding to create expanded research facilities, recognizing the scale of action required in tackling multiple factor problems.

Finally, and not unrelated to the immediate challenge of environmental research, the task group considers it imperative that judicious attention be given to matching training programs to the latest research developments and insights. Additionally, every effort should be made to expose students in basic disciplines to the potentials of involvement in environmental programs.

Recognizing the existence of certain well-defined biochemical, physiological, behavioral, and structural features characteristic of living systems, we recommend research in biological exchange useful in influencing environmental quality, to obtain information on:

+ Representative multiple component marine systems

  Selection to be based on
  - latitudinal coverage,
  - capacity to expose links between coastal, open ocean and depth zones, and
  - interaction with human interests and activities (intense and minimal).

  Data to be collected on the distribution and fluxes of selected pollutants in
  - water,
  - sediments,
  - suspended particulate matter,
  - dissolved organic matter,
  - biota: plankton, nekton, benthos, and
  - major organisms in each group based on:
    trophic position,
    size,
    feeding habits,

quantitative importance,
dynamic importance, and
economic importance.

+ Specific processes (largely in the laboratory)

  Exchange kinetics as affected by:
  - age,
  - pollutant concentration,
  - major environmental variables,
  - form in which pollutant occurs, and
  - co-existence of pollutants.

  Organism to organism transfer in relation to, for example, trophic concentrations of pollutants, and decomposition.

  Basic nature of transfer - physical, chemical or biochemical; cellular and organ sites of accumulation; nature of biochemical association.

+ Integrative techniques based on modeling and useful in prediction and management.

Basic knowledge of biological organization is incomplete. However, emphasis should be placed on research that can make effective use of existing knowledge at all levels.

RICHARD T. BARBER
IZADORE BARRETT
JOHN BLAXTER
HOLGER W. JANNASCH
JOHN A. MCGOWAN
JAMES G. QUINN
LAWRENCE POMEROY
LUIGI PROVASOLI

CHAPTER V

THE EFFECTS ON MARINE ORGANISMS

INTRODUCTION

THE BASIC OBJECTIVE

Society, particularly the components of society responsible for the political and economic management of the oceans, needs information on the biological effects of pollutants that can be used to make management decisions that allow and ensure the continued existence of a functioning and productive ocean. Without this information, the decisions that affect the oceans will be made (and have been made in the past) on economic and political considerations alone. We clearly recognize that we cannot propose with certainty research concepts that will "protect" the essential productive functions of the oceans, but we believe strongly that the currently used methods of assessing pollutant effects are inadequate and that a more complete conceptual framework for designing this kind of research can be recommended. The following report gives our recommendations for the kind of work that will lead to improved environmental management.

BIOLOGICAL TRANSFER TO MAN VERSUS BIOLOGICAL EFFECTS

The problem of tracing a chemical pollutant through a food chain is distinct from evaluating the effect of a chemical pollutant on a food chain or population of organisms. The toxic effects of a chemical pollutant on a natural system and the rate of transfer of that pollutant through the system are inversely related. If a pollutant significantly reduces reproduction, development, or another vital function of an organism, then the amount of the pollutant that can be concentrated and passed through the populations will be less. This observation suggests that organisms most likely to return concentrated chemicals to man are those organisms that are least affected by the pollutant. Studies that indicate that a particular level of a pollutant has no discernible impact on an organism do not indicate that there is no human threat from that organism. The public health threat is related to the concentration and transfer of pollutants in economically important food chains. Woodwell (1970) has proposed that the most complex organisms in an affected assemblage will be the most sensitive to stresses such as radiation. If toxic pollutants behave analogously to radiation then man may be proposed as a very sensitive member of certain marine food chains. (Whether man is necessarily the most sensitive organism of these food webs is not known but can be experimentally evaluated.) This line of reasoning suggests that, if the release of pollutants into the environment is regulated in such a way that human health is protected, a certain level of protection for ocean systems will result. In the absence of better knowledge on biological pollution effects, this strategy is certainly an acceptable one to use.

The inverse situation should also be considered. If the larval development of one of the crustacea in an economically important food chain is the most sensitive link (e.g., Mirex and stone crab larvae; Bookhout *et al.*, 1971), the resulting food resource will decline. Man will suffer from an economic and, in some areas of the world, health threat as a result. The potential health threat of

starvation from the loss of marine protein is no less a threat than the return of a toxic pollutant. Research programs should consider both the *transfer* of pollutants and the *effects* of pollutants.

INADEQUACY OF ACUTE TOXICITY TESTS

In the past, water quality has been evaluated almost exclusively by acute toxicity experiments in which a limited range of test organisms has been subjected to toxicants for a certain time (arbitrarily decided) and the dose required to kill 50 percent (LD_{50}) used as the basis for a standard. Some of the shortcomings of the traditional approach are:

A limited range of test species is used.

Hardier laboratory organisms are used, which are likely to be less sensitive to pollutants.

Adults are used rather than the more susceptible embryos and larvae.

The influence of long-term sub-lethal concentrations on behavior, survival, reproduction, and community structure have not been determined.

In phytoplankton toxicity tests with axenic cultures, no account is taken of bacterial transformation of pollutants as in natural conditions.

The density of phytoplankton in toxicity tests is often unrealistically high, (e.g., over 10^4 cells/ml).

The quality of control media is inadequately monitored, so that the media may contain low levels of other pollutants.

The emphasis of LD_{50} data results in part from legal requirements for evidence that a given concentration of a pollutant will kill organisms.

Research is needed to define more sensitive, but legally functional, criteria that take into account the subtle and long-term effects that will degrade or destroy ecosystems. These criteria have to be developed with both a knowledge of the ecological subleties involved and with a realization of the ultimate use of the criteria required to make and enforce anti-pollution laws.

SELECTING ORGANISMS AND SYSTEMS FOR STUDY

The greatest scientific benefit will result if the intensive research is focused on relatively few kinds of organisms and systems. We are aware of the risk of extrapolating from one organism to another, one population to another, and from one geographical locality to another. These extrapolations must be made because we cannot study all the components of a biological system. The inability to generalize results from specific observations is a major stumbling block in the use of ecological information for environmental management. We suggest that the problem be formally recognized and specific emphasis be given to make each study as widely useful as possible.

We suggest the following criteria for the selection of subjects for study in rank order:

1. Systems (or species) with large amounts of baseline data available (survivorship curves, age, and growth);
2. Systems (or species) of economic importance;
3. Systems that are relatively homogeneous over large areas and therefore have a large absolute flux of materials; i.e., the central oceanic gyres; and
4. Systems of opportunity or exemplary systems that are of interest because their simplicity or uniqueness would give insight into more complex processes of transfer or accummulation of pollutants.

Table 1 indicates organisms for study that fulfill these criteria.

IMPORTANCE OF A CONCEPTUAL FRAMEWORK

For purposes of both planning and analysis, formal statements about the structure and function of the system of concern, be it an organism or an ecosystem, are useful. Such formal statements take many forms: metabolic maps, species lists, compartmental diagrams, or population models. All such statements serve the primary purpose of helping us to organize our plans around the complete system and to focus on the most significant features of the system. One of the most versatile formal statements is a mathematical model. Such a model serves to focus attention in a systematic way and permits us to carry out simulated perturbations of the system that may tell us what the effects of pollutants will be. It is also possible to perform a sensitivity analysis of such a model, which will tell us which components of the system are most sensitive to any perturbation.

Models should be constructed during the planning and proposal stages of pollution research. These may be only compartmental models in which the fluxes and stocks are identified but not yet quantified. In practice, it would not be possible to construct a compartmental model for some systems (e.g., the bathypelagic community) in which all fluxes are identified. However, by carrying this exercise as far as possible we can best define our ignorance of the system and begin to identify what kinds of information are most needed. As the information becomes available, the model is modified (sometimes in unexpected ways), and it can be tested by computer simulation. Specialists in modeling and programming are vital to this phase of the research and should be brought into the research group at the outset to overcome interdisciplinary communication problems.

TABLE 1 Suggested Study Organisms that Fulfill Selection Criteria

	Coastal Pelagic	Coastal Demersal	Oceanic Pelagic	Anadromous Catadromous
WARM-BLOODED	Seal Marine birds		Seal Marine birds	
FISH	Anchovy Herring	Halibut Haddock Plaice	Scombroids *Coryphaena* Migrating myctophids	Salmon Eel
CRUSTACEANS	*Pleuronocodes* *Centropages* *Calanus* *Euphausia pacifica*	Barnacles King crab Blue crab Peneids	*Nannocalanus* *Haloptilus* *Euphausiids*	
MOLLUSCS	Squid (Loliginids ommastrephids)	Oyster Mytilids	Squid (Ommastrephids enoploteothids)	

Examples of models that have functional utility for environmental management at the present time include the population models of fisheries (Beverton and Holt, 1957), hydrodynamic models of water bodies that incorporate biological terms for nonconservative properties (O'Connor, 1965), and models of nutrient flux and energy flux through marine ecosystems (Dugdale and Whitledge, 1971; Patten, 1971; Pomeroy, *et al.*, 1971).

IMPLEMENTATION OF THE CONCEPTUAL FRAMEWORK

Observational and experimental information can be gathered on five levels. These levels have biological connotations; that is, they are the levels of biological organization as well as time relationships. Workers at each level should consider the information needs of the workers above and below them in the following organizational scheme.

Level	Biological Organization	Time Required for Study
I	Biochemical - cellular	Minutes to hours
II	Whole organisms	Hours to months
III	Organisms in communities under controlled conditions	Days to years
IV	Population dynamics under natural conditions	Months to decades
V	Community dynamics and structure under natural conditions	Years to decades

Environmental management must be based on an evaluation of the effects of pollutants on organisms at each of the five levels. The following specific recommendations are proposed for each level to determine the effect of pollutants.

SPECIFIC RECOMMENDATIONS FOR EACH LEVEL

LEVEL I-a, BIOCHEMICAL-CELLULAR (MICROORGANISMS)

Short-term experiments with microorganisms (bacteria, fungi, protozoans, and phytoplankton) provide a quick and relatively simple method of uncovering the toxic or inhibitory effects of any type of suspected pollutant. However, failure to show an effect does not prove the long term safety of the substances tested. The short-term parameters usually measured are respiration and photosynthetic ^{14}C uptake. The ATP method of Holm-Hansen and Booth (1966) and the electron transport method of Packard (1969; Packard *et al.*, 1971) provide two new techniques that should also be used. Past experiments have used two methods of exposure to the pollutants:

exposure to the pollutant for a given period followed by some measurement of biological activity, or

simultaneous addition of the pollutant and measurements of biological activity.

There is no way to predict which method is most relevant to the effect of pollutants on natural population of microorganisms. We suggest that both methods of exposure be used. In experiments involving preconditioning of natural populations, possible changes in species composition should be monitored during the exposure period.

LEVEL I-b, BIOCHEMICAL-CELLULAR (HIGHER ORGANISMS)

Hisopathology, morbid anatomy, and biochemical or physiological disfunction all provide an early warning system for the detection of pollution effects before it is possible to measure the presence of the pollutant chemically in the environment.

The effects of heavy metals on specific enzymes and of petroleum, PCB's, and fat soluble pesticides on lipid metabolism, membrane permeability, and membrane function should be examined. We recommend especially the development of tissue-culture.

techniques for early warning and high sensitivity detection of pollution effects on marine organisms.

LEVEL II-a, WHOLE ORGANISMS (MICROORGANISMS)

Chemical pollutants may be nutrients or toxins. The detection of pollution effects should be carried out on pure cultures, on mixtures of axenic cultures as well as on bacterized cultures and, when appropriate, on natural communities (see Level III). Desirable experimental conditions include:

Constant flow systems for maintaining constant concentrations of pollutant throughout the experiment as well as batch exposures that simulate conditions where the pollutant is degraded or consumed;

Initial concentrations of the inoculum similar to those in nature (e.g., 10^4 cells/liter or less);

For unialgal experiments, a comparison of growth curve and final yield of control and experimental cultures; and

For mixed cultures and natural populations, initial and final assessment of species composition (the change in species composition is as important a parameter as the change in specific growth rate).

LEVEL II-b, WHOLE ORGANISMS (HIGHER ORGANISMS)

Organisms in culture can be used for classical mortality LD_{50} studies. Such studies should be done on the most sensitive and ecologically important organisms even when this demands further research effort into culture techniques. Experiments should also be conducted over much longer periods of time than those used at present.

Threshold determinations should be studied by presenting the organism with increasing concentrations of pollutants below the lethal level. This extension of the LD_{50} concept provides

information useful for early warning, shows the influence of sub-lethal levels, and provides rate information for necessary modeling and waste disposal management.

Thresholds can be of two types: all-or-none and graded (Figure 1).

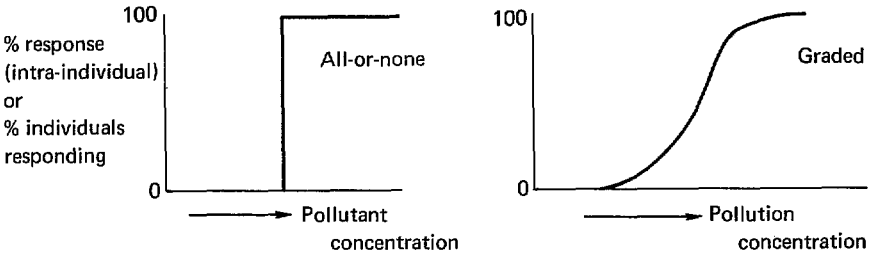

FIGURE 1 Two types of thresholds.

While the abscissae represent increasing pollutant concentration, the ordinates can represent either changing response within an individual organism or numbers of individuals responding. The former has significance at the organism level, the latter at the population level. Threshold studies can be conducted in biochemical, physiological, behavioral, and developmental areas. The following areas are selected as providing the best return in knowledge and as being critical aspects of an organism's biology.

Physiology - We recommend study of the effects of pollutants on membrane function, for example osmoregulation (especially as reflected in salinity tolerance), because membrane function is vital to the integrity of the organism.

The effects of pollutants on temperature optima and temperature tolerance are important because temperature varies so widely in the marine environment and is so important in controlling distribution.

The effects of pollutants on metabolic rate, respiratory quotients, digestion, and food conversion are important because metabolism is a

sensitive indicator of general health, of activity levels and of stress.

Sensory physiology - Pollutants may interfere with sensory perception because behavior and orientation are dependent on input from the chemical environment to the sense organs. For example, interference with chemoreception could influence food selection, homing, and responses dependent on pheromones. High sensitivity assays of nerve function are available to provide a level of analysis not exploited previously in pollution studies.

Behavior - The modifications of behavior by pollutants should be examined because behavior is an integrated organism's total response to the environment. The following areas should be considered:

- locomotor performance and activity levels,
- chemotactic responses in gradients of pollutants,
- extinction and modification of learned responses especially by conditioning techniques (as an experimental tool), and
- unit behavior such as feeding and schooling.

Reproduction and development - Reproduction and early development have been shown to be particularly sensitive to chemical pollutants (Bookhout and Costlow, 1970; Bookhout, *et al.*, 1971). The following aspects of reproduction and development should be examined:

- fecundity
- fertilization rates
- hatching success
- larval development
- larval behavior
- abnormalities
- growth rates

LEVEL III-a, ORGANISMS IN COMMUNITIES UNDER CONTROLLED CONDITIONS (MICROORGANISMS)

Research is needed to develop methods of assaying long-term response of phytoplankton, bacteria, and protozoa to pollution. This should be done directly on natural populations or, possibly, on a mixture of cultured organisms. If culture organisms are used, the response of the test mixture to pollutants would have to be compared initially with the response of natural populations. If a test mixture were developed that showed sensitivity comparable to real systems, it would provide a technique that could be used widely as a routine bioassay.

We recommend that natural communities of marine organisms be cultivated under controlled conditions over periods equal to several or many life cycles or many cell division cycles to permit measurements of the effects of low concentrations of toxic materials. For photosynthetic, chemosynthetic, and heterotrophic plankton organisms, the chemostat offers maximum control of conditions for periods of weeks or months. A considerable number of marine phytoplankton species have been successfully brought under monospecies or axenic cultivation and are available in type culture collections. Harvesting at suitable frequency supplies an abundance of organisms for measurement of important characteristics expected to vary with time and concentration of pollutants. Complex techniques, such as providing an extensive free surface for exposure to petroleum fractions and chlorinated hydrocarbons, are imaginable. The usable results include knowledge of growth rates of individual species and of pathological phenomena at different low concentrations of toxic substances and indices of hazard to organisms for a number of substances and concentrations within 2-3 years. Larger plankton can be cultivated, sampled, and controlled in running water aquaria, by a quasi-chemostatic technique. At this level of operation, the disposal of the toxic substance added to the sea water passing through the tank requires care.

Studies of real communities, because they are taxonomically complex, require the availability of skilled specialists. Long term experiments require measurement of changes in both growth rate and in the taxonomic composition. Such experiments may be difficult to evaluate because substantial changes in taxonomic composition may occur in a period of days in the control as well as in the test conditions. Because pollutants may have a differential effect on certain species, enrichment experiments or pollution assays that measure a parameter such as photosynthesis over a period of days should include observations on the changes in species composition.

It does not seem practical to recommend specific microorganisms for study. Microorganisms selected should represent important taxa (diatoms, dinoflagellates, coccolithophores) and be representative of the latitude and water type considered. Nannoplankton, micro-flagellates, and micro-zooplankton (both pigmented and non-pigmented) are poorly represented in culture collections. Because there is evidence that they are important movers of energy and materials in the open sea (Johannes, 1964; Beers *et al.*, 1967; Pomeroy and Johannes, 1966), they deserve special attention, which they have not yet received, in pollution studies. Present methods for the study, preservation, and culture of these organisms are not sufficiently well established to permit us to assess the impact of pollution on them in a rapid, straightforward manner. General basic research on these components of the ocean ecosystem must be encouraged, so that we can eventually understand the effect of pollution on these important lower trophic levels.

Accurate techniques of measuring activity and population size of microorganism-degrading pollutants must be elaborated. Such techniques will permit studies on the effect of a variety of pollutants and their concentrations on specific microbial populations including the effect of environmental factors on a quantitative basis. It will be important to evaluate the role of the benthic microbial populations as opposed to the microbial activity in the water column.

The microbial attack on, and ultimate removal of, pollutants by microorganisms is closely related to physiological and biochemical processes. Based on Monod's original principle on repression of microbial enzymatic activities (Monod and Wollman, 1947) and subsequent work on metabolic regulation, information should be gathered on the effect of mixtures of pollutants on the over-all degradation rate. Multiple substrates (pollutants) may supplement each other or compete with regard to microbial metabolism. Experimental research on growth and substrate conversion by pure and mixed populations of microorganisms, as initiated by Stumm-Zollinger (1966 and 1968), should typify beneficial and detrimental combinations of pollutants.

Microbial succession during breakdown of complex organic molecules of pollutants should be studied in order to evaluate the appearance of intermediate products. Secondary pollution might occur from microbial growth on such intermediate products. Secondary products of microbial transformations might be more toxic than the primary pollutant. Multistage chemostats will be used to attack these problems. Successive populations can be isolated and studied separately.

Recent microbiological studies have shown a striking slowdown of bacterial activities in the degradation of organic matter in the deep-sea (Jannasch *et al.*, 1971). Studies should be continued in order to come to a clear understanding of advantages, disadvantages, and possible dangers of discharging degradable organic wastes into the deep sea.

LEVEL III-b, ORGANISMS IN COMMUNITIES UNDER CONTROLLED CONDITIONS (HIGHER ORGANISMS)

Commercial fish culture techniques include raising populations of fish in ponds where populations of organisms at several trophic levels are integral components of the system. Nektonic, planktonic, and benthic organisms may be present by design at any level. Commercial practice may include the use of nutritious substances supplementing or effectively replacing one of the higher food

levels, or of only mineral fertilizers, or of native foods brought by currents. On the other hand, unwanted classes or organisms (e.g., benthic flowering plants) may be discouraged or removed by appropriate means. Hall, Cooper, and Warner (1970) demonstrate that valuable scientific data can be obtained by thoughtful application of these techniques. Use of natural, artifically-enclosed, or excavated replicate pools in suitable estuarine environments is recommended to hold wholly or largely native communities under controlled tidal flushing for periods of several months while subjected to chemical treatments held at effectively constant levels.

The population size of each of a considerable number of species of fish, large zooplankton, and smaller forms should be measured at frequent intervals. The age distribution including numbers of eggs and larvae, should be measured. Important characteristics expected to vary with time and concentration of pollutants as previously determined by work on biological functions of individual species should be observed on a statistically significant number of each important species. With associated experiments, birth rate, mortality, and recruitment can be estimated. In pond experiments attention should be paid to the bottom sediments, their biota, and the processes occurring there.

Under these circumstances, it may be possible to observe, at low pollutant concentrations, departures from the usual relative abundance of different components of the community. Because of variability in abundance occurring under the most uniform conditions possible, it will often be difficult to distinguish changes due to pollution. However, this experimental approach should provide other data not obtainable under less natural conditions (e.g., observation of aberrant hunting and avoidance behavior). Great care will be required in managing the effluents from such an experiment.

A pond experiment of the type described above is a relatively long-term project (5-10 years), but it is a valuable means of linking observations on single species or on very simple artificial communities to those on naturally occurring communities.

LEVEL IV, POPULATION DYNAMICS

Our concern about pollution problems stems basically from the fear that populations will be affected. Therefore a number of attributes of species populations should be determined as one important means of judging the magnitude of the threat. The measurements should be made on samples taken from the target populations. Sampling in all cases should be done so that statistical confidence limits and an index of dispersion ($\frac{s^2}{\bar{x}}$, or some other suitable measure) can be calculated.

A number of population variables must be measured:

+ Biogeographic maps of the species average distribution and spatial variations in abundance should be constructed. For many species it is possible to do this with data already extant. Whenever possible, indications of both the total range and reproductive range should be included. Such maps should be constructed every few years, using new data.

+ Population size estimates, including eggs (where appropriate) and larvae, from time series samples should be made, perhaps using a spatially stratified random procedure.

+ The age structure of the population should be determined from time series.

+ The sex ratio of the population should be determined from time series samples.

+ The pollutant "load" of the population should be determined from time series.

+ Fecundity of the populations may be estimated by ovary and testis size (or weight) as a function of size (or weight) of the individuals in the time series samples. In some cases this can and should be expressed as a function of age. Other estimates of fecundity, such as egg counts, may be better.

+ The condition of the organisms in the time series samples should be noted (e.g.,

fatness, thinness, any departures from normal shape, and color).

+ Gut contents should be determined from the organisms in the samples. This should be detailed, detecting, at least, major qualitative shifts in food availability and preference.

+ Pathological examinations of the time series samples should be made.

+ Observations on the behavior of the organisms (before sampling in the field) should be made whenever possible.

Many of the above are already being done, while others can rather easily be added to existing programs of research on the recommended species. In all these programs, very careful attention must be given to the statistical design of the sampling program, so that confidence limits can be calculated for every measurement. Furthermore, every attempt should be made to select sampling strategies that will reduce the confidence limits. Detailed measurements of the physical environment should be taken to correspond to the biological samples taken.

LEVEL V, COMMUNITY DYNAMICS AND STRUCTURE

Our understanding of community structure, dynamics, and stability is not well developed for most neritic and oceanic pelagic areas. In spite of the rather primitive state of our knowledge in this field some important facts are known and some useful techniques and measurements are available. Recurrent groups (i.e., communities) of a limited number of zooplankton and diatom species have been identified in the oceanic North Pacific. Principal components (i.e., communities) of a limited number of zooplankton species have been identified in the oceanic North Atlantic. These studies have, essentially, outlined the ranges of major communities in these two areas. Within these two oceans, and in each of the major community habitats two

types of time series measurements should be made for phytoplankton and macrozooplankton.

Measurements of community complexity and degree of equitability of species abundance can be expressed by the Shannon-Wiener Diversity Index (Shannon and Weaver, 1963). This measurement should be combined with measurements of community stability, expressed by an index, such as the Whittiker Percent Similarity Index (Whittiker, 1962). These measurements could provide a feasible and relatively cheap indication of gradual, subtle, or abrupt changes in community structure in response to fallout pollution. These measures are probably less valuable in neritic zones, which show great statistical variability, than in the pelagic zone. Although similar studies on the deep sea benthos are technically more difficult and more expensive, they should be made. While the study of microzooplankton and nekton should be included, taxonomic and sampling difficulties may make this impracticable at present. Such study is a desirable goal to insure effective understanding of pollution effects.

G E N E R A L R E C O M M E N D A T I O N S

FORTUITOUS EXPERIMENTS

Studies of community and population dynamics must take place over relatively long time spans so that information for management may not be available when needed. However, it may be possible to take advantage of experiments that have already been performed fortuitously by the massive introduction of pollutants into the system. Some of these fortuitous experiments have been documented and could be used for long term studies. We emphasize the value of these events and the need to compile and review carefully the available history of changes in populations that have resulted from local or regional pollution.

THE VALUE OF HISTORICAL COLLECTIONS

Museum collections provide the only means of observing the gradual build-up of persistent global pollutants. We recommend that large collections of organisms be stockpiled now to provide a baseline for observation of the accumulation of new or newly recognized chemical pollutants that will be released into the global environment in the years ahead. We recommend that material from a variety of types of systems (see the section entitled Selecting Organisms and Systems for Study) be collected as rapidly as possible and stored in ultra low temperature freezers until more specific storage recommendations are available.

DONALD W. HOOD
WILLIAM O. FORSTER
VICTOR LINNENBOM
MICHAEL WALDICHUK
PATRICK L. PARKER
JOSEPH L. REID
KARL TUREKIAN
RICHARD PERKINS

CHAPTER VI

THE ULTIMATE FATE OF SUBSTANCES THAT RELATE TO THE QUALITY OF THE MARINE ENVIRONMENT

GENERAL INTRODUCTION

Our task group investigated the ultimate fate of natural or man-made substances that find their way to the marine environment with the potential of harming life processes. We had difficulty distinguishing between the intermediate or transient fate of a substance and the ultimate fate. Some substances may cycle through the marine biosphere for a long time; some, such as heavy metals, may become deposited in the streams, lakes, or estuaries near the source. Still other substances are removed from the cycle by biological and chemical reactions. Because it is sometimes necessary to consider the biota and the water column as well as the sediments as sites of deposition, some duplication with other chapters is unavoidable.

The wide variety of physical and chemical properties of the potential pollutants requires that different ultimate fates be considered for different classes of substances. These substances fall broadly into three groups: nondegradable constituents, degradable constituents, and decomposition products of organic matter.

NONDEGRADABLE CONSTITUENTS

Substances that will not degrade with time or that degrade so slowly relative to the life of man

that they may be considered stable include trace metals, inorganic nutrients, the solid minerals associated with dredging, ash, and a variety of inorganic chemicals and very long-lived radioisotopes. The ultimate fate of these materials is best understood by taking a geochemical approach, involving estimates of input, determination of concentrations, evaluation of rates of movement and geochemical reactivity. The field of marine geochemistry is highly developed, so that such an approach promises to yield useful results within a few years for certain critical pollutants.

DEGRADABLE CONSTITUENTS

Among substances that will degrade to simpler, harmless materials within a short time period are petroleum, petrochemicals, drugs, pesticides, sewage organics, and organic detergents. The fate of some of these substances, such as petroleum, can be studied in relation to organic and marine geochemical information that has become known during the past decade. However, evaluation of the impact and fate of many of these substances, such as the man-made petrochemicals (e.g., chlorinated hydrocarbons), will require new concepts, improved measurement techniques, and extensive field studies.

DECOMPOSITION PRODUCTS OF ORGANIC MATTER

Substances resulting from the degradation of degradable constituents are the ultimate form of decomposition of organic matter. The major component of this group is carbon dioxide. Carbon monoxide, nitrogen oxides, sulfur compounds, atmospheric dusts, and partially oxidized intermediates of organic molecules also occur in quantities sufficient to be of environmental importance. However, because the oceans contain overwhelming amounts of these materials or their derivatives as normal components, most of them will probably have little impact on the oceans. In the atmosphere, the concentration of most of these materials is

controlled through exchange reactions at the air-water interface. It is, therefore, important to study the dynamics of these ocean exchanges to understand and predict the quality of the future world atmosphere.

POLLUTANTS

NONDEGRADABLE CONSTITUENTS

A number of pollutants are indestructible, including heavy metals and dredge spoils that are essentially free of organic contamination or of the products of organic decomposition. They may be converted into different compounds, some of which are more toxic than the element or its original compound, but they are never biologically or chemically decomposed. Characteristically these pollutants have no organic component.

The radionuclides decrease in concentration according to physical laws controlling their half-lives. Biochemical activity may change the site or local concentration of the nuclide but has no effect on the total amount of the radionuclide in a system.

INORGANIC CHEMICALS

The oceanic fate of inorganic pollutants, such as heavy metals and what are sometimes referred to as trace elements, may be dynamic and will depend on the chemical and physical properties of the materials entering the ocean and on their subsequent oceanic chemistry. For example, particulate material entering the oceans may remain in the solid form and reach the ocean floor by direct sedimentation, it may be taken up by filter feeders to become associated with detrital material, or it may dissolve immediately to participate in both chemical and biochemical cycling processes. If a pollutant has a mean residence time in ocean water

of thousands of years, dynamic cycling within the ocean is considered its final fate.

Even the natural level of some pollutant elements in the ocean is of concern. The President's Council on Environmental Quality (1971) has recently listed 14 elements (Hg, As, Ba, Be, Cd, Cr, Cu, Pb, Mn, Ni, Se, Ag, V, and Zn) considered to be potentially dangerous to health and the environment. The following criteria assist in determining if these or other inorganic pollutants would probably affect the environmental quality of the ocean:

+ Is the artificial rate of addition of these elements high compared to their natural addition rates? and

+ Are they in a different chemical form than the naturally occuring element that may be more readily available and more toxic to ocean organisms?

Greatly increased concentration of inorganic pollutants has been frequently documented in estuaries and occasionally documented along coastal areas. For the open ocean, only anthropogenic Pb has been demonstrated to be added at rates that are high compared with natural Pb.

A pollutant element that enters the ocean in a chemical form that is different from that already present may be taken up at a much faster rate, and, therefore, its potential hazard is much greater. For example, available data indicate that the specific activity of ^{55}Fe, with a half-life of 2.7 yr, is 100 to 1000-fold higher in Pacific salmon than in seawater (Palmer, et al., 1968). These observations have been confirmed (Preston, 1970) by measurements in Atlantic cod. One concludes from this that fallout ^{55}Fe is in a chemical or physical form that is far more available for biological uptake than the natural iron in the oceans. Further studies of Pacific salmon have shown that their ^{55}Fe content is decreasing at the same rate at which stratospheric ^{55}Fe enters the troposphere (Jenkins, unpublished data), suggesting that all of the ^{55}Fe is rapidly taken into the biosphere or otherwise made unavailable.

A pollutant element may be taken up preferentially by the ocean biosphere and not be diluted by the natural concentration of that element in sea water. Several radioelements that enter the ocean from their stratospheric reservoir could be used as tracers to define the oceanic behavior of their trace element pollutant counterparts. These include ^{110}Ag ($t_{\frac{1}{2}}$ = 1 yr), ^{108}Ag ($t_{\frac{1}{2}}$ = 107 yr), ^{60}Co ($t_{\frac{1}{2}}$ = 5.24 yr), ^{125}Sb ($t_{\frac{1}{2}}$ = 2.6 yr), ^{65}Zn ($t_{\frac{1}{2}}$ = 265 d), and ^{54}Mn ($t_{\frac{1}{2}}$ = 310 d).

The following research is recommended:

+ The chemical and physical forms of the anthropogenic components must be determined as well as those of the components naturally present in the ocean and entering the ocean from natural weathering processes.
+ The changes in chemical form of these elements occurring with time must be determined.
+ The concentrations of these elements in organisms, particulates, and bottom sediments must be established.

In estuaries, reducing environments are important in the control of heavy metal concentrations. Heavy metals are being introduced into near-shore waters at increasing rates because of human activity. Some of this material escapes the near-shore environment and some is trapped there in sediments. Metals injected into surface waters at other points in the ocean ultimately make their way to potential sedimentary traps in the estuaries. If we presume that an important locus of heavy metal removal is the estuarine environment, the following specific problems need to be assessed:

+ What is the actual method of transport of these elements to the bottom? In particular, what is the flux from direct injection of metal-rich sludges and the flux from trace element incorporation in sinking organic debris produced in the estuarine water column? Is there a role played by the scavenging action of freshly precipitated iron

oxide? Are detrital sediments, especially clay minerals directly injected into the coastal waters without traversing a riverine system, a source of metal released on contact with sea water, or are they potential sinks?

+ What methods can be used to determine rates of accumulation of sediment on the time scale of human modification of the environment? In particular, can ^{228}Ra ($t_{\frac{1}{2}}$ = 6 yr) in shells or ^{210}Pb ($t_{\frac{1}{2}}$ = 20 yr) in sediments be used?

+ What is the actual form of retention of trace elements in estuarine sediments? What is the role of sulfide deposition from *in situ* H_2S production? What is the role of insoluble organic complexes?

+ What are the geographical locations of trace element concentrations within estuarine sediments and how are they related to potential sources of supply by trace-element-enriched streams or sewer outfalls? How well do estuarine dispersion processes obscure point-source supplies of trace elements brought in solution?

+ What proportion of injected trace elements bleeds out of an estuary to the open sea? MnS and FeS have high solubilities in reducing environments, so that Fe^{+2} and Mn^{+2} are released to the overlying water. Compared to tidal flushing times, the rate of oxidation of these metals and of flocculation of their oxides is assumed to be slow. As flocculation occurs, some trace elements will be adsorbed and removed from the system. One method of measuring the quantity of metals transported from an estuary is to assay deep-sea sediments that are iron-rich. This method is difficult because the iron oxide flocs are probably reduced and dissolved and reoxidized and flocced many times before reaching the deep ocean bottom. Another method is to sample the water and very fine-grained iron oxide particles leaving an estuary, thereby determining composition and flux.

RADIONUCLIDES

In the next three decades, an estimated 5000 tons of mixed-fission products representing 860,000 megacuries of radioisotopes of diverse chemistries, such as ^{90}Sr, ^{137}Cs, ^{85}Kr, ^{3}H, ^{95}Zr, ^{95}Nb, ^{103}Ru, ^{141}Ce, and ^{144}Ce, will have to be disposed of in a way that preserves the low background level of the oceans. The ^{90}Sr and ^{137}Co that reach the oceans as soluble radioisotopes will move with the water from those coastal point sources to the offshore mixed layer. During transport, organisms will remove insignificant amounts of the radionuclides. The volatile radioisotopes ^{3}H and ^{85}Kr will be caught in the prevailing winds and enter the surface waters downwind from the injections. The other fission products will be quickly lost from the water as they settle out on particles. Very little biological cycling of these elements will take place in the benthic communities. The greatest biological uptake at all trophic levels will be from the variety of neutron-induced products that are also associated with these fission products, i.e., ^{54}Mn, ^{55}Fe, ^{59}Fe, ^{60}Co, and ^{65}Zn.

DEGRADABLE CONSTITUENTS

This class of pollutants includes synthetic components and mixtures that undergo biological, chemical, or biochemical degradation. The degradation may be rapid microbiological decay, as for ordinary agricultural products, or slow chemical or biochemical change as for the persistent chlorinated aromatic hydrocarbons. Some organic pollutants (e.g., human wastes) may decompose directly to the original building blocks--carbon dioxide, water, and nutrients. Others form intermediate products that may have ecologically harmful properties (e.g., DDE from the degradation of DDT). Other pollutants, such as crude oil, that fractionate by evaporation and partial microbial destruction leave the more refractory components for longer-term destruction.

CHLORINATED HYDROCARBONS

Many synthetic chemicals are being introduced into the environment. Some were developed with a degree of persistence in order to eliminate certain pests. Others, like the polychlorinated biphenyls (PCB's), were developed for particular industrial purposes with long-lasting characteristics. Several of these synthetic organic chemicals have appeared in the marine biota.

The questions that must be answered are:

+ What are the rates of change of chlorinated hydrocarbons in the water, sediments, biota, and atmosphere?
+ What are the processes producing the change?, and
+ What are the sinks?

DDT is chosen as an example to follow through from source to sink because it represents a group of chlorinated hydrocarbon pesticides that have been best documented. Because of their similarity to DDT in properties and behavior, the PCB's probably follow the same pathways and end up in the same sinks.

The National Academy of Sciences Panel on Monitoring Persistent Pesticides in the Marine Environment (NAS, 1971a) evaluated available data on chlorinated hydrocarbons in the marine environment, to determine their mass balance, to predict their behavior and ultimate fate, and to recommend needed action.

The panel members estimated that:

Twenty-five percent of the DDT produced to date has been transferred to the sea, and, even if DDT use stopped immediately, the remaining 75 percent in land reservoirs could lead to increased damage in the sea;

Of the annual production of DDT, 0.1 percent reaches the sea by surface runoff and 25 percent by the atmosphere;

Although chlorinated hydrocarbons have a great affinity for lipids, less than 0.1 percent of

the total production of DDT is present in the marine biota; and

A large proportion of the marine DDT must be in the upper mixed layer of the sea, in surface films and sediments.

The validity of the basic assumptions made in the above study is uncertain and some data have to be checked (i.e., the average concentration of DDT residues in plankton; the average concentration of DDT residues in fish; and the DDT distribution in the upper mixed layer of the sea). In addition, knowledge of the following lacks any degree of certainty and is required, among other things, for more accurate mass balance evaluations:

+ Average DDT concentrations in open ocean waters;
+ Average DDT concentrations in marine sediments, and any variations in areal distribution;
+ Rate of transfer of DDT from water to biota and from biota to sediments;
+ Exchange of DDT between sediments, water, and biota and equilibrium concentrations of DDT in water overlying the sediments;
+ Degradation rate of DDT, as well as that of other chlorinated hydrocarbons, in the marine environment;
+ Partition of DDT and other chlorinated hydrocarbons between the water and surface films;
+ Concentrations of degradation products of the chlorinated hydrocarbons in the open sea water, biota, and sediments (saturation levels of DDE and DDD in sea water are still unknown); and
+ The amount of DDT and its metabolite taken up by the sea birds and recycled through deposition of excrement and bird carcasses on land.

PETROLEUM AND PETROCHEMICALS

The determination of the ultimate fate of petroleum, petrochemicals, and similar degradable materials requires an understanding of chemical and biological decomposition processes and of physical transport processes. Sediment and biota must be considered as possible significant sites of deposition of these substances. The extent to which petroleum and petrochemicals have intruded into the normal marine carbon cycle is important and should be considered at two levels:

Has there been a gross shift in the carbon cycle due to this new carbon source in estuaries; and

Has there been a significant introduction of specific petromolecules into a meaningful number of marine organisms.

Petroleum is a complex mixture containing several types of potential pollutants. Petroleum consists of paraffins, aromatics, asphaltics, and a variety of minor constituents. Petrochemicals are equally complex. Hundreds of synthetic organic chemicals are included in the more than 100 million pounds produced in the United States every year. Some of the substances are potential pollutants, especially in the near-shore environment. Chemical and biological stability, amount released, and biotoxicity are the guides that should be used to evaluate which of these materials may affect the marine biota.

Although it is not feasible to recommend a complete and inclusive research program for organic chemicals in the marine environment, certain specific investigations are needed.

The amounts of total dissolved organic carbon (DOC) and particulate organic carbon (POC) in the open sea are well documented, except perhaps in the major shipping lanes. The highly restricted estuaries which are naturally more variable and difficult to describe, have received less study. A major effort should be made to establish the DOC and POC levels in the major restricted estuaries of the US with potential pollution by petroleum.

The gross impact of man-induced organics on open-sea sediments is probably small except for very local situations. However, the sediments of estuaries are most probably serving as gross reservoirs for the large inputs of organic material.

Several synthetic and natural organic chemicals, particularly chlorinated hydrocarbons such as DDT and PCB, have appeared in the marine biota. Studies are urgently needed both in the open sea and in near-shore waters to determine which of the thousands of synthetic organic chemicals have made a significant appearance in the marine biota.

Petroleum is the raw material for the petrochemical industry and the major source of energy for society. It represents the most massive amount of organic material being injected into the marine environment. In fact, the introduction of petroleum into the marine environment has aroused the concern of the President, the Congress, and the general public more than has any other environmental pollutant. Fortunately, much is known about the composition and chemical and physical properties of petroleum. Much is also known about the natural lipid composition of marine biota and sediments. The question that remains to be answered is: To what extent have petroleum-type molecules appeared in marine biota and sediments? A research program should include the following elements:

+ Systematic studies of oil spills. The processes that degrade an oil spill should receive particular attention. These should include dispersion due to physical processes, rates of chemical and biological oxidation of oil under marine conditions, rates of evaporation and dissolution, and rates of uptake by sediment.

+ A search for specific indicator petroleum molecules in open sea and marine organisms. These should include a readily degraded molecule type, such as normal paraffins, and a resistant molecule, such as a polycyclic aromatic.

+ Improved analytical methods, especially for the higher molecular-weight fraction of petroleum.

NUTRIENTS

Phosphate and nitrate additions to the ocean from man-made sources are of considerable significance to the quality of local coastal environments, including estuaries, bays, coastlines, and (in some instances) the near-shore continental shelf. However, these additions are probably of little significance to the total oceans. If a world population of 6×10^9 people were to inject their metabolic wastes into the ocean, it would require 100,000 years to increase the present fixed nitrogen components by 100 percent.

The major effect of excessive additions of nutrients to the coastal zone is excessive growth of non-endemic plants leading to a change in food chain components for indigenous organisms, frequent increase in the biochemical oxygen demand, lowering of the transparency of the water, and general deterioration of esthetic, recreational, and commercial value of the area. Nutrients discharged into the world's drainage systems reach the marine environment or are incorporated into bottom sediments in fresh water streams or lakes. These nutrients may cycle through several biotic stages in their journey through streams, lakes, rivers, and estuaries. Either through this indirect route or by direct transport, a large portion of them will eventually reach the open ocean to participate in oceanic processes along with the abundant supply already present. Nutrients seem to offer little threat to the world ocean environment. The problem is related largely to the effect of nutrient additions to local areas.

Adequate knowledge is available on the effect of nutrients on plant growth, nutrient cycles, sediment-water relationships, the ratio of nutrients required for growth, the effect of added organic load on the oxygen requirements for metabolism, and engineering know-how for handling of material. To cope with the local nutrient problem techniques need to be developed to enhance flushing or dilution rates of local areas, either by using natural circulation of the system to better advantage or by enhancing dilution by proper outfall design. A better understanding of the

consequences of coastal nutrient enrichment in offshore regions and much more thorough knowledge of the transport of coastal water to the deep sea is needed.

MUNICIPAL AND SOLID WASTES

Several general types of materials are derived from the discharge of municipal and solid wastes in coastal waters:

+ Organic wastes that deplete dissolved oxygen and cause damage to bottom fauna;
+ Toxic materials such as heavy metals, pesticides, petrochemicals, and other industrial wastes;
+ Bacterial and viral contaminants from sewage that give rise to a potential public health problem;
+ Excess nutrients that can cause over-stimulated growth of certain life species; and
+ Dredge spoils that by their mere bulk alone can cover appreciable bottom areas and affect unfavorably the benthic communities.

The eventual fate of the decomposable organic fraction of the wastes depends entirely on the ability of the surrounding waters to handle the chemical and biological oxygen demand associated with the waste. If the rate at which the material is being added exceeds the rate of oxidation (which is true in many localized situations), the degradation of the bottom environment becomes irreversible and anoxic conditions eventually result, leading to formation of noxious hydrogen sulfide and continued accumulation of organic sludge. If the dumping is stopped, can the situation be reversed? The rates of recovery of a dumping area after discontinuance of the dumping will depend on local conditions, rate of renewal of oxygenated waters near the bottom, the type of waste dumped, and natural silting processes. In general, the surface layers of the sludge will begin to oxidize at a

rate dependent on that of renewal of oxygenated waters. Eventually, the anoxic condition of the bottom waters will disappear. However, the organic material buried beneath the surface layers will tend to remain virtually unchanged, because oxidation rates will be limited by the extremely slow processes of diffusion. A similar situation will be obtained if inert material (i.e., certain types of dredge spoil or natural siltation involving materials such as clays and sand) is deposited on top of the organic sludge.

In general, toxic materials entrapped in municipal and solid wastes will be released only from the surface layers. Little is known about the rate of release, which depends on localized conditions.

With the exception of toxic elements and nutrient chemicals, dredge spoils are mostly inert and exert their effects through physical processes such as increased turbidity from suspended particulates and destruction of bottom life by physical burial. Factors determining the rate of recovery of an area where dumping of dredge spoils has been discontinued are relatively unknown; the turbidity effects are presumably short-lived, but the rate at which bottom life is able to re-establish itself may well be slow.

END PRODUCTS OF DEGRADATION

The average concentration in the atmosphere of gaseous products resulting from degradation of organic materials has been estimated by the MIT working group on "Man's Impact on the Global Environment" (SCEP, 1970) to be 315 ppm for CO_2, 0.20 ppm for H_2O, 6.8 ppb for CO, 6.8 ppb for NO and 0.16 ppb for SO_2. All of these gases are important to the global environment, and changes in their concentration will affect its quality. Each has its own peculiar interactions with the oceans, but studies on any of these will probably follow the same general pattern for investigation as that outlined below for carbon dioxide.

CARBON DIOXIDE

The surface mixed layer of the ocean from surface to 200 meters contains about the same amount of carbon dioxide as the atmosphere. The deep ocean contains about 50 times this amount. The circulation between the mixed and deep ocean is remarkably slow. The time scale of CO_2 injection into the atmosphere from man's additions, coupled to the slow turnover rates of the ocean, places a heavy burden on the atmosphere as a reservoir for excess carbon dioxide created by man's activities. Broecker, Li, and Peng (1971) estimate that the atmospheric concentration will be twice its present value in the early 2000's. Others (SCEP, 1970) have provided a longer estimate of the doubling time. There are many assumptions connected with the available estimates, and input to the models and rates of exchange are made from limited data.

The importance of atmospheric concentrations of carbon dioxide to man's future life on the earth cannot be questioned. Its distribution between the ocean and the atmosphere is mainly an oceanographic problem, and it is therefore the responsibility of the ocean science community to gain a clear understanding of the behavior of carbon dioxide in the hydrosphere and its rates of exchange with the atmosphere on a worldwide basis.

The following questions must be answered to determine the fate of carbon dioxide in the oceans and atmosphere:

What are the rates of exchange of carbon dioxide through the sea surface?

What are the physical and other processes of the ocean that transport carbon dioxide both horizontally and vertically, and how rapidly do these occur?

Has carbon dioxide a potential for lowering the pH of ocean water or for affecting ocean chemistry in any way to cause a release of carbon dioxide from other carbon dioxide reservoirs, such as calcium carbonate?

Will shifts in pH due to addition of carbon dioxide at the surface of the sea cause changes in the surface chemistry of the ocean? and

What are the dynamics of carbon dioxide exchange through the ocean surface?

Sufficient information pertinent to oceanography is now available on the composition of the atmosphere. Long-range changes in the atmosphere are necessary, of course, to check ocean exchange models and material balance computations. The distribution of carbon dioxide pressures in surface waters of the world ocean, especially the identification of sinks and sources, such as upwelling, is incompletely known, however, the need for additional broad surveys seems unnecessary. Our understanding of the chemistry of the carbon dioxide system of sea water and techniques for measuring the various components with a high degree of accuracy is mostly satisfactory.

Rate-of-exchange data over a natural ocean or even freshwater lakes are almost totally lacking. Development of techniques for measuring to a high precision the CO_2 pressures near the sea surface is needed for both the air and water phase to obtain concentration-gradient data from which exchange rates can be calculated. The effective film thickness for CO_2 at the sea surface must be calculated. More must be learned about the composition and physical chemistry of the sea surface. The importance of upwelling of waters from below the well-mixed layer rich in CO_2 to the total atmospheric and oceanic reservoirs should be studied. The present concepts of the kinetics of the exchange of components within the carbon dioxide system should be reviewed to determine if the theory fits the environmental observations.

RECOMMENDATIONS

The fate of anthropogenic substances in the oceans defines their immediate and long-term effect on environmental quality. This fate is controlled by chemical, geochemical, and biological processes that must be thoroughly investigated with emphasis on the role of pollutants.

We should take the opportunity to study selected pilot areas where harmful substances have never been added to the environment but are expected to be introduced within a few years. Within limits of present technology such studies should aim to establish baseline data that can show the effect of later stress imposed by man.

GENERAL

All marine studies of the fate of pollutants should include the following information:

+ A baseline survey of existing concentrations in the waters, in the biota, and in the sediment;
+ The effect of the pollutant on the metabolic processes of selected indigenous organisms;
+ Dilution rates, physical transport rates, and, where applicable, the flushing rate of the system;
+ Transfer rates of the material in question between the water, biota, and sediments, and the residence time in each of these reservoirs; and
+ The chemical and biological reactions, the rates involved, and, for degradable materials, the products of decomposition.

SPECIFIC RESEARCH PRIORITIES

+ Petroleum:

  The decomposition rates of representative petroleum fractions in the environment;

  The amount and kind of major fractions of petroleum in water, biota, and sediments;

  Physical processes leading to dispersion, transport, and disposition; and

  Losses due to evaporation.

+ Chlorinated Hydrocarbons:

  Degradation rates of the chlorinated hydrocarbons and their metabolites in the marine environment;

  Rates of sedimentation of chlorinated hydrocarbons through the water column, including the biota; and

  Transfer rates of DDT and other chlorinated hydrocarbons at the air-sea interface, in the presence and absence of an oil slick, and at the water-sediment interface.

+ Municipal Wastes:

  The persistence of bacterial and viral components in sea water;

  The rate at which toxic elements and harmful chemicals leach out of the solid wastes; and

  The rate of recovery of a dumping area after dumping activities have ceased.

+ Radionuclides:

  Cycling of ^{3}T, ^{85}Kr, and ^{239}Pu in the marine environment; and

  Continued studies of pathways of ^{59}Mn, ^{55}Fe, ^{60}Co, and ^{65}Zn in the marine environment associated with that of natural isotopes of these elements.

+ Heavy Metals:

  Chemical and physical forms of anthropogenic material entering the ocean and of natural marine counterparts;

  Movement of heavy elements through the principal marine biota in the food web; and

  Kinetics of transfer processes.

+ Carbon Dioxide:

  Rates of exchange of carbon dioxide between sea and atmosphere; and

  Physical chemistry of the air-sea interface.

REFERENCES

Barger, W. R., W. D. Garrett, E. L. Mollo-Christensen, and K. W. Ruggles. 1970. Effects of an artificial sea slick upon the atmosphere and the ocean. J. Appl. Meteorl. 9:396-400.

Beers, J. R., G. L. Stewart, and J. D. H. Strickland. 1967. A pumping system for sampling small plankton. J. Fish. Res. Board, Canada 24: 1811-1818.

Bertine, K. K., and E. D. Goldberg. 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173:233-235.

Beverton, R. J. H., and S. J. Holt. 1957. On the dynamics of exploited fish populations. Fish. Invest., Ministry of Agriculture, London. Ser. 2, no. 19.

Bookhout, C. G., and J. D. Costlow, Jr. 1970. Nutritional effects of *Artemia* from different locations on larval development of crabs. Helgoländer wiss. Meeresunters. 20:435-442.

Bookhout, C. G., A. J. Wilson, Jr., T. W. Duke, and J. I. Lowe. 1971. Effects of Mirex on the larval development of two crabs. *Submitted* to Water, Air and Soil Pollution.

Bowen, H. J. M. 1966. Trace elements in biochemistry. Academic Press, New York. 241 p.

Brezenski, F. T. 1970. Estuary water quality and Salmonella. Proc. National Specialty Conference on Disinfection. Amer. Soc. of Eng., New York. p. 481-493.

British Medical Journal. 1968. Sewage in the sea. Brit. Med. J. 4:466.

Broecker, W. S., Yuan-Hui Li, and Tsung-Hung Peng. 1971. Carbon dioxide--man's unseen artifact, p. 287-312. *In* D. W. Hood [ed.], Impingement of man on the ocean. Wiley & Sons, New York.

Chow, T. J., and C. C. Patterson. 1966. Concentration profiles of barium and lead in Atlantic waters off Bermuda. Earth and Planetary Science Letters 1:397-400.

Clarke, N. A., G. Berg, P. W. Kabler, and S. L. Chang. 1964. Human enteric viruses in water: source, survival and removability, p. 523-536. *In* Advances in water pollution research, Proceedings of the Second International Conference in Tokyo, Aug. 1964. Vol. 2. Pergamon Press, New York.

Council on Environmental Quality. 1971. Toxic substances. US Government Printing Office, Washington, D. C. 25 p.

Dugdale, R. C., and T. Whitledge. 1970. Computer simulation of phytoplankton growth near a marine sewage outfall. Revue Int. Oceanogr. Med. 17: 201-210.

Egorov, V. V., T. N. Zhigalovskaya, and S. G. Malakhov. 1970. Microelement content of surface air above the continent and the ocean. J. Geophys. Res. 75:3650-3656.

Emery, K. O., W. L. Orr, and S. C. Rittenberg. 1955. Nutrient budget in the ocean, p. 229-309. *In* Natural sciences in honor of Captain Allan Hancock. Univ. of Calif. Press, Los Angeles.

Feely, R. A., W. M. Sackett, and J. E. Harvis. 1971. Distribution of particulate aluminum in the Gulf of Mexico. J. Geophys. Res. 76(24): 5893-5902.

Food and Agriculture Organization. 1971. Report of the seminar on methods of detection, measurement, and monitoring of pollutants in the marine environment--supplement to the report of the technical conference on marine pollution and its effects on living resources and fishing. FIRL/R99, Suppl. 1. Food and Agric. Organ. of the U.N., Rome. 123 p.

Garrett, W. D. 1965. Collection of slick-forming

materials from the sea surface. Limnol. Oceanogr. 10:602-605.
Geldreich, E. E., and D. J. Van Donsel. 1970. Salmonellae in fresh water pollution. Proc. National Specialty Conference on Disinfection. Amer. Soc. of Civil Eng., New York. p. 495-514.
Hacker, D. 1971. Garbage on the high seas. National Observer 10(29):1,14.
Hall, D. J., W. E. Cooper, and E. L. Werner. 1970. An experimental approach to the production dynamics and structure of freshwater animal communities. Limnol. Oceanogr. 15:839-928.
Hartung, R., and W. Klingler. 1970. Concentration of DDT by sedimented polluting oils. Environ. Sci. Tech. 4:407-410.
Harvey, G. R., V. T. Bowen, R. H. Backus, and G. A. Grice. 1971. Chlorinated hydrocarbons in open ocean Atlantic organisms. *In* Proc. of Nobel Symposium, The changing chemistry of the oceans. Gothenberg, Sweden. Aug. 16-20. *In press.*
Harvey, G. W. 1966. Microlayer collection from the sea surface: a new method and initial results. Limnol. Oceanogr. 11:608-613.
Hoffman, G. L. 1971. Trace metals in the Hawaiian marine atmosphere. Ph.D. thesis, Univ. of Hawaii.
Holm-Hansen, V., and C. R. Booth. 1966. The measurement of adenosine triphosphate in the ocean and its ecological significance. Limnol. Oceanogr. 11:510-519.
Hosty, T. S., W. J. Beck, C. B. Kelly, T. G. Metcalf, A. Salinger, R. Shelton, L. W. Slanetz, and A. D. Tennant. 1970. Recommended procedures for the examination of seawater and shellfish, 4th ed. Amer. Pub. Health Assn., New York. 105 p.
Jannasch, H. W., K. Eimhjellen, C. O. Wirsen, and A. Faramfarmaian. 1971. Microbial degradation of organic matter in the deep sea. Science 171: 672-675.
Johannes, R. E. 1964. Phosphorus excretion and body size in marine animals: microzooplankton and nutrient regeneration. Science 146: 923-924.
Johnson, U. G., N. H. Cutshall, and C. L. Osterberg. 1967. Retention of Zu-65 by Columbia River

sediment. Water Resources Res. 3(1): 99-102.
Kanazawa, J., K. Yushima, and K. Kiriya. 1971. Pollution of ecosystems by pesticides, II. Kagaku (Science) 41:384-391.
Kautsky, H. 1966. Possible accumulation of discrete radioactive elements in river mouths, p. 163-175. *In* Disposal of radioactive wastes into seas, oceans, and surface waters. IAEA, Vienna.
Ketchum, B. H. 1969. Eutrophication of estuaries, p. 197-209. *In* Eutrophication. National Academy of Sciences, Washington, D. C.
Kharkar, D. P., K. K. Turekian, and K. K. Bertine. 1968. Stream supply of dissolved silver, molybdenum, antimony, seleneum, chromium, cobalt, rubidium and cesium, to the oceans. Geochim. et Cosmochim. Acta 32: 285-298.
Liv, O. C. 1970. Viral pollution and depuration of shellfish. Proc. National Specialty Conference of Disinfection. Amer. Soc. of Civil Eng., New York. p. 397-428.
Lloyd-Jones, C. P. 1971. Evaporation of DDT. Nature 229:65.
Lovelock, J. E. 1971. Atmospheric fluorine compounds as indicators of air movements. Nature 230:379.
Metcalf, T. G., and W. C. Stiles. 1968. Enteroviruses within an estuarine environment. Amer. J. of Epidemiol. 88:379-391.
Monad, J., and E. L. Wollman. 1947. L'inhibition de la croissance et de l'adaption enzymatique chez bacteria infectees par le bacteriophage. Annu. Inst. Pasteur 73:937.
Mosley, J. W. 1967. Transmission of viral diseases by drinking water, p. 5-23. *In* G. Berg [ed.], Transmission of viruses by the water route. Wiley & Sons, New York.
Mosley, J. W., and M. A. Kendrick. 1969. Hepatitis as a world problem. Bull., New York Acad. Med. 45:143-163.
Murozumi, N., T. J. Chow, and C. Patterson. 1969. Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochim. et Cosmochim. Acta 33:1247-1294.

National Academy of Sciences. 1971a. Chlorinated hydrocarbons in the marine environment. A report prepared by the Panel on Monitoring Persistent Pesticides in the Marine Environment of the Committee on Oceanography. Nat. Tech. Inf. Serv., Springfield, Virginia. 42 p.

National Academy of Sciences. 1971b. Coastal zone baselines and monitoring for pollution and environmental quality. A report to the Coast Guard by the Committee on Oceanography. National Academy of Sciences, Washington, D. C. 23 p.

National Academy of Sciences-National Academy of Engineering. 1970. Wastes management concepts for coastal zone--requirements for research and investigation. A report by the Committee on Oceanography and Committee on Ocean Engineering. National Academy of Sciences, Washington, D. C. 126 p.

O'Connor, D. J. 1965. Estuarine distribution of nonconservative substances. J. Sanitary Eng. Div., Amer. Soc. Civil Eng. 91-SA1.

Packard, T. T. 1969. The estimation of the oxygen utilization rate in seawater from the activity of the respiratory election transport system in plankton. Ph.D. thesis, Univ. of Wash., Seattle. 115 p.

Packard, T. T., M. L. Healy, and F. A. Richards. 1971. Vertical distribution of the activity of the respiratory electron transport system in marine plankton. Limnol. Oceanogr. 16:60-70.

Palmer, H. E., J. C. Langford, C. E. Jenkins, T. M. Beasley, and J. M. Aase. 1968. Levels of iron-55 in humans, animals and food, 1964-67. Radiol. Health Data and Rep., 9(8):387-390.

Patten, B. C. [ed.]. 1971. Systems analysis and simulation in ecosystems, Vol. 1. Academic Press, New York. 607 p.

Patterson, C. C. 1971. Lead, p. 245-258. *In* D. W. Hood [ed.], Impingement of man on the oceans. Wiley & Sons, New York.

Patterson, C. C. 1965. Contaminated and natural lead environment of man. Arch. Environ. Health 11:344-360.

Plotkin, S. A., and M. Katz. 1967. Minimal infective doses of viruses for man by the oral

route, p. 161-166. *In* G. Berg [ed.], Transmission of viruses by the water route. Wiley & Sons, New York.

Pomeroy, L. R., and R. E. Johannes. 1966. Total plankton respiration. J. Deep-Sea Res. 13: 971-973.

Pomeroy, L. R., L. R. Shenton, R. D. H. Jones, and R. J. Reimold. 1971. Nutrient flux in estuaries. Proc. A.S.L.O. Special Meeting on the Limiting Nutrient Controversy. Lawrence, Kansas. *In press.*

Preston, A. 1970. Concentrations of iron-55 in commercial fish species from the North Atlantic. Mar. Biol. 6(4):345-349.

Seba, D. B., and E. F. Corcoran. 1969. Surface slicks as concentrators of pesticides in the marine environment. Pestic. Monit. J. 3:190.

Shannon, C. E., and W. Weaver. 1963. The mathematical theory of communication. Univ. of Illinois Press, Urbana, Ill. 117 p.

Slanetz, L. W., C. H. Bartley, and T. G. Metcalf. 1964. Correlation of coliform and fecal streptococcal indices with the presence of Salmonella and enteric viruses in seawater and shellfish, p. 27-35. *In* Advances in water pollution research, Proceedings of the Second International Conference in Tokyo, Aug. 1964. Vol. 3. Pergamon Press, New York.

Study of Critical Environmental Problems (SCEP). 1970. Man's impact on the global environment: assessment and recommendations for action. The MIT Press, Cambridge, Mass. 319 p.

Stumm-Zollinger, E. 1966. Effects of inhibition and repression on the utilization of substrates by heterogeneous bacterial communities. Appl. Microbiol. 14(4):654-664.

Stumm-Zollinger, E. 1968. Substrate utilization in heterogeneous bacterial communities. J. Water Pollution Control 40(5):213-229.

Tsunogai, S., and K. Ikeuchi. 1968. Ammonia in the atmosphere. Geochem. J. 2:151-166.

US Department of the Interior. 1970a. Mineral facts and problems. Bur. of Mines Bull. 650. US Government Printing Office, Washington, D. C. 1291 p.

US Department of the Interior. 1970b. Minerals Yearbook 1968, Vols. I-IV. US Government Printing Office, Washington, D. C. 3025 p.

US Tariff Commission. 1970. Synthetic organic chemicals, U. S. production and sales, 1968. US Tariff Pub. 327. US Government Printing Office, Washington, D. C. 266 p.

Ward, G. H., and W. H. Espey [ed.]. 1971. Estuarine modeling: an assessment. Capabilities and limitations for resource management and pollution control. Rep. No. 16070 DZV, US Environmental Protection Agency. 126 p.

Weiss, H. V., M. Koide, and E. D. Goldberg. 1971. Mercury in a Greenland ice sheet: evidence of recent input by man. Science. *In press.*

Whittiker, R. H. 1962. Classification on natural communities. Bot. Rev. 28:1-239.

Woodwell, G. M. 1970. Effects of *pollution* on the structure and physiology of ecosystems. Science 168:429-433.