Scientific Problems Relating to Ocean Pollution

Proceedings of a Workshop on

Scientific Problems Relating to Ocean Pollution

Estes Park, Colorado, July 10 - 14, 1978

March 1979

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
Environmental Research Laboratories

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Edward D. Goldberg (Editor)

Boulder, Colorado

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UNITED STATES DEPARTMENT OF COMMERCE
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National Oceanic and Atmospheric Administration
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Environmental Research Laboratories
Wilmot N. Hess, Director

PREFACE

On July 10-14, 1978, a workshop was held in Estes Park, Colorado, organized by Dr. Wilmot N. Hess, Director, Environmental Research Laboratories, NOAA, and Professor Edward D. Goldberg, Scripps Institution of Oceanography. The purpose of this workshop was to (1) write a strong, comprehensive statement of the scientific problems of ocean pollution; and (2) identify research, development, and monitoring programs that should be undertaken in order to solve these problems. This workshop was organized just at the time that Public Law 95-273, dealing with marine pollution, was being passed. The workshop was intended to be a contribution toward the development of a national plan for marine pollution research and development and monitoring. In draft form, this document has been made available to the Interagency Committee on Ocean Pollution Research and Development and its subcommittees to help them prepare their portions of the national plan.

The workshop achieved its objectives. The report offers valuable guidance in the preparation of the Federal plan required by Public Law 95-273. I am grateful for the leadership and initiative of Prof. Goldberg and Dr. Hess in organizing the workshop and promptly preparing this document.

Ferris Webster

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Assistant Administrator for
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OCEAN POLLUTION RESEARCH, DEVELOPMENT, AND MONITORING NEEDS

Report on a Workshop at Estes Park, Colorado
July 10-14, 1978

REVIEW AND OVERVIEW

Edward D. Goldberg

1. INTRODUCTION

The scientists who convened at Estes Park in July 1978 to prepare a research and monitoring program in marine pollution were guided by several prevailing moods. First, there was an overwhelming, and possibly overemphasized, sense of the complexity of both the marine environment and its pollutants. Hosts of interactions take place between the organisms of the sea, their environment, and people. Formulating effective laboratory experiments or making relevant field measurements tries the abilities of our most competent workers. Marine pollutants may act individually or in concert; natural phenomena are often difficult to distinguish from human-induced changes.

Second, in a more positive vein, the scientists recognized that the marine system must be treated as a resource for humans, and that the ability of the waters and sediments to accept wastes must be assessed continually. These two concerns influenced the setting of priorities for research.

The scientists who met at Estes Park sought tactics for early recognition of potential pollutants in the coastal zone. In the past we have recognized some and managed them effectively, for example, the radionuclides introduced from the nuclear fuel cycle. For others a catastrophe has provoked action; for example, the Minamata Bay epidemic poisoning led to identification of mercury methyl compounds, and the impact on non-target organisms caused concern about DDT and other biocides.

The ultimate goal is to keep the resources of the oceans renewable. By doing this we are protecting our ability to utilize foods from the sea without jeopardizing public health, to maintain healthy ecosystems, which in turn provide food resources, to utilize the oceans as recreational areas without fear of poisoning by pollutants, and to enjoy the beauties of the marine system.

Each panel studied one significant set of pollutants. A few phenomena sometimes considered to be polluting such as heat, beach erosion, and sedimentation by river plumes, were not studied. The panel recommendations presented in the report propose research activities that are relevant to recognized and potentially solvable problems in marine pollution. This review highlights the more important recommendations of the panel.

2. SOURCES OF POLLUTION

2.1 Synthetic Organics

Synthetic, organic chemicals present a "text-book" example of the complexities involved between the antagonists, the pollutants, and the protagonists, the organisms they affect. It is tragic that, so far, we have identified these pollutants only through catastrophic events. As a consequence, the proposed research activities center about strategies to manage and manipulate the existing and forthcoming data that relate to both pollutant concentrations and their biological effects.

The pesticide DDT was the first synthetic organic to be regulated as a result of its effect on non-target organisms. Marked decreases in the reproductive success of spotted seatrout, a commercially important marine fish on the south Texas coast, were associated with high DDT residues in the fishes' eggs; fish productivity rose after the United States banned DDT usage in the early 1970's. Of readily recognizable economic concern is the recent "Kepone incident" in which the synthetic organic pollutant was identified as dangerous through the morbidity of people engaged in its manufacture. Wastes from the production facility were released into the James River and subsequently entered the Chesapeake Bay estuary. The levels of Kepone in some fish exceeded the permissible FDA levels. The commercial fishery was closed for many species with losses not only to fishermen but also to dock-workers, restaurants, truckers, railways, boat dealers, and tackle and bait suppliers. Several decades must pass before the estuary is cleansed enough to bring the Kepone residues in fish below the maximum permissible levels.

The synthetic organic chemicals of concern contain chlorine atoms and are analyzed by gas chromatographic techniques. The spectra issuing from these instruments contain many unidentified peaks. Peaks may represent substances that occur naturally, or those introduced by human activity. (The polychlorinated biphenyls (PCBs), chemicals that have been extensively used in industry, were identified as pollutants through the widespread occurrence of their peaks in environmental samples.) To determine the compound represented by an unknown peak may cost thousands of dollars and many months of study.

REC 1 The development of a national, computerized network for accumulation and storage of information about spectral peaks on gas chromatograms is the primary research activity proposed relative to pollution from synthetic organics.

By developing standardized methods of analysis, each peak can be assigned a number characteristic of its appearance in the gas chromatograms. The number for each environmental sample can be stored in a computer system as a function of the date and site of collection.

When a peak occurs in only one area, a point source of pollution is indicated, which can be investigated. Cosmopolitan occurrences of peaks suggest widespread pollution or naturally occurring material. Biological disasters in a given area may be considered in the light of information within the computer. The identification of problems before they reach crisis proportions is the desired result.

2.2 Chlorination Products

In the future the coastal ocean may be used mainly as a reservoir for excess wastes and heat produced by human activity. The transfer of heat and some wastes to the marine system is producing another category of pollutants--the chlorination products. Chlorine is introduced to waste waters to disinfect them partially and to cooling waters of electric-power generating plants and other industrial facilities to minimize slime and other types of biofouling. The chlorine interacts with the organic materials of seawater to produce chlorinated substances and with the bromate ion to produce bromine and hence brominated organic compounds. Among the compounds formed are chloroform and bromoform, both of which have carcinogenic and mutagenic properties. The use of chlorine is expected to increase in the future, and hence it is a cause for concern.

Scattered but increasing evidence indicates that undesirable impacts on marine organisms are associated with the use of these chlorination products. Lethal effects were found in a California commercial mariculture enterprise that used chlorinated power plant effluents. Oysters, which exhibit measurable uptakes of halocarbons (such as chloroform and bromoform) provide a potential route to humans for these toxic substances. Waste waters with no measurable chlorine residuals caused measurable shifts in the colonization and composition of communities of marine algae. Current regulations are based solely on residual oxidant levels and not on oxidation (chlorination) products and thus may need evaluation.

REC 2 It is recommended that priority attention be given to problems concerning the composition and formation of the higher molecular weight organic halocarbons.

The production of specific products is governed by temperature, salinity, light intensity, and other factors that have not been characterized. Perhaps toxicity of effluents can be reduced under some conditions. Once oxidation products are identified, studies of their impact on marine ecosystems and their fates and persistences in the marine system can be undertaken.

REC 3 Studies are needed to determine the reactions of anthropogenic organics in waste water to the treatment process.

More toxic substances may result from the treatment process, such as the chlorination of phenol which produces chlorophenols, or the pollutant may be destroyed, as by the oxidation of a pollutant metal from a bio-available to a less bio-available form.

2.3 Dredging and Large-Volume Waste Disposal

REC 4 New sites must be designated for disposal of increasing volumes of dredged materials and solid wastes in the future.

REC 5 To accomplish this, criteria must be developed for new site selection, and new techniques must be developed for disposal of materials.

Since sites and the material to be disposed have unique characteristics choices must be made between containment and dispersal of the material to be disposed, and each site must be evaluated for its capacity to retain discharged materials, on the basis of its physical, biological, and geological characteristics.

REC 6 Dredged materials and barged wastes must be characterized as to their physical and chemical properties so that their fates at a given site can be predicted.

REC 7 Pollutants identified in this report should be assayed to ascertain if any public health or ecological risks are involved in their disposal.

Contact should be established with major United States chemical companies and industrial facilities to determine the amounts and types of wastes they expect for the future and their plans for disposal.

REC 8 To formulate appropriate models to evaluate the adequacy of potential disposal sites, on-site investigations of long-term changes of materials are needed, especially with regard to the release of pollutants and to any increased turbidities due to chronic dumping in the areas.

Procedures for cleanup or rehabilitation of severely polluted areas are urgently needed. Examples of severe pollution include Kepone in the James River, polychlorinated biphenyls in the Hudson River, and mercury in Lake St. Clair and the Detroit River. Remedial activities have been delayed because no substantial scientific base has been developed to guide operations.

REC 9 To develop clean-up and rehabilitation procedures, research programs should be initiated with feasibility studies, followed by pilot scale operations, and, finally, formulation of contingency plans.

2.4 Litter

Litter is any solid anthropogenic or natural product that is out of place in the environment. Litter encompasses a variety of substances: plastics and synthetic organic materials, glass, metals, wood, petroleum products in the form of tar balls, grease balls, and the natural organic articles. Litter can be found in beaches, coastal and open ocean waters, in or on bottom sediments, and in marine organisms. Its sources include recreational activities on land and on sea, ship discharges, industrial inputs, and sewage-related additions such as storm system overflow and by-pass of treatment systems.

Although litter has been found in the internal organs of marine organisms, there is no clear evidence of morbidity or mortality from its ingestion.

REC 10 Experiments are recommended to assess the effects of ingestion of litter by birds and fishes.

The accumulation of litter on beaches is a major aesthetic problem. The cost of clean-up is high, and economic losses to beach-related industries for a single beach can reach annual values of tens of millions of dollars, as noted on Long Island.

REC 11 Comprehensive, quantitative studies of the types, fluxes, and persistence of litter must be made.

REC 12 Most important, ways must be developed to keep litter out of the oceans, especially litter that fouls beaches or jeopardizes the health of marine organisms.

REC 13 Studies on the persistence of plastics in the marine system (i.e., studies of photo-oxidation, biodegradability, and mechanical breakdown) should be made to indicate directions of regulatory action.

2.5 Artificial Radionuclides

The management of releases of artifical radionuclides into the environment is a classic case of using scientific information to minimize losses or restrictions on the use of environmental resources. Soon after production of nuclear energy began, the question was asked: What amounts of artificial radionuclides can be accommodated in the marine system without danger to public health, marine ecosystems, or marine organisms? With the minimal information available in the 1950's, guidelines for acceptable levels were formulated; they were modified as better and more complete data became available. Monitoring and surveillance programs provided descriptions and then predictions of the distribution of radionuclides in the oceans. To date, no impacts on human health have been documented; no effects harmful to marine organisms are known, even at the sites of large discharges, such as the reprocessing plant in Windscale, England.

The Estes Park panel on artifical radionuclides posed as the major problem the assessment of the deep ocean floor for the emplacement of high-level radioactive waste. Sub-seabed storage is an alternative to terrestrial depositories.

REC 14 For information adequate to predict the consequences of inadvertent releases of radioactive material to the deep-ocean environment, research programs are needed in geology, geophysics, sediment physics and chemistry, oceanography, abyssal ecology, and radio-ecology.

REC 15 The speciation of many artificial radionuclides in marine waters must be determined, especially for transuranic elements (i.e., plutonium, americium, and curium).

Such information is essential to predict the elements' behavior in the coastal ocean and their availability to marine organisms. The behavior of a species with respect to sedimentation is important to ascertain the species' persistence in the aqueous state.

REC 16 Finally, existing dump sites should be watched for leakage of radionuclides to test the validity of present assumptions about the retention of disposed materials in the sediments and to provide a basis for the selection of future disposal areas for low-level radioactive wastes.

2.6 Microorganisms

Microorganisms released into coastal waters by discharges of human and lower animal wastes can jeopardize public health, since some of these organisms are agents of both human and faunal disease. Hepatitis A and gastroenteritis, probably caused by the Rotaviruses and Parvo-like viruses, are the most common enteric diseases associated with recreational water use or consumption of shellfish harvested from coastal and estuarine waters.

REC 17 The development of recovery and enumerative methods for these viruses constitutes a priority research need.

REC 18 In addition, an assessment of epidemiological data to ascertain the relationship between populations of organisms and effects on human health is needed.

REC 19 Risk analyses of the data are essential.

Recent investigations suggest that infectious diseases in fish, crustaceans, and mollusks, caused by viruses, bacteria, fungi, and protozoa, are more prevalent in degraded marine environments. Fin rot is significantly more common in demersal flatfishes from areas receiving domestic wastes than in those from more pristine areas.

REC 20 Research is recommended to investigate the relationship between degraded environments and the occurrence of infectious disease, with emphasis upon the vulnerable stages of organisms, the larvae and juveniles.

Finally, there is a concern about the effect of wastes on the existing populations of marine micro-organisms. If the load capacity of the oceans is exceeded, the marine ecosystem may be drastically altered, perhaps with the loss or restricted use of food or recreational resources.

REC 21 Research is needed to ascertain the load capacities of coastal waters and to determine the rates at which existing marine populations degrade wastes, such as petroleum products, pesticides, and organic industrial effluents.

The delineation of areas that can accommodate greater waste burdens may result from such studies.

2.7 Trace Metals

During the past 5 years marine chemists have found that the concentrations of some trace metals in sea water are one or several orders of magnitude less than had previously been believed. The ability to sample sea water and to analyze it accurately for its trace metal without introducing contaminants has led to this discovery. As a consequence, human mobilization of metals such as lead, cadmium, copper, zinc, and chromium may be as great or even greater than movement of the metals in the major weathering cycles. Several areas of concern have developed: the impact on human health of the ingestion of seafoods enriched in trace metals, the toxicity of trace metals to marine organisms, and the disruption of ecosystems through trace-metal caused alterations of phytoplankton populations.

A notorious case of metal poisoning of humans through the consumption of seafood is the Minamata Bay incident in which methyl mercury chloride was released from a chemical plant into the bay, then consumed in seafood, causing fatalities and morbidities. No metal pollution episodes have been reported for United States coastal waters. However, researchers must be aware of potential dangers because many sea organisms consumed by people are able to concentrate such toxic metals as mercury, cadmium, lead, and selenium.

There are reports of an abalone kill from pollutant copper and of the loss of detoxification abilities of mussels by overexposure to trace metals. But perhaps of greater importance is the possibility that such metals as zinc and copper can alter the assemblages of phytoplankton species. The form of an element determines its toxicity. For example, the toxicity of copper is related to the abundance of free copper ions, which is decreased through complexation with natural and anthropogenic organic compounds.

REC 22 Research should include accurate measurements of metals in coastal waters and the fluxes of such metals from anthropogenic inputs.

REC 23 We must determine the forms of metals in sea water and their relative availability to marine organisms, especially phytoplankton, which will make possible prediction of their potential impacts on food chains.

2.8 Biostimulants

A continually increasing input to coastal waters of substances that enhance the growth of marine plants has altered marine ecosystems, usually in an undesirable way. These biostimulants, which include compounds of nitrogen, phosphorus, silicon, and metals, as well as dissolved organics, are introduced primarily in sewer outfalls. Perhaps their most dramatic effects are alterations in the composition of the food chain base and increases in the plant population. Usually, the small microscopic plants, the diatoms, which are the food of filter-feeding fishes and zooplankton and hence support large fish populations, are displaced by flagellates (marine weeds), poor foods for many of these grazers. The increased plant life can result in excessive oxygen consumption in the waters, leading to anoxic conditions, a situation that has been reported to result in fish kills, often of commercially important species. Anoxic conditions also discolor and cause unpleasant odors in waters and render them unpleasant for aesthetic and recreational uses.

There are many widespread and well-documented examples of biomass increases, anoxia, and changes in community structure resulting from the anthropogenic inputs of biostimulants: Chesapeake Bay, New York Bight, California embayments, San Francisco Bay, Kaneohe Bay, Lake Erie, and Long Island's Great South Bay and Moriches Bay. Ocean dumping has little effect on these problems in the New York Bight; biostimulants introduced from outfalls have caused the trouble.

REC 24 The priority research problems are distinguishing between natural and anthropogenic biostimulus to coastal ecosystems and assessing the magnitude of each.

The interactions among biostimulants, toxic pollutants, food chains, and physical parameters make the problem especially complex. Solutions may be found in coupling predictive models with necessary inputs from field and laboratory studies. Although variations in many of the parameters tend to make each model site-specific, general models of wide applicability should be sought. The complementary laboratory and field studies should provide an understanding and quantification of the interactions among the phytoplankton, biostimulants, and the physical forcing functions. Models will enable researchers to gauge the trend of a coastal water zone toward either a healthy situation or one approaching eutrophication, the overstimulation of plant activity.

2.9 Fossil Fuel Compounds

Petroleum compounds and their degradation products are the main components of this group of pollutants. Petroleum usage is predicted to decrease substantially in the next 30 years or so; simultaneously, use of coal and oil shale will increase as energy sources and feedstocks for the production of chemicals. Coal gasification and liquefaction, shale processing, and combustion and transport introduce many of the same compounds into the environment that petroleum does. Thus, a knowledge of the fates and impacts of petroleum hydrocarbon in the marine environment will be a basis for understanding coal and oil shale problems.

REC 25 The accumulation of data about sources of inputs of fossil fuel is a priority research activity.

Such information is necessary to describe present distributions more adequately and to predict future ones. The following sources of fossil fuel compounds have already been identified: marine transportation and operations, offshore production, atmospheric transport from fossil fuel combustion, land-based discharges via rivers and industrial and domestic outfalls, and dumping. In addition, it is necessary to identify fluxes of hydrocarbons from seeps, forest and grass fires, and vegetation, to distinguish natural from pollutant inputs.

To construct descriptive and predictive models, the fates of the petroleum hydrocarbons in the marine system must be understood. Their destruction or alteration by biological and inorganic processes is of first-order interest.

REC 26 Recommended for priority study are the rates of microbial degradation of petroleum components and the role of photochemical reactions in altering or destroying hydrocarbon compounds.

Although acute, biological effects of oil pollution, such as mass mortalities, require immediate remedial measures,

REC 27 future research should emphasize long-term, interdisciplinary studies of sublethal biological effects of oil pollution.

Since not all compounds or organisms can be studied, initial efforts should be directed toward persistent toxic substances or compounds that produce toxic substances upon degradation. Because petroleum compounds have shorter residence times in water than in the sediments, benthic organisms are subjected to greater exposure than are pelagic organisms. Hence,

REC 28 benthic organisms should be emphasized in either individual organism or community studies.

3. BIOLOGICAL EFFECTS

Researchers have not identified biological effects, other than the very obvious mass mortalities, associated with the entry of pollutants into the marine system. Not only is there a complexity associated with the interactions between the organisms constituting a community but there is a complexity concerning the pollutants themselves. Do they interact independently or are there synergistic or antagonistic effects through exposure to two or more contaminants? The following variety of available approaches further complicates a research program: studies on single organisms, food chains, communities of organisms, and entire ecosystems by investigations that may be physiological, behavioral, biochemical, or ecological.

The Estes Park Workshop Panel on Biological Effects submits that the outstanding problem is determining whether pollution is the cause of a significant alteration in ocean life, even when pollution is clearly associated with an environmental change.

REC 29 The panel proposes that long-term studies of the natural variation in unpolluted marine ecosystems be initiated so that we can ascertain what types of changes are normal.

To accumulate enough significant data, the studies should continue through a decade, although three-to five-year programs would provide the stepping stones for future work. The study sites should be representative and easily accessible. They would include an intertidal muddy site such as a salt marsh (e.g., Savannah River Estuary); a nearshore mud bottom community; an intertidal rocky coast community; a nearshore sand bottom community; a pelagic community in a bay or estuary. A species list would be prepared for each site studied. The list would provide a basis for studying the community structure and the flow of energy through it during longer time periods. Surveys would be made at frequent intervals. Thus, the range of natural variations could be determined.

REC 30 Complementing these ecological studies would be investigations involving the manipulation of small ecosystems by introducing pollutants, followed by studies of their effect.

The goal would be the determination of how pollutants, singly and in combination, affect ecosystem structure and function. Ecosystem studies of this type have been carried out for the forests at Hubbard Brook, for salt marshes at Cape Cod, and for lakes in Manitoba.

REC 31 Whole ecosystem studies, although more expensive and more complicated to manage, are recommended, rather than the large-scale enclosure studies popular at the present time.

4. MONITORING

REC 32 Complementing the proposed research programs must be surveillance programs to monitor pollutant levels at given sites during extended time periods.

The ongoing Mussel Watch project measures pollutant levels for heavy metals, petroleum hydrocarbons, synthetic organics, and artificial radionuclides at 120 coastal stations, using bivalves (e.g., oysters, mussels, clams) as sentinel organisms (Goldberg, 1975, 1978). Surveillance techniques must be developed to study pollutants that cannot be monitored by bivalves, e.g., litter microorganisms, biostimulants, dumped wastes, and oxidation products. Since pollutants may stress organisms or ecosystems in cumulative ways, coordinated programs in coastal marine monitoring are essential. To ascertain whether any biological impacts have occurred at a site, all monitoring data should be stored in one place and be made available to investigators. Comprehensive and flexible information systems must be developed concurrently with the monitoring programs.

Countries sharing coastal waters must depend on each other for monitored pollutant data that in turn may be used to formulate guidelines for marine pollutants. The increasing uses of materials and energy by most countries has led to increasing disposal of pollutants in coastal waters, and the marine pollution of one country may be created by another. The International Atomic Energy Agency has written guidelines for the oceans' abilities to handle radioactive wastes, but such information is lacking for other pollutants.

Research and monitoring strategies formulated by United States efforts will provide patterns for their extension to global or regional programs.

5. REFERENCES

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SYNTHETIC ORGANICS

Philip A. Butler, Robert Huggett, Kenneth Macek,
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1. INTRODUCTION

1.1 Problem Identification

Synthetic organic compounds are now universally distributed in the world's oceans. Contamination levels in the coastal zones are substantially higher, and, in recent years, excessive pollution by the synthetic organic compounds has closed some major fisheries (e.g., Michigan, New York, and Virginia; Boyle, 1975; U.S. EPA, 1978). The economic consequences have been severe. Action in response to these events has always been a reaction to crisis situations. It is now our task to develop a more rational approach to these problems.

Global production of synthetic organic chemicals continues to increase at a rate considerably higher than the population growth. New chemicals, including byproducts and wastes of manufacturing, are entering the environment in proportion to the production. In response to past events, including the history of PCB contamination, and in response to growing public awareness and concern, new laws have been promulgated on state, national, and international levels with the intent to prevent the release of potentially hazardous chemicals into the environment. Such laws, however, offer no guarantees that the past will not be repeated, nor do they guarantee that "mirex" and "Kepone" will be the last mistakes.

No longer is dilution the solution. Once introduced into aquatic environments, synthetic organics partition, depending partly on their polarity, to all components of the ecosystem. Concentrations in some biota, such as fish, may be unexpectedly high. The dynamics of transport of a synthetic organic pollutant in estuarine and marine environments are diagramed in Fig. 1. For some pollutants, such as PCB's and DDT, atmospheric input into the marine environment is significant. Eventually the more persistent of these pollutants are permanently deposited in the bottom sediments but only after cycling through the biota, perhaps many times.

In the past 10 years information concerning the dynamics and the biological effects of certain synthetic organics in the environment has had a strong influence on the development of pollution-related legislation. For example, the use of the pesticide DDT was banned in 1972, and the uses of a number of other chlorinated hydrocarbon insecticides have

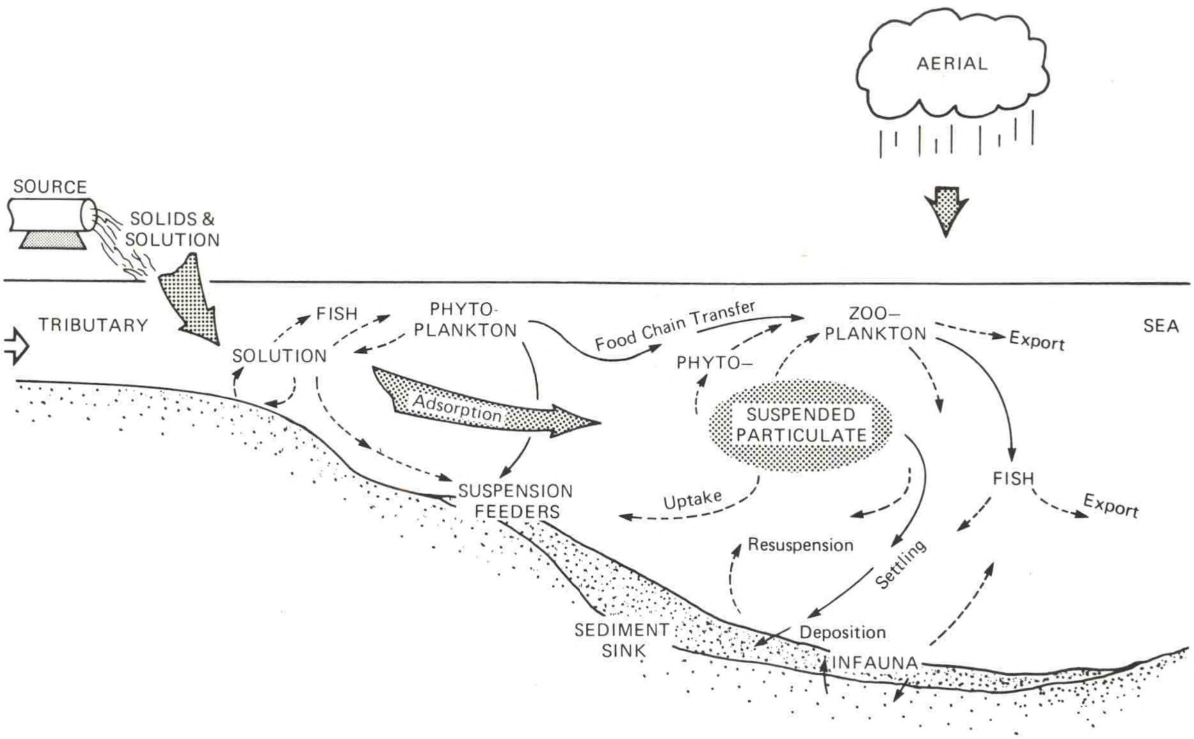

Figure 1. Dynamics of transport of a synthetic organic pollutant in estuarine and marine environments.

either been banned or severely restricted as a consequence of their impacts on non-target organisms. Also, the production of PCB's in the United States has been restricted. In addition, information obtained in the past 10 years concerning the dynamics and biological effects of synthetic organics has been used in the development and/or reassessment of water quality standards and FDA food tolerance levels.

Past experiences with synthetic organics in aquatic systems should be used as guidelines for studies involving these materials. In the future we cannot allow, as we have in the past, synthetic organic compounds to accumulate in the aquatic environment to the point that they have detrimental effects. Our past experience suggests we must develop methods to inventory the increasing numbers of synthetic organics that are being detected in the aquatic environment, and we must develop a priority system for determining the order in which these materials are to be tested for their effects on aquatic organisms. At present, the state-of-the-art in pollution work involving the detection of synthetic organics is much more advanced than our capabilities for determining the effects of these materials on the environment.

1.2 Biological Effects

Deleterious environmental effects of synthetic chemicals have been well documented in the scientific literature, but the press and popular literature have frequently reported suspected effects which have not since been confirmed.

The principal, known environmental effect of synthetic chemicals has been poor reproductive success, associated with eggshell thinning, of species of fish-eating and raptorial birds. The only chemical found to be responsible is the DDT degradation compound, DDE. Osprey populations in the coastal zone of New England declined sharply throughout the 1960's. Since 1973, reproductive success has improved and population is increasing as environmental DDE levels decline. Peregrine falcon populations have been reduced in the United States south of Alaska to a few pairs in relatively uncontaminated areas. Eggshell thinning has been demonstrated in island populations where the only source of DDE is atmospheric fallout. Massive inputs of DDT into the Southern California coastal waters from a manufacturing plant caused extensive shell thinning and reproductive failures among the brown pelicans and other species of fish-eating birds in the late 1960's and early 1970's (Keith et al., 1970). When input of DDT ended, the birds began to recover. The bald eagle has been another species affected by this syndrome, including populations in coastal areas.

Documenting these effects and determining that they were associated with DDE, and showing that other environmental chemicals were not responsible, have required extensive scientific investigations of species that are relatively easy to study. DDT effects on crabs at a Long Island locality and on reproduction of lake trout at Lake George in New York have been documented (Burdick et al. 1964). Substantial declines in reproductive success in spotted sea trout, commercially important marine fish on the south Texas coast, have been associated with high DDT residues in their eggs. Productivity returned to normal levels following the ban on DDT (Butler et al., 1972). In general, however, it is extremely difficult to detect biological changes in populations of marine species that might be related to pollution, let alone to determine which pollutant among a complex mixture is responsible. The absence of demonstrated effects is not therefore equivalent to the absence of effects.

Pollution of the coastal and marine zones by synthetic organics has already caused vast economic losses to the citizens of the United States. For instance, an extremely successful salmon fishery was developed in Lake Michigan in the early 1960's. However, adult salmon and lake trout soon were found to contain concentrations of chlorinated hydrocarbon insecticides and PCB's that all averaged above the FDA action levels set for these synthetic organics (Reinert and Bergman, 1974). This stopped the development of a potential multimillion dollar industry designed to use part of the spawning salmon for human and pet food consumption. Because of the high concentrations of these synthetic organics in chubs, the interstate shipment of these fish was banned. This action resulted in the great economic loss to the fishery.

In Lake Ontario it was discovered that fish contained mirex, a synthetic organic used as a fire-retardant or to control fire ants in the Southeast. The compound entered by way of the Niagara river which in turn has been contaminated by an industry that produced it (Kaiser, 1974). The concentrations of mirex in the fish were above the FDA action level, and as a consequence commercial fishing on the lake was stopped. This resulted in the loss of millions of dollars to the fishery.

In the summer of 1975 a number of workers at a chemical plant in Hopewell, Va., were found to be suffering from poisoning by a synthetic organic called Kepone (Cannon et al., in press). Sampling of the estuarine environment showed that the compound had contaminated nearly every segment of the ecosystem and spread throughout the food chain. These data and results of carcinogenic bioassays resulted in action levels which, in effect, have closed the James Estuary to commercial fishing for many species. When the residue data first became available, the impact on the economy of the Chesapeake Bay Fishery was immense. People stopped buying seafood from the Bay because of fear of being poisoned. Not only were the fishermen of the James River affected but also the docks, restaurants, truckers, railways, boat dealers, tackle and bait suppliers. Although the total economic cost of this incident is unavailable, it certainly amounts to tens of millions of dollars.

Although contamination of the estuary was not recognized until 1975, archived samples of shellfish and sediments dated 1967 revealed substantial concentrations of Kepone. Therefore, contamination of the estuary began shortly after production started (1966) and continued to the present, for a period of 11 years. If the workers had not become ill, the problem probably would still be undetected because of the lack of an adequate monitoring program for synthetic organics.

The full economic impact of Kepone has not yet been felt, and the pollution of the estuary still exists. A recent study completed by the Environmental Protection Agency (U.S. EPA, 1978) estimates that if the James River is left alone decades must pass before the fish in the James will contain Kepone residues below the present FDA action level. If, on the other hand, attempts to clean the river are undertaken, the costs will run into billions of dollars plus perhaps the destruction of the existing biota. Even more frightening is the potential, however small, that the thousands of pounds of Kepone residing in the James River may move into the Chesapeake Bay. Already the finfish of the Bay are contaminated even though below the action level. The final costs as yet cannot be evaluated, but may be in the tens of billions of dollars.

2. PRIMARY RESEARCH

2.1 Utilization of Analytical Data

The detecting and measuring of biological changes and determining if they are associated with pollution remains a primary task in assessing the effects of synthetic chemicals in the environment. For example, the dungeness crab population has declined in the San Francisco area. However, the population decrease has not been linked to pollution; neither has it been shown that the effect is not pollutant-related.

A major difficulty is analyzing the complex mixtures of pollutants in environmental samples, and storing and retrieving this information in ways that the information can be used. New techniques, including capillary gas chromatography, can resolve these mixtures into many more components than was previously possible. Figure 2 shows a flame ionization gas chromatogram of an environmnental sample in which almost all the components are unidentified. Even by employing more sophisticated equipment such as mass spectrometry, the cost of identifying an unknown peak may be thousands of dollars and may require months of time. Any one of the unknown compounds may be of environmental concern. Therefore, a mechanism must be developed to keep track of these potential problem compounds even though their full identity is unknown. For instance, an electron-capture gas chromatogram of an extract of fish from a relatively uncontaminated area would rarely show prominent peaks. The presence of such peaks in a fish extract would probably imply the presence of pesticides or similar pollutants. To ignore them is folly if the intent of a monitoring program is to protect the environment and public health.

Much of the information obtained from analyses is not usable at present, but could be invaluable in the future. Research is needed to develop ways of using already developed technologies to manage, by computerization, chromatographic data concerning potential problem compounds. Each peak can be assigned a relative retention time characteristic of a given column type; this number and the integrated area can be stored in a computer system; software can be developed to compare the occurrences of an unknown in various samples as a function of either sample type, space or time. These comparisons can lead to intelligent choices of which unknowns require absolute identification.

With limited time and money the strategy to handle the data is important. Monitoring programs are recommended to acquire background data concerning synthetic organics in water sediments, and biota. If, in any single monitoring program with arrays of sampling locations in space and time the unknown peaks were computerized, then an unknown peak increasing with time would tell the investigator that the compound should be identified. Likewise, a peak that occurs in only one system (e.g., a river) would indicate that a pollution source is nearby and the compound should be identified. As future "Kepones" or other carcinogens are detected, or when a biological effect is suspected to result from a

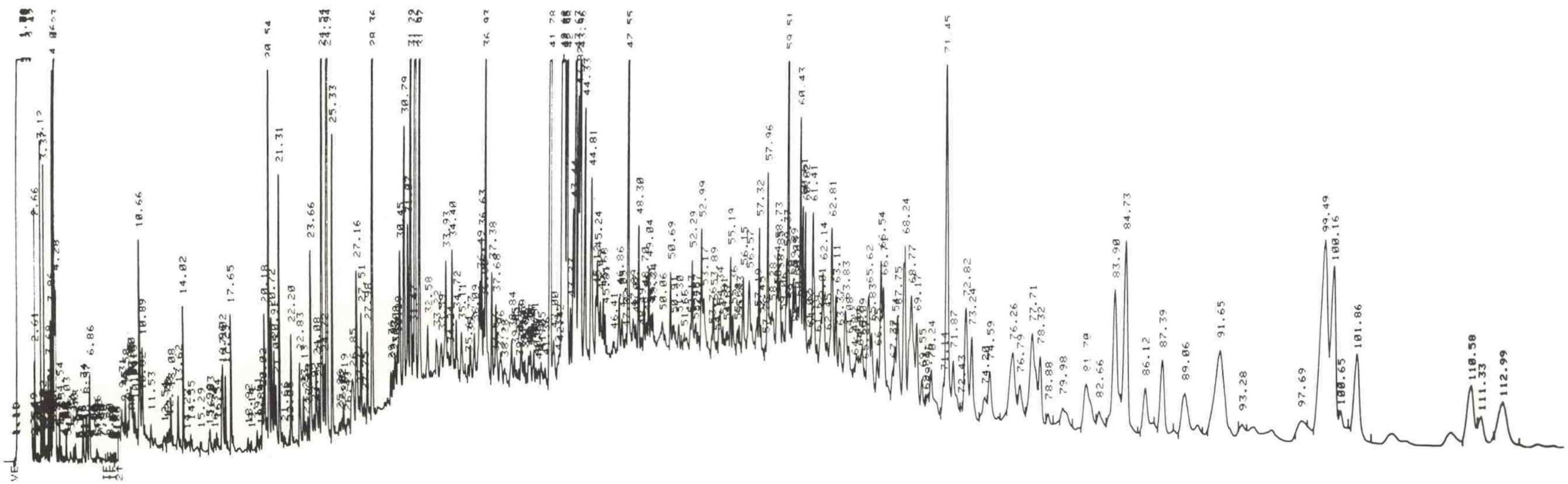

Figure 2. Flame ionization gas chromatogram of an extract of mussels, <u>Mytilus californianus</u>, containing a mixture of biogenic and pollutant compounds. Mussels were obtained in Carmel Bay, California, on July 18, 1977. Analysis with a SP-2100 glass capillary column, in a Hewlett Packard 5840 gas chromatograph, at the Bodega Marine Laboratory.

particular chemical, all gas chromatographic runs in the data system could be searched for the possible presence and amount of the chemical in question. Compatible files of mass spectrometric data could confirm identity.

In retrospect, had this type of program been ongoing 12 years ago in the Chesapeake Bay, Kepone could have been detected less than a year after pollution started.

With any program we will be unaware of deficiencies that will surface with new technology or information. Therefore, it is necessary to be able to perform retrospective analyses. It is recommended that samples of organisms be stored in a manner to ensure the integrity of the sample for retrospective analyses. This is being done in the U.S. National Mussel Watch Program, now the only national pollution monitoring program in the marine coastal zone (Goldberg et al., 1978).

In summary, we are now utilizing only a small amount of the available data generated by existing monitoring and research programs. Among the contaminants in the marine or coastal environment, we are identifying only those that have already caused a problem by harming either the ecosystem or man. In essence this is a "feed backwards" program, and to protect our marine and coastal resources we need one that will identify problems before they reach crisis proportions--one that is "feed forward."

2.2 Monitoring Strategies

Monitoring strategies for synthetic organics in coastal and marine environments might apply equally well for petroleum and fossil fuel combustion products. Sampling and analytical methodologies have much in common.

In formulating a strategy, previous and existing monitoring programs in the coastal environment might first be examined. Between 1965 and 1972 estuarine bivalves were collected monthly at 180 sites to determine spatial and temporal distribution of chlorinated hydrocarbon pesticides (Butler, 1973). The Mussel Watch Program, begun in 1976 by the Environmental Protection Agency, is examining all detectable synthetic organics and petroleum in mussels, *Mytilus sp.*, as well as metals and artificial radionuclides. Oysters are sampled in southern areas where *Mytilus* does not occur. Approximately 150 stations are sampled once a year; one west coast and one east coast station are sampled monthly. The samples are archived for future reference, and more samples are archived when calibration programs are in progress among participating laboratories.

In designing a monitoring strategy, two initial questions must be addressed:

Which data should be collected over a temporal and/or spatial framework to answer the question of interest?

Would the statistical design result in acceptable levels of uncertainty?

Spatial and temporal changes are only two of the components of variance. When looking for relatively small differences, determination of analytical variance becomes important. The sampling variance must be either determined or accounted for. How well does a group of 10 or 20 oysters represent the population that is sampled? In many cases, the sampling error can be made insignificant in comparison with the analytical variance by pooling individuals; the sampling variance then decreases by a factor of N, the number of individuals in the pool.

The choice of species sampled and the temporal and spatial intervals of sampling therefore depend on the questions that are posed. For instance, bivalves are suitable for higher molecular weight compounds in the marine coastal zone, but are not good bio-indicators of lower molecular weight synthetic and petroleum compounds. Nor are they suitable for marine environments remote from the coastal zone nor for many questions of local concern.

A significant part of the effort in monitoring water, sediments, and biota for synthetic organics is associated with sample collection. Normally when these samples have been examined for their intended purpose (usually the quantification of known hazardous compounds) they are discarded along with information on chemicals toward which analysis was not directed. A new strategy to correct this problem has evolved over the past several years and involves the concept of an environmental specimen bank. Samples, which have been carefully selected on the basis of previously discussed factors, go regularly into this bank. Once in the bank, the sample is split into three fractions if it is sufficiently large. One fraction is analyzed for "known" contaminants, which are defined as those which we know are hazardous. These include compounds with existing action levels for human consumption or those that can have documented biological impacts. Acceptable analytical methods exist for many, if not most, of the compounds in this class and it would satisfy the needs of regulatory agencies to know continuously the levels of "known" contaminants in the coastal and marine environment. A second fraction of the sample is analyzed after extraction and separation by perhaps several methods using high resolution gas chromatography. The resulting data or fingerprints for each sample are stored as analog signals by computerization. The manipulations of these data and the advantages of doing them are discussed in the text. Once a suspicious pollutant is detected, samples of additional species, of sediments, and of the water column can be examined to provide additional information on local distribution and abundance of the pollutant.

A third fraction of the sample is stored in a manner to preserve its integrity for decades, probably by freezing. The logic for this is that our methods of analysis for the vast array of unknown organics will undoubtedly be only semiquantitative. As future needs dictate or as our knowledge and instrumentation improve, samples can be withdrawn from the bank and subjected to refined quantitative analysis.

In essence this program satisfies the need for current knowledge of known contaminants, a forward-looking program to head off pollution crises, and the ability for retrospective analyses.

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CHLORINATION PRODUCTS

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1. INTRODUCTION

1.1 Problem Identification

The use of chlorine and other biocides in various water treatment processes is causing the formation of many biologically active compounds (toxic, carcinogenic, teratogenetic, or mutagenic) that are released into the estuarine and coastal waters of the United States. The significance of the impact of current usage or probable future increased usage on marine resources or on public health from the ingestion of seafood cannot be adequately assessed with existing information. However, present evidence should dispel any complacency; effects are taking place, although major crises are not apparent.

Major water treatment processes include drinking water disinfection, waste-water partial disinfection, and prevention of slime or other biofouling in electric-power generating plants. The two kinds of evidence that health and resource damages may be occurring are chemical identification of biologically active compounds in the effluents and bioassay observations of responses by organisms exposed to the effluents from these activities. The formation of chloroform and haloforms during drinking water chlorination (Rook, 1974; Bellar et al., 1974) has raised questions regarding possible impact on human health. Chloroform, bromoform and other haloforms have been found in power plant effluents (Jolley et al., 1978b). The carcinogenic and mutagenic properties of these substances have been described recently (Simmon and Tardiff, 1978) and form the basis for concern about these compounds in marine systems.

Direct evidence for effects on marine organisms (mortality of oyster larvae, *Crassostrea virginica*) from exposure to chloroform, bromoform, and bromate ions has been described very recently (Stewart et al., 1978). Bromate formation in chlorinated seawater exposed to sunlight (Macalady et al., 1977) and in ozonized seawater even in the dark (Crecelius, 1978) under conditions simulating power plant operation suggests that this compound should be considered in assessing environmental effects of coastal power plants.

Identifying biological effects is complex and difficult. Finding halo-organic compounds in the drinking water of 80 United States cities represents discovery of the tip of the iceberg in our chemical and biological conceptualization of the problem. One workshop (Block et al., 1977) and two symposia (Jolley, 1978; Jolley et al., 1978a) have collected and summarized most of the major aspects of processes, effects and byproducts from chlorination practices. Recent events and studies have given us a number of clear signals of potential problems that call for additional, carefully executed research:

(1) Lethal effects were experienced in a California commercial mariculture enterprise that used chlorinated power plant effluents (S. Henderson, 1978, personal communication to W. Blogoslawski). In contrast, a Long Island, N.Y., shellfish hatchery has continuously used heated nonchlorinated power plant effluents with success in rearing bivalve shellfish (Phillip Campbell, 1976, personal communication to W. Blogoslawski).

(2) Measurable shifts in colonization and in the composition of communities of marine algae and organisms resulted from chlorination doses that yielded no detectable residual levels (Davis et al., 1977). This demonstrates that toxicity is not related solely to residual oxidants. Thus current regulations based solely on residual oxidant standards are inadequate.

(3) Chlorination of estuarine waters in a flowing water experiment, followed by dechlorination, resulted in uptake of measurable halo-organic compounds in edible tissues of such organisms as oysters (Scott et al., 1978, personal communication). These bivalves provide a potential route to humans for halo-organic compounds.

These studies, together with investigations of fresh water (Brooks and Seegert, 1978) and marine waters (Davis and Middaugh, 1978) describe a broad spectrum of effects of chlorination on biota. However, only recently have investigators attempted to distinguish between the effects of oxidative compounds and the effects of other chlorination by-products. A substantially increased research effort comprehensively integrating biological and chemical studies is needed to evaluate recent findings.

1.2 Waste-Water Quality Criteria

State and federal agencies must develop permissible or allowable discharge regulations for water treatment by-products to protect human health and environmental quality. Integrated laboratory and field investigations are needed, to obtain information sufficient to establish realistic water quality criteria. To formulate broad ranging tactics for enforcement without careful research could create more problems than solutions. For example, finding certain levels of fecal coliform or pathogens in waters or in shellfish traditionally has resulted in application of biocides to control or reduce the micro-organism population. The by-products from such treatments were not of concern since our awareness of their toxicity did not then exist.

As a specific example, the arbitrary requirement of waste-water chlorination to levels of 2 mg/ℓ "residual chlorine" by the state of Virginia caused unanticipated, extensive damage to the oyster beds of the James River estuary (Bellanca and Bailey, 1975).

Information exchange between industry, waste treatment engineers, researchers, and regulators must be maintained by workshops and symposia producing refereed, published reports.

1.3 Sources and Types of Environmental Discharge

Most municipal waste treatment plants that discharge into rivers and estuaries treat the effluent with biocides. Chlorine is the principal biocide currently used and 1% to 2% of United States production of chlorine is used for this purpose (White, 1978; Jolley et al., 1978a). However, disinfection by ozonation and ultraviolet irradiation is practiced at several sites in the United States. Chlorine-containing organics are produced in the chlorination disinfection process (Jolley, 1973; Jolley, 1975; Glaze and Henderson, 1975; Jolley, 1978; Jolley et al., 1978a). Therefore, discharged chlorinated wastewater effluents contain relatively stable chlorine-containing organics as well as a reactive chlorine residual. This reactive chlorine residual is dissipated in the receiving water system by further reactions. The toxicity of the chlorine residual in chlorinated effluents has been documented extensively in both fresh and marine waters (Brooks and Seegert, 1978; Davis and Middaugh, 1978). Chlorine residuals from waste-water effluents consist principally of reaction products of chlorine with ammonia. When treatment effluents are discharged into marine systems, further reactions of the residuals with a bromide ion produce new toxic components, some of which are yet to be identified. The chlorine-containing organic compounds in chlorinated, waste-water effluents include such toxic chemicals as chlorophenols and mutagenic chemicals such as chlorinated pyrimidines (Jolley et al., 1978b; Glaze and Henderson, 1975). However, the majority of the chlorine-containing, organic constituents in chlorinated effluents are unidentified.

Several municipal waste-water treatment plants disinfect effluents with ozone; for example, Springfield, Mo., Chino Basin, Calif., and Woodlands, Tex. If waste-water treatment plants using ozonation are located at estuarine and ocean-shore sites, the ozonated waste-water effluents may contribute to marine pollution. Ozonation of seawater or waters containing significant bromide concentrations produces hypobromous acid and hypobromites in a manner analogous to their production by chlorination (Helz et al., 1978; Blogoslawski et al., 1976). Therefore, many of the brominated organic compounds produced by chlorination of sea-water could be anticipated from ozonation of seawater.

Sources of chlorinated effluents can be attributed to industrial activity, the paper, textile, and chemical industries for example. The pulp and paper industry uses 16% of the chlorine produced in the United States (White, 1978). Chlorine-containing organics have been detected in effluents from several pulp and paper industries (Keith, 1976). Therefore, chlorinated effluents from this industry may represent a significant source of chlorine-containing organic constituents for estuarine and marine ecosystems. Industries may chlorinate seawater extensively either to prevent biofouling or in industrial processes (Mangum and McIlhenny, 1975). To the extent that these industries discharge effluents to saline waters, they can contribute substantial amounts of halogenated organic compounds to the ocean. Forty to fifty percent of the textile-company-operated waste treatment plants use chlorine and discharge effluents to aquatic ecosystems (Tincher, 1978).

Maintenance of high efficiences in power production at electric power plants dictates that biofouling of condenser systems be prevented or controlled. The principal antifoulant currently used is chlorine. Alternate biocide usage in power plants has been summarized by Waite et al. (1978) (Fig. 1). Chlorination of once-through cooling waters produces both volatile halo-organic compounds (e.g., chloroform or bromoform) and non-volatile compounds (e.g., chlorophenols (Jolley et al., 1978b; Jolley et al., 1978c; Bean et al., 1978; Carpenter and Smith, 1978; Helz et al., 1978). Therefore, chlorinated cooling waters, both estuarine and marine, introduce known carcinogens and mutagens and other halogen-containing compounds into the ocean environment.

Other minor sources of oxidizing chemicals include the use of bromine for disinfection processes for marine vessels and the use of bromine chloride for waste-water treatment processes.

The proposed Ocean Thermal Energy Conversion (OTEC) technology possibly represents a significant future source of ocean pollution. For example, one proposed use of chlorine for antifoulant treatment of the cooling systems for a 100-MW OTEC facility ranges from a low of 6,000 tons/year to a high of 48,000 tons/year for continuous treatment (Hamilton, 1978). These values represent 25% to 200% of the total chlorine used in the United States for electric power plants in 1974, as indicated by the Federal Power Commission (Hamilton, 1978). Thus, this future technology represents a possible impact of considerable proportions on the ocean.

2. THE PRIORITY PROBLEMS

2.1 Chemistry of Water Treatment

The chemistry of water treatment practices is poorly understood with respect to the reactants, products, and variables affecting the reactions. In addition, the interaction of the treatment chemicals with other anthropogenic pollutants needs study.

STUDY AREAS / TREATMENT CHEMICAL	CHLORINE (Cl_2, OCl^-, HOCl)	CHLORINE DIOXIDE	OZONE	BROMINE (Br_2)	BROMINE CHLORIDE	IODINE	PERMANGANATE	FERRATE	PEROXIDE	MIXED HALOGENS	DECHLORINATION (Sulfur)	DECHLORINATION (Activated Carb.)	ORGANIC BIOCIDES AND BIOSTATS
BIOCIDAL EFFECTIVENESS													
Dispersed Microorganisms	A	C	A	B	B	B	B	B	B	B	(–)	(–)	C
Microbiological Films	B	X	C	X	X	X	X	X	X	X	(–)	(–)	X
Biocide Activity in Presence of Inert Matter	A	C	A	C	C	B	C	X	X	C	(–)	(–)	C
Temperature Dependency	A	C	A	C	C	B	C	X	C	C	B	B	C
pH Dependence	A	C	A	B	B	A	C	C	C	C	B	C	C
AQUATIC CHEMISTRY													
Solubility and Temperature Relationships													
• Fresh Water	A	A	A	A	A	A	A	A	A	A	B	C	B
• Salt Water	C	C	C	C	C	C	C	B	C	C	C	X	X
Species Dist. in Aqueous Systems													
• Fresh Water	A	B	A	A	A	A	A	A	B	C	C	C	C
• Salt Water	C	C	C	C	C	C	C	B	X	X	X	X	X
Reactions with Organic and Inorganic Constituents													
• Fresh Water	B	C	A	A	A	B	C	C	C	B	C	C	C
• Salt Water	C	X	C	C	C	C	X	X	X	C	C	X	X
ENGINEERING CONSIDERATIONS													
Application Procedures and Equipment	A	B	B	C	B	B	A	X	A	C	B	A	B
Occupational Safety and Handling	A	A	A	B	B	B	A	C	A	C	A	A	C
Availability of Chemical for Commercial Use	A	B	A	B	B	B	A	X	A	C	A	A	C
Cost	A	B	A	B	B	B	A	X	A	C	B	A	C
Scaling or Corrosion Problems	A	C	C	C	C	C	X	X	C	C	B	A	C
ENVIRONMENTAL EFFECTS													
Persistence of Oxidized Species													
• Fresh Water	A	B	A	B	B	A	B	B	B	B	A	B	C
• Salt Water	C	C	C	C	C	C	C	X	X	X	C	X	C
Formation of Environmental Toxins													
• Fresh Water	A	C	A	C	C	C	X	X	C	C	C	C	C
• Salt Water	C	C	C	C	C	C	X	X	X	X	C	C	C
Toxicity to Aquatic Biota													
• Fresh Water	A	C	A	B	B	C	C	X	C	C	C	C	C
• Salt Water	C	C	C	C	C	X	C	X	X	X	C	C	C
MONITORING OF RESIDUALS													
Fresh Water	A	C	A	A	B	B	A	A	C	C	A	A	C
Salt Water	A	C	A	B	B	C	C	C	C	C	A	A	C

LEGEND:
A – Large amount of information currently available
B – Some information, usually not in reviewed journals or books
C – Very little information published, or only preliminary investigations
X – Information completely lacking
(–) – Not applicable.

Figure 1. Cooling water chemical treatment alternatives (Waite et al., 1978. Figure reproduced with permission of the publishers, Ann Arbor Science Publishers, Inc.).

Studies of the products of water treatments have been limited mainly to those produced from chlorination practices in fresh water and to a lesser extent in seawater (Jolley et al., 1978c). Some results have been reported on the identification of products from fresh water ozonation as well (Sievers et al., 1977). The formation of haloforms from chlorination of natural waters is well established, but little information exists concerning the formation and the composition of the higher molecular weight organohalogen materials. The slow pace of research progress is related to the complex nature of the products of the water treatment, with each of many hundreds of components being present in very small concentrations. The important work of product identification requires the use of the sophisticated trace analytical techniques including capillary gas chromatography, mass spectrometry, and high resolution liquid chromotography. Identification by these methods is difficult because usually no analytical standards exist. Additional long-term research concerning water treatment products is needed in all aspects of analysis: sampling, concentration, separation, and identification.

Research is needed on the basic organic chemistry of water treatment technologies--the chemistry of oxidative reagents in aqueous systems. Studies of the interaction of treatment reagents with groups of materials possessing similar reactive groups would aid the chemist in designing his analytical approaches to search for expected products. Fundamental information is needed regarding the important reaction variables (e.g., temperature, concentration, salinity, organic carbon content) and the effects of changing these variables on product concentrations.

Our knowledge of the impact of treatment processes on aquatic systems that bear a large burden of anthropogenic pollutants is virtually nonexistent. Presumably, the effects might be beneficial as well as undesirable. An example of an undesirable effect is the conversion of phenol introduced by human activities to a chlorinated phenol, which is more toxic. A desirable effect might be the oxidation of a metal from a bioavailable valence to a less bioavailable one. Research projects addressing the combined effects of chlorine and some metallic pollutants are currently in progress, but the effort is at present sparse, and is confined to a few isolated laboratories.

2.2 Environmental Transport

Little information is available concerning the mechanisms that govern the distribution of chlorination byproducts throughout the environment. Interdisciplinary research including biology, chemistry, oceanography, and meteorology is imperative to determine the mechanisms and rates of distribution of chlorination byproducts.

An example of what could be accomplished rather quickly under such a program is the formation of volatile haloforms from chlorination. With the data and methods currently available our understanding of the aquatic and atmospheric transport of haloforms could be rapidly developed. However, the relative importance of the various transport mechanisms in the distribution of the nonvolatile products of effluent treatment is not known, and will require extensive research.

2.3 Toxicity

The environmental toxicology of the oxidation products, especially from long-term studies, needs investigation. Ozone and chlorine react with bromide in seawater to produce various bromine-containing compounds such as hypobromous acid and bromate. There is a direct short-term toxicity of these substances to oyster larvae (Stewart et al., 1978). Lobster larvae are killed in chlorinated seawater (Cappuzzo et al., 1976; Capuzzo, 1977) and oyster eggs develop abnormally in ozonized seawater (MacLean et al., 1973). Roberts et al. (1975) showed that chlorination is very toxic to both oyster and clam larvae.

Several bromine-containing compounds (e.g., bromoform and 5-chlorouracil) are considered mutagenic on the basis of an Ames-type test (Simmon and Tardiff, 1978; Kraybill, 1978; Cumming, 1978); these compounds may also be mutagenic to marine organisms. Long-term studies must be conducted on the larvae of marine species sensitive to bromine compounds. Larvae seem more susceptible than adults are to toxic materials. As a first step in assessing overall ecosystem effects, an indicator marine species must be identified for short-term and long-term bioassay studies. The oyster larva is well suited since its biology is well known. It can easily be cultured year-round and it is sensitive to most pollutants at the mg/ℓ level (Calabrese et al., 1977; Davis, 1969; Longwell et al., 1967). Finfish and crustaceans such as the striped bass and blue crab, which are economically important marine animals, should be critically examined as potential indicator species.

2.4 Bioaccumulation

Research is recommended to assess the potential enrichment of oxidation products in higher ranks of the food web.

The question of potential bioaccumulation of chlorination byproducts and subsequent food web transfer arises from experience with pesticides and industrial chemicals. To assess this potential requires prior development of reliable analytical procedures, which has barely begun. Many of the measurements of halo-organic compounds in the effluents of municipal treatment plants already exceed "allowable" levels for total halo-organic compounds.

Young and Heesen (1978) report bird deaths among captive cormorants and gulls in the Los Angeles City Zoo that have been fed fishes captured within 20 km of Palos Verdes Peninsula ocean outfall. Adjacent caged pelicans fed different fish species from another source area suffered no mortality from the high levels of pesticides/halo-organic compounds associated with the cormorant and gull deaths. Previous monitoring programs have tracked specific halo-organic substances (DDT, PCB's, Kepone) among selected marine organisms. Because of the variety of by-products and the dynamics of marine ecological systems, careful planning and experimental design are needed before attempting to trace chlorination-produced substances in marine food webs.

2.5 Fate of Water Treatment Products

Knowledge of the persistence of water treatment products in coastal waters is essential for the prediction of future work.

As water treatment becomes more common worldwide (Orihuela et al., 1978; Hamilton, 1978), we must determine the environmental assimilatory capacity for the products of water treatment processes and learn the physical, chemical, and biological mechanisms determining the ultimate fate of these chemicals. Such information may well determine choices and operating conditions of the water treatment processes.

Certain chlorinated hydrocarbons, such as PCB's, are persistent and ubiquitous in environments because of their resistance to chemical alteration and microbial attack. The relative contribution of water treatment processes such as chlorination or ozonation to the environmental budget of refractory chemicals is unknown.

A research program on the environmental chemistry of water treatment process effluents must include capabilities in physical chemistry, photochemistry, microbiology, and sediment-water interface processes. Initial focus in the program may be directed toward screening changes in physical and chemical properties of effluents under different microbial, photochemical, or chemical conditions. More specific studies should be initiated as information about the composition of effluent streams is generated.

Besides the laboratory studies, field studies specifically directed toward understanding the environmental fate of effluent components must be integrated and factored into design and execution of monitoring programs.

2.6 Formulation of a Monitoring Scheme

We must plan monitoring programs closely coupled with research programs. Conceptualization of the natural processes is necessary before a monitoring program can be designed. The present knowledge of water treatment byproducts that are being discharged is so inadequate that useful monitoring programs cannot be formulated. It seems probable that some of the important byproducts are altered by metabolism and exert their impact either during or as a result of metabolism. The pitfall of collecting uninterpretable data should be avoided.

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DREDGING AND DISPOSAL OF ITS LARGE-VOLUME WASTE

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1. INTRODUCTION

1.1. Problem Identification

Dredging of navigation channels and major commercial ports is necessary to maintain marine and Great Lakes commerce, to improve and extend recreational boat harbors, and to recover sand and gravel for construction purposes. These activities involve removal of about 300 million cubic meters annually in the United States (Boyd et al., 1972). Dredging of at least this volume will continue indefinitely and may increase when harbors and navigation channels are deepened for deep-draft bulk cargo carriers and when dredging projects, deferred in the early 1970's, are undertaken. Dredging and disposal of dredged materials are among the largest waste-producing and waste-disposal operations in the United States. In the New York Bight, for instance, dredged material disposal exceeds river discharges of sediment or coastal erosion by a factor of about 8 (Gross, 1976). In short, dredging and large-volume waste-disposal problems are ubiquitous, usually expensive, and likely to increase in importance.

Most dredged materials consist primarily of natural sediments from upland areas where disposal need not create any particular environmental problem. However, when pollutants are added to the natural sediments by municipal and industrial discharges to the harbor areas they can create severe environmental stresses and consequent problems in handling and disposal of dredged materials. Extreme examples of such pollutants include mercury in Lake St. Clair and Detroit River sediments, Kepone in James River muds, and polychlorinated biphenyls in Hudson River deposits. Organic substances in dredged materials from urban runoff, drainage channels, and sewers may cause oxygen depletion and damage to benthic organisms in disposal areas.

Various wastes, such as sewage sludges or industrial wastes, are also produced in large volumes. Because of the volumes involved, such wastes are often placed in upland, intertidal, or open-water sites. Although much of the following discussion is phrased in terms of dredged materials, the basic principles and processes may also apply to other wastes (Gross, 1976).

Until recently, it was common practice to dispose of dredged materials and other wastes at open-water sites or the nearest convenient upland or intertidal area. Because of environmental concerns many disposal areas used in the past will not be available in the future and new disposal sites or management schemes must be developed to permit dredging or waste-disposal operations to continue.

Criteria have been developed for designation of new disposal areas and for the classification of dredged materials to be placed in them. A sound scientific basis for many of these criteria is lacking because the criteria have not been derived from the physical and chemical processes that actually occur in open ocean, coastal, estuarine, or Great Lakes environments. Classes of parameters may be developed to describe a particular site's ability to contain, disperse, or absorb contaminants and to aid in the intercomparison of disposal sites.

Besides traditional dredging and disposal operations, new applications of these or improved techniques are needed to deal with severely polluted sediment deposits ("hot spots") and to rehabilitate ocean bottom areas disturbed by mineral production.

The following discussion primarily concerns dredged material. Dredged material typically is composed mostly of inorganic sediment and often contains less than 10% organic matter by weight. However, some dredged material may contain domestic waste products. In some urban harbor areas subject to the discharge of large quantities of municipal wastes, sewage sludge may be a major component of dredged materials. Although typical dredged materials are not sewage sludge, many strategies are related to disposal of both organic-rich and organic-poor dredged sediments. Therefore, the disposal of dredged sewage sludge is included within the general framework of dredged material disposal. The discussion also considers incineration of wastes at sea, although it differs in many respects from dredging and related disposal activities.

1.2 Types of Disposal Areas

Four types of disposal areas may be designated in the ocean, Great Lakes, or coastal zone to receive dredged materials or other large-volume wastes:

Upland areas - above the influence of the tides; e.g., strip mines, quarries, sand-and-gravel pits, agricultural lands.

Intertidal areas - subject to tidal flooding, including wetlands.

Subaqueous areas - below the low tide level (always flooded), including the continental shelf and continental rise.

Sub-bottom areas - excavated on the ocean bottom (e.g., sand-and-gravel mining) or natural holes that may be filled with dredged materials or other wastes and covered.

Not all regions have the capacity to accommodate the full range of disposal options. In addition, some areas are more appropriate than others for disposal of certain wastes to avoid (or minimize) public health risks or marine resource conflicts. Furthermore, the cost of transporting dredged material from the dredge site to the disposal site severely limits site selection. Therefore, each disposal option exhibits certain benefits and certain risks that should be quantified. For example, disposal of contaminated dredged materials at an upland site has the potential of contaminating ground water. Some of these issues are addressed in the following problem statements.

2. THE HIGH-PRIORITY PROBLEMS

The problems have been categorized into high-priority and second-priority groups. Discussions of the four high-priority problems are followed by discussions of five second-priority problems.

2.1 Disposal Strategy: Dispersal vs. Containment

Onshore and subtidal disposal areas are becoming increasingly scarce and costly to acquire and maintain. As a result, new disposal areas must be designated offshore to handle quantities of dredged materials now produced and likely to be produced in the future (Pequegnat et al., 1978). Two options are available for the disposal strategy: producing the maximum dilution and dispersion of the dredged material, or containing and isolating the dredged material on the disposal site. The choice depends on the load of contaminants. Criteria need to be developed for selecting appropriate disposant sites and disposal methods.

The fundamental question is whether specific dredged materials or large-volume wastes should be contained or dispersed. An obvious first step is to determine to what extent we need expensive containment procedures to avoid adverse environmental impacts.

There are several associated questions:

(1) How can various types of material be appropriately classified with respect to their composition and pollution potential?

(2) How do characteristics of various large-volume wastes fit the different disposal strategies identified?

(3) How can appropriate disposal areas be selected?

(4) What are the long-term effects of various disposal alternatives? How reversible are these effects?

Techniques for dispersing fine-grained dredged material are available (Barnard, 1978). However, when materials are released into the water column their motion is uncontrolled and is determined primarily by currents, settling, and consolidation characteristics. Thus the ability of a particular disposal area to distribute the material and the capacity of the site to absorb the disposed material must be assessed (Carpenter, 1973).

Long-term effects of sustained low levels of contamination of the ecosystem are not well-defined, although substantial studies are beginning to address this problem. Existing disposal philosophies imply that the preferred approach is containment and total isolation of severely polluted materials from the biosphere. Placing such materials in diked, enclosed areas or in sealed sites in the ocean bottom or upland is often expensive, and appropriate disposal sites are scarce. Disposal of unpolluted ("virgin") materials from new construction ("new work") might be designed to maximize dispersion or mixing with other materials. Likewise some materials may readily decompose in the environment or may even be beneficial to marine resources, by providing food for desirable marine organisms, for example.

At open-water sites it is desired to minimize the contact between polluted waste materials and the receiving waters. The degree of retention of fine-grained material (and its associated contaminants) at an open-water disposal site depends primarily on the sedimentary regime at the site and the geometry of the waste deposit (Bokuniewicz and Gordon, 1978). Particulate material can be placed accurately at a desired location on the bottom by using existing technology (Bokuniewicz et al., 1977; Custar and Wakeman, 1977). The stability of the deposit, however, depends on consolidation rates and a complex interaction of biological, geochemical, and physical processes.

Although progress is being made to understand specific sedimentary processes (e.g., Rhoads et al., 1976; Young and Southard, 1978), the need remains to examine long-term manifestations of sedimentary processes in specific coastal environments (Schubel, Bokuniewicz, and Gordon, (1978). In particular, research should be directed toward evaluating the capacity of disposal sites to retain material discharged in them. At this time no consensus exists among scientists and environmental managers or decision makers regarding basic disposal strategies. Furthermore, data are rarely available to characterize the wastes, and few wastes have distinctive textures and composition. For instance, the degree of containment may be dictated by the pollutant level in the dredged materials. But it is impossible to specify the relationship between the level of contamination of the wastes and the degree of containment or dispersal that is appropriate.

A critical research need in ocean disposal of barged dredge spoils, sewage sludge, and other large-volume wastes is to determine the relative costs and benefits of dispersal vs. containment. Extensive studies of incidental dispersal of sewage sludge in the New York Bight and offshore from the Delaware Estuary, and deliberate dispersal of chemical wastes in a number of areas have revealed no rational basis for determining which disposal strategy should be used where. The next approach should be to synthesize existing United States and foreign case study information and to develop a prediction model that would provide a first approximation of relative advantages of dispersion vs. containment in specific cases. Priority should be given to sites that are needed to replace existing ones that are no longer usable.

2.2 Characterization of Dredged Materials and Large-Volume Wastes

Data should be obtained in the following ways to guide the future dredging activities in United States waters:

(1) Inventory past dredging projects and future dredging requirements for major port areas, on a regional basis.

(2) Characterize dredged materials on physical and chemical bases, especially for the major sources such as the Mississippi River.

(3) For one or more dredging and disposal operations, characterize the wastes, and develop and test predictive models for such processes as water transport and post-depositional dispersal on the bottom.

In obtaining the above data, the following information-gathering activities should be included:

(1) The critical constituents in wastes should be identified on the basis of their public health risks, aesthetic implications, and effects on marine resources.

(2) Chemical analytical techniques should be developed for critical constituents in dredged materials and wastes. Analytical results should be checked by developing appropriate analytical standards and by having frequent intercalibration activities among involved laboratories.

(3) Data on post-dredging projects and future dredging requirements should be collected and analyzed to determine which areas have been most affected in the past and which ones are likely to be affected in the near future. Areas should be selected for investigation on the basis of projected dredging requirements.

(4) Predictive models should be tested by observing the behavior of the materials during actual disposal operations and by follow-on studies after disposal operations have ceased.

2.3 Long-term Changes in Disposal Sites

Investigations of long-term changes (up to 10 years) of materials in disposal sites (upland, intertidal, subaqueous, sub-bottom) are urgently needed for evaluation of public health risks, conflicts with marine resource utilization, and possible beneficial effects.

Insufficient information exists on long-term changes involving various types of dredged material disposal sites (upland, intertidal, subaqueous, sub-bottom) for evaluation of the effects of waste deposits on marine resources and public health. Disposal areas no longer in use should be examined to see how they can be rehabilitated, as was done for areas that were surface-mined for coal (Riley, 1977).

Considerable attention has been directed toward the environmental impacts of dredged material disposal on the marine ecosystems through the U.S. Army Corps of Engineers Dredged Material Research Program (DMRP). In general, results have indicated that during the time of disposal and for a short time thereafter, some releases of materials (e.g., nutrients, polychlorinated biphenyls, potentially toxic metals) do occur but have little environmental consequence (Wright, 1978; Burks and Engler, 1978; Brannon, 1978). The limited duration of the DMRP program did not permit an adequate assessment of long-term effects on marine resources. For example, previous research dealt with effects of increased turbidity and smothering in the disposal site on marine organisms (Hirsch et al., 1978). Other studies evaluated recruitment in disposal sites and pollutant uptake from dredged material by organisms shortly after colonization (Hirsch et al., 1978). Little attention, however, has been given to the long-term chemical, physical, and biological changes in these deposits that may influence marine resources or public health. The following technical questions concerning these changes must be answered:

(1) What are the rates and mechanisms of biological, chemical, and physical processes that lead to stabilization of dredged material disposal sites?

(2) Can stabilization processes be modeled adequately to identify needed field investigations?

(3) Have inputs to disposal sites been cataloged adequately to permit identification of sites appropriate for detailed investigations?

(4) How transferable are results from one site to another?

(5) Does waste disposal result in any long-term benefits or detriments to marine resources or the marine environment or human health?

(6) What fraction of the disposal material is mobilized at the disposal site? Where and at what rate does this material migrate?

We must base our approach to obtaining an adequate understanding of long-term changes in dredged-material disposal sites on our present knowledge of impacts and short-term changes and develop models to guide further field studies. Field studies should use existing disposal areas of various types (e.g., upland, intertidal, sub-aqueous, and sub-bottom) and pilot studies in which new types of disposal environments are considered. Specifically the approach should include the following components:

(1) Studies of various types of previously used or newly introduced disposal sites to determine changes with time and the processes involved (trends and rates). For example it would be useful to evaluate effects of Hyperion sludge outfall (off Southern California), and the 170-km dumpsite (off the U.S. Middle Atlantic coast).

(2) Development of hypotheses and predictive models (physical, chemical, biological) to guide field studies.

(3) Development of better records of quantity and composition of materials discharged to sites.

(4) Use of pilot projects in newly designated disposal sites (in areas not previously used).

2.4 Alternative Procedures for Cleanup or Rehabilitation of Severely Polluted Areas

The long-term objective of this research is to provide technological, environmental, and economic data on alternative procedures for cleanup or rehabilitation of severely polluted bottom areas in coastal waters of the United States. Severe pollution of bottom muds has been caused by discharge of toxic materials into many environments, including Kepone in the James River, polychlorinated biphenyls in the Hudson River, and mercury in Lake St. Clair and the Detroit River. Remedial and maintenance dredging have been delayed because of possible effects of potentially toxic materials that might be mobilized by dredging and disposal operations.

Regions of high priority include (1) the connecting channels of the Great Lakes, (2) Atlantic and Gulf Coast areas with broad continental shelves, (3) the West Coast and island areas with narrow shelves.

Treatment or disposal options include those in or near the affected waters, including transportation to deeper waters. The research and development will include a first-phase feasibility study (discussed herein), followed by second-phase pilot-scale operations in selected areas, and third-phase development of contingency plans.

The Phase I strategies for the feasibility study might encompass the following studies, focused toward pilot studies in Lake St. Clair and the Detroit River, the James River, and the Hudson River:

(1) Evaluate current practices and results of bottom sediment rehabilitation such as that in Yakkaichi Bay south of Tokyo.

(2) Evaluate technological proposals made for Environmental Protection Agency, Corps of Engineers, and other agencies for cleanup of priority areas such as southern Michigan (polybrominated biphenyls).

(3) Characterize sedimentation and hydrographic properties of various estuaries, bays, and harbors that are especially likely to experience releases of toxic chemicals.

(4) Consider technologies for disposal and containment of dredged materials. These could include, but are not limited to the following:

- on-site, barge-mounted incineration, alkaline hydrolysis, or other treatment with residual disposal either on- or off-site.
- blanketing with coarser-grained, unpolluted sediment.
- construction of a cofferdam or other stream realignment procedure followed by permanent sealing of the toxic muds.
- off-site land containment of dredged material.
- offshore disposal to deep water in sealed disposable concrete containers.
- offshore disposal to deep water through pipeline.
- permanent grouting of polluted sediments.
- permanent paving of polluted area.
- temporary grouting or freezing of polluted sediments to permit their removal with minimum resuspension.
- accelerated in-situ degradation of toxic material in sediment.

3. THE SECOND-PRIORITY PROBLEMS

3.1 Fluid Muds

Fluid mud flows may be a major dispersal mechanism for dredged materials and particle-associated pollutants. Production of fluid muds during dredging is likely to increase as channel depth increases. Areas available for upland disposal are increasingly limited so that dredged materials likely to produce fluid muds when discharged may be placed in open-water sites more often, in the future.

Dense slurries of contaminated fluid mud, which accumulate in coastal harbors and shipping channels, are difficult to contain in open-water dump sites (Barnard 1978; Nichols et al., 1978). The fluid mud spreads over broad areas as mudflows or density currents, threatening clam and oyster beds and fishery spawning grounds (May, 1973; Diaz and Boesch, 1977). Because fluid mud persists and is often enriched with trace metals, toxic materials, and organic matter devoid of oxygen, it has a high potential for degrading marine resources in or near the disposal sites.

Answers to questions about fluid mud influence waste-disposal strategies. Research should be directed toward the following questions:

When dredged material consists of fluid mud (slurries of high suspended solids), how can one predict the dispersion of a fluid mud mass in space and time with varied geometric and hydraulic conditions in the environment?

What are the effects of fluid mud on benthic organisms and community structure?

How can fluid mud dispersion be controlled and the mud stabilized to alleviate impacts on biota and release of pollutants into overlying water?

3.2 Effects of Excess Turbidity

Investigations to evaluate potential damages of turbidity to the ocean environment are urgently needed. Certain marine habitats (for example, coral reefs, kelp beds, and sea grass areas) may be especially vulnerable to the effects of high concentrations of suspended particles, such as those that may be produced by dredging disposal operations. Adverse effects of suspended particles and nutrient enrichment have been documented for a coral environment in Hawaii by Johannes (1978); high concentrations of suspended materials can inhibit photosynthetic activity of aquatic plants. However few quantitative field or laboratory data are yet available concerning the spatial and temporal effects of known concentrations of suspended materials on ocean habitats.

In general, adult aquatic animals (fish, crustacea, mollusks) can tolerate high concentrations of suspended material for short periods of time. For example, Saila et al. (1968) exposed lobsters (Homarus americanus) to concentrations up to 3200 ppm of silt for 24 hours with no apparent ill effects. Sherk et al. (1975) showed that early life history stages are more susceptible to damage by suspended material, which may cause sublethal effects on certain species. The tolerance of many important aquatic organisms to turbidity is fairly well known. However, the behavioral response of certain economically or recreationally important organisms to turbidity is very much in need of study. In addition, quantitative data are needed on the specific effects of turbidity produced from contaminated versus uncontaminated sediments.

Both field and laboratory studies are needed to provide information on the quantity, kinds, and duration of exposure to demonstrate specific adverse effects to various coral species, kelps, and sea grasses. Laboratory studies are needed on the behavioral response to turbidity by fish species that undergo seasonal movements and/or migrations in coastal areas. Such species include the striped bass, scup, and menhaden.

3.3 Sand and Gravel Mining

Construction aggregates are a vital part of the United States economy. In 1974 more than 900 million tons of sand and gravel were produced by about 5600 commercial operations (NOAA, 1976). The U.S. Bureau of Mines expects the demand for sand and gravel to grow at a rate of about 3% per year through the year 2000.

In many urban areas, land-based deposits are either being depleted or made inaccessible by urban expansion, are too expensive because of land values, are being restricted by legislation, or are located in very remote areas. Hess and Cruickshank (1975) suggested that new sources of supply that can be mined economically with a minimum of environmental impact must be developed to avert serious shortages. Critical shortages already exist in Puerto Rico and the Virgin Islands, and existing supplies are nearly depleted in New England.

Commercial sand and gravel mining operations are foreseeable along the Atlantic continental shelf within 5 to 10 years. In fact, United States reserves of sand and gravel might be increased by a factor of up to 25 if seafloor deposits are considered. The United States sand and gravel industry will probably eventually follow the development of several European countries and Japan, which now have economically viable marine sand and gravel operations. The technical capability exists to mine deposits in water depths to about 30 to 45 meters (Hess, 1971).

Alterations and disturbances to the marine environment associated with offshore mining operations are not well understood. Even around existing operations, environmental effects have not been documented sufficiently to permit resource development without concern over risk to ocean resources or shore erosion. Some aspects of the potential environmental impacts are being addressed by the Coastal Engineering Research Center in its evaluation of beach nourishment and offshore dredging. Other aspects of environmental impacts associated with dredging and disposal of dredged material have been evaluated within the Dredged Material Research Program (Boyd et al., 1972). In addition, studies in France (Cressard, 1975) may provide some results applicable to the United States.

General concerns involve the lack of understanding of biological and physical characteristics and processes in the marine environment that will be affected by sand and gravel mining. For example, the value of different types of continental shelf areas to various ocean resources is not known. Because of these uncertainties, the industry has been reluctant to develop systems and equipment for offshore mining without some form of government assurances. The relevant environmental problems must be solved, and a favorable legal climate and workable leasing/permit provisions must be created if a marine sand and gravel industry is to develop.

Besides the mining operation itself, the creation of borrow pits may cause environmental changes. The effect of unfilled borrow pits (created during the mining operations) on sedimentation, circulation, water chemistry, or benthic recolonization is poorly understood. There are also questions about whether these borrow pits can be used to contain contaminated or uncontaminated finer-grained dredged material with or without cover. The technology for borrow-pit disposal of dredged material was considered by the DMRP (Johanson et al., 1976). Whether fine-grained fill will have a beneficial effect on the benthic productivity is yet to be ascertained. In addition, we do not know whether experiences from other foreign operations (Hess, 1971) can be transferred to United States environments. If they can be, research requirements may be reduced.

Sand and gravel mining and dredged material disposal may be complementary activities. Future research should consider the possibility of filling the borrow pits with fine-grained dredged sediment and capping the deposits with sand. Although there are technical problems to be solved, this procedure might both remove the borrow pit and isolate and contain the dredged sediment.

We recommend syntheses of available information on sand and gravel mining operations in the North Sea, study of existing borrow pits in United States coastal areas, and testing the response of coastal shelf and environment ecosystems to filling of existing borrow pits with fine-grained dredged material. With results of such studies the effect of mining operations and the desirability of borrow pit filling can be evaluated. Pilot operations should be closely monitored and evaluated as a means of resolving the technical, legal, environmental, economic, industrial, socio-political and legislative problems associated with mining and borrow pit filling in offshore areas.

3.4 Incineration at Sea

The United States is a member of the Intergovernmental Maritime Consultative Organization (IMCO), which is a United Nations agency whose concerns include at-sea incineration. With increased limitations on terrestrial waste disposal, it is important to evaluate the environmental effects of ocean-based incineration of wastes. Incineration of wastes at sea in designated areas is under consideration for such materials as toxic industrial wastes, contaminated waste solids, and domestic and industrial refuse. First (1972) documented some physical, meteorological, chemical, and economic aspects of solid waste incineration at sea.

We recommend meterological studies of potential oceanic incineration sites to permit predictions of atmospheric dispersal of incineration plumes and to minimize hazards to marine traffic and to land areas exposed to the incinerator plumes. We recommend other studies to consider the fate of various types of particulate incinerator residues discharged at sea.

Pilot studies should be made to evaluate any problems involved with ocean incineration. Some model studies of atmospheric plume dispersion are desirable. A systems model of an operational procedure can be a useful prerequisite to pilot studies.

3.5 Episodic Release and Transport of Contaminants

Although contaminants may be delivered to the marine environments continuously or periodically, there is increasing recognition of the importance of controlling occasional, episodic events to control the contaminant budget in the marine environment. Floods, hurricane surges, tsunamis, and such episodic events can produce exceptional conditions for release and dispersal of contaminants with possible jeopardy to health and marine resources (Bokuniewicz et al., 1977; Gorsline and Swift, 1977). For example, more sediment was transported into Chesapeake Bay during a few days of flooding than during many years of normal river inflow (Schubel, 1974; Nichols, 1977).

Major efforts need to be directed to studying the impact of unexpected, catastrophic events, and contingency plans should be developed to deal with them.

Investigations should be directed to answering the following questions:

(1) Given a source of contamination, how much material is released or mobilized by the event? Where does it go and at what rate?

(2) How great are the changes relative to long-term average releases?

(3) What are the corresponding effects on or responses from marine resources?

(4) How long does it take for the affected resources to recover or to come into a new equilibrium?

(5) Are continuous data collection systems useful for monitoring and detecting the effects of unusual conditions?

Policy considerations might involve the following additional concerns. Local research facilities could be identified to deal with unexpected events in given areas. A funding mechanism could be developed to supply short-term, low-level support, within hours if necessary, for the study of unusual conditions. To prevent duplication of effort, existing programs need further coordination.

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LITTER

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1. PROBLEM IDENTIFICATION

For this report, litter is defined as any anthopogenic or natural solid product that is out of place in the marine environment. It consists of plastic and other synthetic, organic materials, glass, metals, wood, petroleum products in the form of tar balls, grease balls, and natural organic articles resulting from improper disposal. These materials are widespread in the sea and can be found on beaches, in coastal and open ocean waters, in or on bottom sediments, and in marine organisms. Sources of marine litter include commercial shipping (including discharges and cargo handling), recreational users of beaches and waters, solid-waste handling operations, industrial inputs, and sewage-related effluents, particularly storm sewer overflows and sewage treatment bypassing.

Our knowledge of the role played by litter in marine ecosystems is extremely limited. This section summarizes our current understanding of the litter problem, exposes critical areas that need further investigation, and recommends ways of monitoring this chronic type of pollution. Following are the major problems deserving attention:

(1) Identifying and quantifying specific litter materials found on widely varied areas, such as the seabed, the beaches, and the sea surface.

(2) Determining the sources of these materials and the associated pathways and mechanisms of transport in the marine environment.

(3) Understanding the fate of these forms of litter, particularly the persistence of these materials in marine areas.

(4) Assessing the impacts of these materials on marine organisms and on recreational and commercial users of the sea.

2. DISTRIBUTION OF LITTER IN THE MARINE ENVIRONMENT

Litter concentrations and other quantitative information are provided in Tables 1, 2, and 3. A bias is apparent in the data since some areas that potentially have large litter concentrations have remained unstudied. Also investigators tend to study areas that are already known to be polluted.

2.1 Beach Litter

Litter is distributed ubiquitously over the world's beaches. Sources and types of litter vary with beach location (Table 1). For example, in Narragansett Bay, R. I., Cundell (1973) noted that most beach litter came from either fast-food refuse or recreational boating. In contrast, in northern Scotland a large portion of the litter was of foreign origin and probably came from commercial ships (Scott, 1972, 1975). On many other beaches the litter originated from industrial sources (Hays and Cormons, 1973) or from sewer outfall discharges (Swanson et al., 1977).

The types and concentrations of litter have been quantified on only a few beaches. Some areas in Scotland and England (Scott, 1975; Dixon and Cooke, 1977) contain more than 1000 items/km of beach, and in New Zealand the concentration may be more than 40×10^6 plastic particles/km. Plastic particles seem to be the most common beach litter; however, we again note that very little information is available on the concentrations and kinds of beach litter.

2.2 Litter on the Ocean Surface

The world's oceans are also littered with a variety of plastic particles. In 1971 the Sargasso Sea contained an average of 3,500 pieces and 290 grams of polyethylene plastic per square kilometer (Carpenter and Smith, 1972). Along the east coast of the United States the ocean surface concentrations range from means of about 10 to 80 g/km^2. This same type of litter has been collected in surface waters of much of the open north Pacific Ocean (Venrick et al., 1973; Wong et al., 1974) and the coastal northwestern Atlantic. Small plastic particles have also been collected in plankton trawls in Bristol Channel, U.K. (Morris and Hamilton, 1974).

2.3 Litter on the Ocean Floor

References to benthic litter in the scientific literature are few. Nevertheless, media and personal accounts of litter on the sea bottom around public wharves abound. Scuba divers are particularly aware of

Table 1. Litter (Excluding Tar) on Beaches

Region	Site	Category	Concentrations*	Reference
New England	Coanicut Island, Narragansett Bay, R.I.	Recreational	9.6 g of plastic	Cundell (1973)
Mid-Atlantic	Amboy, N.J. Fire Island, N.Y.	Plastic particles (Industrial?)	Not quantified	Hays and Cormans, (1973)
	Long Island, N.Y.	Sewage	Not quantified except as totals	Swanson et al. (1977)
Gulf of Mexico	Corpus Christi, Tex.	Plastic particles	Not quantified	Colton (1974)
	Padre Island National Seashore	Clandestine waste dumping	1.39 55-gal. drums/km	Matthews (1975)
Washington	Kalaloch Beach	Plastic particles	Not quantified	Colton et al. (1974)
Alaska	Amchitka Island	Fisheries	0.125 tons of gill nets/km 72.9 gill net floats/km	U.S. Dept. of Commerce (1973)
Canadian South Beaufort Sea	Yukon and Tuktoyaktuk Peninsula Coast	Seismic flagging	0.15 g/m of beach	Wong et al. (1976)
United Kingdom	Loch Scavaig, Scotland	Com'l. transport	0.90 plastic items/m (8/71) 4.66 plastic items/m (8/74)	Scott (1975)
	Kent Beach, England	Com'l transport	236.3 plastic items/m 960.0 glass items/km 154.0 metal items/km 24.4 paper items/km 7.9 other items/km	Dixon and Cooke (1977)
	Bristol Channel	Plastic particles	Not quantified	Morris and Hamilton (1974)
Continental Europe	Lisbon, Portugal	Plastic particles	Not quantified	Colton et al. (1974)
South America	Barianquilla, Columbia	Plastic particles	Not quantified	Colton et al. (1974)
New Zealand	Selected Auckland beaches	Plastic particles 5-6 mm diameter	Generally >100/m; sometimes >2000/m	Gregory (1977)

*Concentrations per km or m of beach front.

Table 2. Litter (Excluding Tar) on the Ocean Surface (km^2 or m^2) or in the Water Column (m^3)

Region	Site	Category	Concentrations	Reference
NW Atlantic	Sargasso Sea	Polyethylene particles about 5 to 6 mm dia.	$\bar{x}$ = 290 g/km^2 $\bar{x}$ = 3500 $pieces/km^2$	Carpenter and Smith (1974)
	Eastern U.S. seacoast, excluding Florida	Plastic particles	77.7 g/km^2	Colton, Jr. (1974)
	Bahamas and north of Caribbean Islands	Plastic particles	18.1 g/km^2	Colton, Jr. (1974)
	Caribbean Sea	Plastic particles	10.5 g/km^2	Colton, Jr. (1974)
United Kingdom	Bristol Channel	Polystyrene spherules	Up to 198 $spherules/m^3$	Morris and Hamilton (1974)
NE Pacific	NE of Hawaii	Visible flotsam	4.2 $items/km^2$	Venrick (1973)
	NE of Hawaii (35°N, 150-140°W)	Plastic particles	34,000/km^2 (max) 3.5 mg/m^2 (max)	Wong et al. (1974)
	35°N, 140° E to 130°W (North Pacific Current)	Plastic particles	0.3 mg/m^2 (av)	Wong et al. (1974)
	35°N to 49°N, 125°W (West Coast, U.S.)	Plastic particles	0.0 mg/m^2	Wong et al. (1974)

Table 3. Litter on the Ocean Floor

Region	Site	Category	Concentrations or Semi-Quantitative Results	Reference
New England	Chicoppee River, Mass.	Plastic particulates	$0.88/cm^3$ and $529.2/cm^2$	Hays and Cormans (1973)
	Connecticut River at Saybrook	Plastic particulates	$8.4/cm^3$	Hays and Cormans (1973)
Northeast Gulf of Alaska	60°00'N, 147°30'W to 59°38'N, 140°00'W (Northeastern Gulf of Alaska)	Primary plastic	Of 58 trawls (av. length 5.92 km) 33 contained refuse	Jewett (1976)
Bering Sea	Approximately the southern Bering Sea fishing area	Metal, rope (synthetic), plastic, or glass bottom debris	Of 106 trawls (av. area 0.039 m^2) 43 contained refuse	Feder et al. (1978)
United Kingdom	Bristol Channel	Polystyrene spherules	Up to $20,000/m^2$ near Holm Islands and up to $100,000/km^2$ in Bridgewater Bay	Morris and Hamilton (1974)
Netherlands	Continental	Industrial materials	27 to 136 articles/km^2, 15% to 58% man-made	Van Banning (1972)

this problem, which for the most part is out of sight of the general public. Bottom trawls in the northeast Gulf of Alaska in 1975 (Jewett, 1976) collected a variety of litter consisting mainly of plastic materials, such as refuse bags, bait wrappers, and cargo binding materials. The presence of many plastic articles of Japanese and Korean origin and cargo binding material indicate that seaborne commerce is one source. Bottom trawls in 1975 and 1976 (Feder et al., 1978) collected a large variety of litter most of which could be attributed to fishing activities in the area. A similar benthic study by Van Banning (1972) on the Netherlands' continental shelf showed the presence of a large number of man-made articles, such as packing materials, bottles, and metal drums.

Kinds of plastic particles that have been found on beaches and the ocean surface have also been discovered in some instances in the benthic sediment of the Bristol Channel (Morris and Hamilton, 1974) and in rivers of New England (Carpenter, personal observation).

3. SOURCES OF LITTER AND ROUTES OF TRANSFER

The sources and transfer routes of litter to the ocean are almost as numerous as the types of materials found. For example, a child throws a can beyond the surf and attempts to sink it with a stone, or an oceanographer uses an expendable bathythermograph and leaves several hundred meters of copper wire in the water. In general, the large coastal population centers of the world, through the estuarine systems around which they are established, are the main contributors of litter. More specifically, litter enters the oceans from indiscriminant handling of materials at their sources (industrial, commercial and recreational) and through inadequate or inefficient sewage and refuse treatment processes. Discussions of some potentially significant contributors of litter to the marine environment follow.

3.1 Industry

Some materials enter the marine environment directly as wastes during manufacturing or indirectly through the industrial consumer chain. Plastic particles such as polyethylene nibs or polystyrene suspension beads that originate from industrial sources have been found far at sea in both the Atlantic and Pacific Oceans (Carpenter and Smith, 1972; Colton et al., 1974). Apparently these materials have come directly from the manufacturer and indirectly through improper waste disposal operations. However, almost nothing is known about the origins, types, and amounts of litter entering the sea from industrial sources.

3.2 Urban Runoff and Combined Sewer Outfalls

Considerable material in the form of street litter, oil, and grease enters the marine environment directly as runoff from land during rains. Oil and grease are considered herein to be litter in the sense that they have the potential to form tar and grease balls. Tar and grease balls typically have high fecal coliform counts and thus are a possible public health threat as well as being aesthetically displeasing when washed ashore. In some cities, such as New York, the storm sewer systems and sanitary sewer systems are combined. When rainfall intensities in New York exceed as little as 0.5 mm/h for an hour or more the sewage treatment plant is bypassed. In addition to the heavy load of street litter, sewage and the associated solid wastes (such as condom rings, diaper liners, tampon applicators) are washed directly into estuarine waters without screening and treatment. In New York City an estimated 81,000 kg of oil and grease flowed from one outfall during a four-hour period (Swanson et al., 1977). Some 14% of the urban areas of the United States and 25% of the population of those areas are served by combined storm sewer systems. The older and larger cities such as New York, Philadelphia, Chicago, and San Francisco are at least in part served by combined storm sewer systems. Elimination or improvement of these systems seems unlikely in the immediate future. As with industrial litter we know little about kinds and amounts of litter entering the sea from urban runoff. One major problem in quantifying such litter is the sporadic nature of the input.

3.3 Wastewater Discharges

Municipal discharges contribute large quantities of oil and grease to receiving water. Up to 191 x 10^3 kg of oil and grease have been estimated to enter estuarine waters in wastewater on a daily basis from the New York metropolitan region (Heaney et al., 1977).

In addition, sewage treatment plants do not always run at 100% efficiency. For example, during the July 1977 New York City blackout about 4 million m^3 of raw sewage that normally would have been treated escaped to the marine environment along with the sewage related artifacts. Metcalf and Eddy (1972) estimate that 37 to 224 m^3 of sewage material is screened from 1 million m^3 of wastewater. An average of 11 m^3/s of raw sewage enters the New York Harbor area. This represents an input of some 35 to 213 m^3 of sewage solids daily.

3.4 Solid Waste Disposal Practices

Cities no longer dispose of garbage and trash at sea. Much of it however is used as landfill in the vicinity of estuarine waters. Routine transfer operations plus the washing of these areas by tide and rain causes considerable but undetermined quantities to escape into the marine environment.

3.5 Commercial Ships and Recreational Boats

For all kinds of craft (passenger, merchant, commercial fishing, military vessels, and recreational boats), the National Academy of Sciences (Matthews, 1975) estimates that 6.2 x 10^6 metric tons of litter are discarded into the marine environment throughout the world. The Coast Guard estimates that recreational boat personnel alone contribute one-half kg of paper, cans, and bottles and one-fourth kg of garbage to the marine environment per person per boating day.

3.6 Debris Harmful to Navigation

It has been estimated that nearly 44 x 10^6 kg of wood and other debris harmful to navigation were removed from eight major harbor areas in 1972 (Matthews, 1975). The lumber industry contributes much of this; however, in our older harbors large quantities are contributed from decaying waterfront facilities and pier fires. If removal is 90% efficient some 5 x 10^6 kg remain as litter. This probably represents a small fraction of the total amount of wood and other debris actually in marine waters.

3.7 Total Input

The National Academy of Sciences (Matthews, 1975) estimates a flux of 6.4 x 10^6 metric tons/yr of litter into the world's oceans. Of that, one-third (2.1 x 10^6 metric tons/yr) is attributed to the United States. Considering that 6.2 x 10^6 metric tons/yr or 97% of the total were estimated to be from the shipping/boating industry, it would appear that some other major sources have been ignored. In the New York metropolitan region it is estimated that at most the shipping industry contributes only one-half the total weight of litter, not including oil and grease. If this is the case, it is possible that the United States contributes nearly 4 x 10^6 metric tons/yr of litter to the marine environment. Industrial inputs, urban runoff/combined sewer systems, and solid waste handling operations are the poorest documented sources at this time.

4. PERSISTENCE OF MARINE LITTER

Man-made and natural litter and debris endure in the marine environment for widely varying lengths of time. Although some products may last only for days, many materials require decades or longer to disintegrate. The impacts of litter must be assessed by understanding the balance between input rates and breakdown time for materials. At present, very little is known about litter dynamics and the adequacy of natural cleansing processes.

The fate of marine litter depends on numerous factors. The chemical and physical structure of a material itself is of prime importance. Most litter materials that constitute a problem are chemically stable. Chemical and biological degradation rates of litter are usually low. Mechanical disintegration is primarily restricted to high-energy shorelines, and breakdown factors are highly dependent on time and place. Because of the variability of the environment and the diversity of materials, it is impossible to predict the fate of litter with any reliability.

Litter materials can be ranked in a general way according to their resistance to chemical and biological degradation in the marine environment:

- High persistence (more than 3 years): plastics and plastic products (i.e., polyethylene, polystyrene, polypropylene, polyvinyl chlorides, and acrylonitrile-butadiene-styrene), glass, ceramics, raw lumber, rubber, metals such as aluminum, stainless steel, iron.

- Moderate persistence (1 to 3 years): petroleum residues, steel cans, cloth, and natural fibers.

- Low persistence (less than 1 year): paper, cellulose, food and vegetable wastes.

Litter tends to be more persistent on seabed, sea surface, and low-energy shorelines; high-energy zones fragment materials or aid in their sinking. Resistance to mechanical abrasion and fragmentation is low for paper, glass, ceramics, and some plastics; it is moderate for wood, rubber, other plastics, petroleum residues, fibers, and cloth; it is high for most metal products.

Plastics have become particularly pervasive. Small production particles and fragments are common on the sea surface (Carpenter and Smith, 1972). Plastic packaging products compose a major portion of beached litter. Studies of weathering of plastic packaging have indicated long-term resistance time (Cundell, 1974; Scott, 1972). Polyethylene and polystyrene foam are persistent with respect to ultraviolet radiation and oxidation. Low-density polyethylene products that are many years old can be found without appreciable signs of disintegration (Scott, 1973). High-density polyethylene, on the other hand, is susceptible to degradation by the action of ultraviolet light. All of these plastic materials show at least long-term effects of disintegration.

Many new plastics, notably polyvinylchloride (PVC) and Teflon, are nearly inert and can be expected to persist for decades, if not centuries. Besides weathering, microbial degradation may have some effect, but probably requires prior chemical oxidative-aging to render the material susceptible to biodegradation (Cundell, 1974). Most research has indicated that synthetic polymers are resistant to microbial attack.

With the production of plastics expected to double in the 1980's (Scott, 1972), increased quantities of these materials can be expected to accumulate in the marine environment. New research is needed on the degradation rates of plastics and their breakdown pathways, as well as the feasibility of substituting photodegradable or water-soluble plastics in the future.

Plastics can also release toxic materials called plasticizers (e.g., phthalates, PCBs) into the marine environment. The extent of the plasticizer problem is not known, although some of these compounds have been detected in sea water.

Petroleum residues (tar balls) are another pervasive form of ocean litter (Wong et al., 1976). Compared with suspended or dissolved oil, these residues are relatively inert in sea water. Weather slowly leaches soluble compounds into the water or suspends fine particulates from the surface of the tar balls. Pelagic tar is moderately persistent and may require 1 to 3 years to degrade. Beached tar is subject to accelerated mechanical action and physical weathering. Petroleum coating rocky shores often leaves a persistent residue that may remain highly resistent to degradation for many years (Butler et al., 1973). Tar coatings of rocks in Bermuda may be up to 10 years old.

Marine litter swept away from one area is deposited in another. Materials sinking from the sea surface are deposited on the seabed. Windward shores tend to accumulate ocean-borne litter. Protected low-energy bays and estuaries often receive the accumulated debris from high-energy shorelines. Despite the long life of plastic products, a recent survey of English beaches found that most containers were significantly less than 3 years old when recovered (Dixon and Cooke, 1977). The effects of mechanical action, such as fragmentation, abrasion, compression, puncturing, and shredding, were evident in 25% of the containers. Beach cleaning, sinking, or long-shore transport may all have helped keep accumulation below worst-case levels. In such instances the fate of the containers is simply fragmentation and/or removal to other sites.

Evidence from trawling, dredging, and scuba diving indicates an increasing pervasiveness of plastic products on the seabed. Metals, synthetic ropes, glass, and especially plastics are the long-lived litter of the seabed (Feder et al., 1978). In the Gulf of Alaska, fully 57% of benthic trawls collected man-made debris, primarily plastic products (Jewett, 1976).

5. EFFECTS OF MARINE LITTER

Some available information suggests that litter may have significant biological effects on some marine organisms. However, virtually no hard evidence clearly documents that litter is deleterious to marine organisms or human health. Most conclusions are based on observations of ingestion of litter. Biological effects may result from direct toxicity or the blockage of alimentary canals. An additional effect of litter is the aesthetic impact on beaches and economic cost of removal. Below we document what is known about the effects of litter in the marine environment.

5.1 Effects of Litter on Birds

Several bird species have been observed to ingest litter. For example, on Great Gull Island in eastern Long Island Sound, both terns and seagulls ingested polystyrene spherules (Hays and Cormons, 1973). The spherules were about 1 to 5 mm in diameter and were noted in the food pellets that are routinely regurgitated by the gulls, but incidence and amount of ingestion were not measured. In a cursory evaluation of the birds the investigators did not observe any harmful effects. However, they were concerned about the ingestion of pellets and urged further study.

Leach's petrels nesting near Newfoundland were examined by Rothstein (1973), and he noted that the gizzards of many birds contained polyethylene nibs (cylindrical pellets about 5 mm in diameter). Petrels generally feed in surface waters far at sea. The nibs were similar to those observed in surface waters of the northwestern Atlantic Ocean by Carpenter and Smith (1972). Like Hays and Cormans, Rothstein did not assess the biological effects of ingesting the plastic particles; however, he was concerned about possible unknown effects.

In Scotland and Norway litter appears to have had a detrimental effect on the native puffin population (Parslow and Jeffries, 1972; Parslow et al., 1972). Puffins ingested elastic threads (like rubber bands) that drift downriver to the sea. The threads appeared to have caused obstruction of the puffins' alimentary canals. Numerous dead puffins with apparently clogged guts have been observed; however, the actual extent of the problem remains to be assessed. It should also be noted here that the British puffin population has undergone marked population decline.

On southern Long Island, N. Y., polyethylene nibs were observed in the crops of deceased black and mallard ducks by Ward Stone, a state wildlife pathologist (Delmar, N. Y.). Here we have no clear cause and effect relationship between the ingestion of plastic and the mortality of birds. However, the possibility exists that the plastic particles were involved in duck mortalities, and it seems clear that further investigations should be carried out on these and other sea birds.

5.2 Effects of Litter on Fish

As with birds, very little is known about the effects of litter on fish. Again, there is the suggestion of possible harm. Carpenter et al. (1972) examined gut contents of larvae of fourteen fish species totaling 270 individuals in Long Island Sound. Of these, eight species contained polystyrene spherules in their gut contents. For some species, such as white perch (Roccus americanus) and silversides (Menidia menidia), a third of the larvae examined contained spherules in their guts. The potential problem is apparent since many of the larvae were only 5 mm in length yet contained spherules 0.5 mm in diameter, a size about half that of the larvae's width. A particle this large would probably cause intestinal blockage in the larvae.

In the Severn estuary in the United Kingdom, Kartar et al. (1973) also noted polystyrene spherules in fish guts. The 0+ and 1+ year class flounders (Platichthys flesus) were observed to contain the spherules. Some larvae only 2 to 5 cm long had as many as 30 spherules each in their intestines. However, the spherules have apparently ceased to be introduced into the estuary; the incidence in flounder dropped from 20.7% of those examined in spring of 1974 to none in spring of 1975 (Kartar et al., 1976).

An attempt was made to assess the effects of ingestion of spherules by young fish (Colton, 1974). Unfortunately, in laboratory studies the five fish species common to the southern New England coastal zone were not observed to ingest spherules. Also, of more than 500 larvae and juvenile fishes (22 species) collected on the east coast of the United States in 1972, Colton et al. (1974) observed no plastics in the gut contents. It is apparent that we know little about the percentage occurrence of litter in fish guts and the subsequent effects on the organisms. It may be that fish in estuaries and near shore as sampled by Karter et al. (1973) and Carpenter et al. (1972) have higher incidences of litter ingestion than those offshore (i.e., those samples by Colton et al., 1974).

One other effect of litter is to provide shelter for smaller fish (Kottcamp and Moyle, 1972). It is also well know that larger debris such as sunken ships provide habitats for larger fish (Brasher, 1973; Salazor, 1973).

5.3 Effects of Litter on Fouling Organisms

Virtually all litter serves as a habitat for fouling organisms. In the north Pacific gyre litter serves as attachment sites for algae and for goose barnacles. Venrick et al. (1973) noted that floating litter provides a long-lived substrate for transport of sessile animal species. However, this probably will not have much effect on populations since there has always been considerable natural introduction of wood into the sea (R. Turner, personal communication) and this must have served much the same role as the floating litter occurring today. We consider the role that litter plays as an attachment site for fouling organisms to be a minor problem.

5.4 Economic Loss Due to Litter

A large economic loss to fishermen occurs from the entanglement of trawl nets on bottom material (Texas A&M, 1973); however, we are unable to quantify this loss.

A considerable economic loss results from floating debris that fouls screws and water intake pipes of ships; however, we have little quantification of the loss. In 1969 the total loss to shipping from debris in American ports handling one-third of all United States shipping tonnage was $17.4 million. On beaches the annual cost of removing litter is high. For example, in 1931 about $10,000 was required per km of beach to remove litter on southern Long Island (State of N.Y., 1931). The annual cost of removing litter from 1 to 3 km of public beaches in Bermuda is more than $100,000 (B. Morris, personal communication). Much of the Bermuda litter is from tar balls and plastic debris. After a two-week washup of litter on Long Island in 1976, $100,000 was required for beach cleanup. The loss to beach-related industries was between $15 million and $25 million (Swanson et al., 1978).

6. PRIORITY RESEARCH

6.1 Concentrations and Types of Litter

Floating litter should be inventoried in the open ocean in both the Sargasso and North Pacific gyre and on the continental shelf and neritic zone. Neuston nets can be used to collect surface litter for identification and quantification. We recommend that litter on the seabed be noted by visual observation from submersibles and by bottom trawling. Beach surveys for large and small litter can be used to assess concentrations in both remote beaches and those near population centers. A general assessment of the litter concentration should be made at about 5-year intervals to detect significant changes in abundance. Neuston samples should be made in and out of the wake of the Hawaiian and the Bermuda Islands. Aerial overflights may be useful in calm weather to assess relatively large pieces of litter.

6.2 Sources of Litter and Prevention of Litter

For assessing the impact of litter on the marine environment, we believe that a better quantification of sources is essential. We also recommend research to develop degradable materials (such as plastics), more effective recycling programs for bottles, cans, oils, and grease, and more effective screening of sources (storm sewers, urban runoff, and landfills) to keep litter our of the environment. Better public awareness of litter problems would be beneficial for encouraging recycling and eliminating improper disposal wastes (such as those by recreational boaters). In some instances financial incentives would be beneficial. However, since the direct approach is not likely to be vigorously enforced, research efforts might provide the basis for more effective management of marine resources. For example, quantification of the volumes and types of litter from major sources, including industrial, urban runoff/combined sewer systems, and solid waste handling activities, would be beneficial to the study of concentration zones, cleanup problems, and effects studies.

Quantification efforts might begin with a literature review before development of any field measurement program. Industrial disposal activities can be surveyed through EPA and state permit programs. Urban runoff/combined sewer systems and solid waste handling activities can be surveyed by reviewing the non-point sources of pollution through the National 208 Program. This program is implemented by the EPA as part of Public Law 92-500 of the Federal Water Pollution Control Act. The purpose of the program is to encourage, facilitate, and implement area-wide waste-treatment management plans.

6.3 Persistence of Litter

We recommend that accumulation of litter materials in the marine environment be studied, using selected study areas and standard sampling protocols. The research should include measurements of rates and pathways of natural weathering processes of problem litter materials. Specific studies will consider the chemical degradation, mechanical breakdown, and decomposition of both newly-made materials and those collected in situ. Studies should incorporate industry knowledge of the chemical and physical properties of plastics, to assess the resistance of these materials to photo-oxidation, biodegradibility, and mechanical breakdown by physical and biotic forces. Laboratory and field studies should also be carried out to determine chemical decomposition pathways, rates of decomposition, formation, fates, and potential effects of intermediate breakdown products of problem litter materials in the marine environment, especially plastic materials and petroleum residues.

6.4 Effect of Litter on Ecosystems and Public Health

We recommend that controlled feeding experiments be carried out to determine the effects of ingestion of litter on seabirds. Initial experiments could use young mallard ducks and seagulls. Litter (such as polyethylene nibs, elastic threads, and polystyrene spherules) could be individually evaluated in separate experiments by mixing it with commercially available food. We recommend using several concentrations of litter. The growth and survival of birds should be assessed in long-term (i.e., 12-month) experiments.

Larval fishes common to the coastal zone should be used in experiments to assess the effect of litter ingestion on growth and survival. Similar experiments were attempted previously in the laboratory but the larvae did not ingest litter (Colton et al., 1974). This may have been because laboratory feeding conditions did not approximate those in the field. The kinds and amounts of natural foods used for both control and litter-treated groups must be as similar as possible to those present in the field. Several fish species should be utilized, especially those with larvae and juveniles present in the coastal zone. Experiments should evaluate growth and survival of treated and untreated larvae.

6.5 Human Health

Sewage-derived litter such as grease balls should be assessed for the presence and viability of pathogens. Grease balls that wash up on public beaches (e.g., southwestern Long Island) can be used by microbiologists to determine whether this form of litter threatens human health.

6.6 Sorption of Anthropogenic Organic Compounds

Many chemicals (e.g., polychlorinated hydrocarbons) are selectively absorbed by plastic. We recommend that samples of plastic from the sea be analyzed to determine their role in concentrating toxic compounds.

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ARTIFICIAL RADIONUCLIDES

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1. INTRODUCTION

The first significant input of artificial radionuclides to the oceans occurred in 1944 when the cooling water was discharged from the military plutonium reactors at Hanford, Wash., to the Pacific Ocean via the Columbia River. Two years later the detonation of two nuclear devices at the Pacific Proving Grounds in the Northern Marshall Islands introduced radionuclides into the north equatorial current of the Pacific Ocean and released significant quantities into the atmosphere. Since that time, fallout from weapons tests conducted by many nations has been deposited globally, and significant quantities of radioactive waste from the emerging nuclear industry in many countries have been discharged to the oceans, either directly or indirectly via rivers.

Since the very conception of atomic energy, it has been recognized that the component radionuclides pose a threat to human health and the environment; therefore, biomedical and radioecological studies in terrestrial, freshwater, and marine environments began at the outset. The quality and quantity of the research has been reported in the numerous publications of the U.S. Atomic Energy Commission and various countries of the world. Two significant publications on artificial radionuclides in the marine environment have been published: one reflects our knowledge of the impact of fallout (National Academy of Sciences, 1957) and the other, the effect of radionuclides from peaceful uses of nuclear energy (National Academy of Sciences, 1971). Although these publications are concerned with potential impacts, they also document the use of these radionuclides by the scientific community as tracers for the study of biological, physical, and chemical processes of the oceans.

Monitoring surveillance and research have provided the data that have enabled us to predict the distribution of radionuclides and their reactions in oceans, and to keep human exposure within the guidelines specified by international and federal bodies. Our predictions have been validated by follow-up surveys. In terms of ecological effects, the consensus of the literature is that radionuclides are not likely to be significantly deleterious in populations of marine organisms at the dose rates estimated for the most contaminated environments. Although predictions are subject to revision in the light of new knowledge, there is no evidence that the past and present practices, or present policies for radioactive waste disposal in the oceans, have jeopardized humans or any marine species (National Academy of Sciences, 1971).

2. PROBLEM IDENTIFICATION

The panel evaluated our present knowledge on artificial radionuclides in the oceans and identified research needs in the following program areas:

- deep-ocean data base for sub-seabed emplacement of high-level radioactive wastes
- long-term monitoring
- chemistry of radioelements
- marine sedimentation and remobilization
- biological effects of chronic low-level exposures
- monitoring of existing dump sites.

2.1 Deep-Ocean Data Base for Sub-Seabed Emplacement of High-Level Radioactive Wastes

Sub-seabed emplacement is an alternative to terrestrial depositories for high-level radioactive wastes. To further evaluate this alternative, we need to determine the parameters for the development of the technology and predict and assess the consequences of release of this material to the ocean waters. Current programs of research in the deep oceans are not adequate to meet these objectives.

2.2 Long-Term Monitoring

Marine processes are dynamic, and relatively long time constants are involved in many of them. Thus, extensive data are needed to establish credible transport parameters, concentration factors, critical pathways, and predictions of biological effects on humans and ecosystems, particularly for those radionuclides that will arise from alternative nuclear power sources and fuel cycles. Even after 20 years of research and monitoring of radionuclides by the United States, our information for selected radionuclides and pathways is not entirely adequate.

2.3 Chemical Form and Speciation

Radioactive discharge into the aquatic environment is of concern because of its potential transfer back to humans in seafood and, for the Great Lakes, in drinking water. The processes that control its transport and fate in these environments need further elucidation.

The concentration of any radionuclide in water, its acculumation by biota, and its transfer to sediments will be governed by its own chemical properties and its interaction with other chemical constituents in the environment. Although the concentrations of radionuclides can be readily measured in water, their chemical form of speciation is difficult to determine and therefore largely unknown. This situation is particularly acute for the transuranic elements (plutonium, americium, and curium) whose chemical properties are not completely known at their concentrations in the oceans. These elements can occur in several different oxidation states, and their stability is governed to some degree by the formation of compounds or complexes with other components in the system. To predict the behavior of each transuranic element in the marine environment, we need to determine their predominant oxidation states and chemical forms.

2.4 Marine Sedimentation and Remobilization

The rates at which radionuclides are returned to the ecosystem from the sediment need to be established, as well as the factors controlling these rates. Sedimentation alters the biological availability of radionuclides, usually resulting in lowered hazard. Studies to date have been primarily concerned with processes that carry radionuclides to the sediments. However, the sediments do not ultimately hold the radioactivity, but act as a storage reservoir from which remobilization can occur. The most important current research needs in sediment pollutant research are the characterization of the physical, chemical, biological, and microbiological processes operating in the sediments after deposition and the assessment of the rates of those processes and the physicochemical form and biological availability of sedimentary material.

2.5 Biological Effects

At present it appears that no damage to populations would be expected at the doses and dose rates estimated from current levels of radionuclides in fallout and in discharges from nuclear facilities. But our assessment of effects is limited by current methodology. We need to develop techniques to assess even more accurately the effects of chronic, low-level exposures on individual organisms, populations, communities, and ecosystems. Future research should address problems of genetic damage (gene mutation, chromosomal abberations) and population changes (population size, biomass, fecundity).

2.6 Monitoring of Existing Dump Sites

There is no apparent danger to humans or the environment from present dose rates at existing dump sites. However, we need data from these sites to test the validity of our assumption of safety. Data can also provide a sound scientific basis for conservation of ocean resources; and they can improve the scientific and technical basis for establishing and evaluating future monitoring operations.

3. PRESENT KNOWLEDGE

3.1 Past and Present Sources and Concentrations

The radioactivity burden of the marine environment falls into two broad categories: natural and anthropogenic. Natural radionuclides found in the oceans are primarily derived from nuclear reactions caused by cosmic-ray bombardment of atmospheric gases (e.g., H-3 and C-14) and from the weathering of rocks (e.g., K-40, Rb-87 and the natural uranium and thorium series). Although natural radionuclides can hardly be termed ocean pollutants, their concentrations and doses to marine organisms are useful for establishing a perspective when one considers the anthropogenic sources. Table 1 lists typical concentrations of the long-lived natural radionuclides in the ocean environment. Table 2 shows the dose rates to marine organisms from those radionuclides.

Table 1. Typical Concentrations of Natural Radionuclides in the Marine Environment (Based on data from the International Atomic Energy Agency, 1976)

	Units	H-3	C-14	K-40	Rb-87	U-238	Ra-226	Pb-210	Th-232
Sea Water	pCi/l	1-3	0.2	300	3	1	$4x10^{-2}$	$1-7x10^{-2}$	$0.1-8x10^{-4}$
Deep Ocean Sediment	pCi/g	---	---	---	---	0.1-1	---	---	0.04-2
Phytoplankton	pCi/kg*	1-3	$3x10^{2}$	$3x10^{3}$	---	50	20	$1.7x10^{-2}$	---
Zooplankton	pCi/kg*	1-3	$3x10^{2}$	$3x10^{-3}$	---	20	20	$1-25x10^{1}$	---
Crustacea	pCi/kg*	$6x10^{2}$	$3x10^{3}$	40	---	---	---	$4-7x10^{1}$	---
Fish	pCi/kg*	1-3	$4x10^{2}$	$3x10^{3}$	25	0.1-30	$2-50x10^{-1}$**	0.2-850†	---

* Based on wet weight
**Soft tissue
† Flesh, stomach, liver, and bone

Table 2. Dose Rates (μrad/h) to Marine Organisms from Internal Natural Radionuclides*
(Based on data from Woodhead et al., 1976)

Radionuclide	Phytoplankton	Zooplankton	Mollusca	Crustacea	Fish
H-3	$1\text{-}3 \times 10^{-5}$	$1\text{-}3 \times 10^{-5}$	$1\text{-}3 \times 10^{-5}$	$1\text{-}3 \times 10^{-5}$	$1\text{-}3 \times 10^{-5}$
C-14	1×10^{-2}	3×10^{-2}	6×10^{-2}	$> \times 10^{-2}$	5×10^{-2}
K-40	2×10^{-2}	1	3	3	3
Rb-87	---	---	10^{-2}	8×10^{-3}	5×10^{-3}
U-238	0.1	0.1 - 0.2	---	---	$1\text{-}300 \times 10^{-3}$
Ra-226	6×10^{-2}	0.2	---	---	$0.2\text{-}5 \times 10^{-2}$
Pb-210**	$3\text{-}18 \times 10^{-3}$	$1\text{-}14 \times 10^{-2}$	$4\text{-}9 \times 10^{-3}$	$3\text{-}6 \times 10^{-2}$	$2\text{-}20 \times 10^{-4}$

* These radionuclides in sea water contribute an additional dose to organisms, equal to or less than that received internally.

**It is assumed that the short-lived daughter Bi-210 is in equilibrium with Pb-210.

There is a relatively long list of anthropogenic sources of radioactivity in the oceans. These sources have been discussed in the literature (National Academy of Sciences, 1971, 1975; Preston et al., 1971; International Atomic Energy Agency, 1975, 1976). We will detail here only those anthropogenic sources which may be perceived to increase measurably oceanic concentrations of radionuclides with a resultant dose to marine organisms and ultimately to humans through the food chain.

3.1.1 Fallout from nuclear weapons testing

In all nuclear weapons tests by all countries more than 20 megacuries (20 MCi = 20 million curies) of ^{90}Sr, 30 MCi of ^{137}Cs and 0.4 MCi of ^{239}Pu were produced. These and numerous other radionuclides were originally emplaced, for the most part, in the high atmosphere and subsequently were deposited on the Earth's surface. The location and altitude of the detonations as well as meteorological processes have resulted in a distribution of substantially more than half of the debris in the Northern Hemisphere; the major portion is located between 30° and 60° N. latitude (National Academy of Sciences, 1975; United Nations Scientific Committee on the Effects of Atomic Radiation, 1977; Volchok and Toonkel, 1974; Feely et al., 1978).

Table 3 lists typical concentrations of some of the long-lived fallout radionuclides in the marine environment. The dose rates to marine organisms from those isotopes (except for ^{239}Pu) are shown in Table 4.

3.1.2 Releases from the nuclear power fuel cycle

Several countries are discharging into the marine environment low-level radioactive wastes from the reprocessing of spent nuclear fuel. These include the United Kingdom at Windscale on the Irish Sea and at

Table 3. Typical Concentrations of Some Long-Lived Fallout Radionuclides in the Marine Environment (Based on data from Woodhead et al., 1976)

	Units	H-3	C-14	Sr-90	Cs-137	Pu-239
Atlantic Ocean Surface Water	pCi/ℓ	20-70	0.01-104	0.02-0.5	0.03-0.8	$0.1\text{-}1 \times 10^{-3}$
Pacific Ocean Surface Water	pCi/ℓ	1-200	≤ 0.04	0.01-3	0.02-5	$0.1\text{-}1 \times 10^{-3}$
Indian Ocean Surface Water	pCi/ℓ	---	---	0.02-0.2	0.03-0.2	---
Phytoplankton	pCi/kg*	---	---	---	---	0.1-80
Zooplankton	pCi/kg*	---	---	---	---	1
Mollusca	pCi/kg*	---	---	---	100-700	0.1-0.6
Fish	pCi/kg*	---	---	---	40-80**	$0.1\text{-}13 \times 10^{-2}$†
Sediment	pCi/kg*	---	0.5-5	20-30	10-100	0.2-0.6

* Based on wet weight
**Muscle
† Muscle and liver

Note: The concentration of plutonium can vary locally in the oceans by many orders of magnitude depending on source. For instance, concentrations in the Irish Sea vary between 0.04 and 1 pCi/ℓ depending on the distance from Windscale.

Table 4. Dose Rates to Marine Organisms from Internal Long-Lived Fallout Radionuclides (μrad/h)* (Based on data from Woodhead et al., 1976)

	H-3	C-14	Sr-90	Cs-137
Phytoplankton	$0.3\text{-}300 \times 10^{-5}$	$0.6\text{-}3 \times 10^{-3}$	$0.5\text{-}9 \times 10^{-3}$	$0.8.60 \times 10^{-2}$
Zooplankton	$0.3\text{-}300 \times 10^{-5}$	$2\text{-}8 \times 10^{-3}$	$0.2\text{-}3 \times 10^{-1}$	0.2-10
Mollusca	$0.3\text{-}300 \times 10^{-5}$	$0.3\text{-}1 \times 10^{-2}$	$0.2\text{-}70 \times 10^{-4}$	$0.6\text{-}3 \times 10^{-1}$
Crustacea	$0.3\text{-}300 \times 10^{-5}$	$0.4\text{-}2 \times 10^{-2}$	$0.1\text{-}20 \times 10^{-3}$	$0.2\text{-}60 \times 10^{-3}$
Fish	$0.3\text{-}300 \times 10^{-5}$	$0.3\text{-}1 \times 10^{-2}$	$0.2\text{-}70 \times 10^{-5}$	$0.2\text{-}40 \times 10^{-1}$

*These radionuclides in sea water contribute an additional dose less than that received internally.

Dounreay in northern Scotland, France at Cap de la Hague on the Channel coast, India at Trombay, and Italy on the Gulf of Taranto.

Probably the largest nuclear fuel reprocessing plant and certainly the best documented in terms of discharge rates and environmental follow-up publications is Windscale. Numerous publications are available describing the outputs (International Atomic Energy Agency, 1976; Hetherington et al., 1975; Mitchell, 1977; Kupferman et al., 1978); others discuss the concentration and potential effects of these radionuclides (International Atomic Energy Agency, 1976; Hetherington et al., 1976; Kupferman et al., 1978; Murray and Kautsky, 1977; Murray et al., 1978).

Table 5 gives the cumulative discharge of some long-lived radionuclides from Windscale. Tables 6 and 7 list concentrations in the environment and doses to marine organisms from released radionuclides near the Windscale outfall. Table 8 indicates average concentrations of some radionuclides in the North Sea and off the west coast of Scotland (the Minch). Nuclear power reactors are designed to release only small amounts of radioactive liquid effluent exclusive of H-3, in contrast to the discharges of chemical reprocessing plants.

Table 5. Discharges of Long-Lived Radioactivity to the Irish Sea from Windscale (Based on data from Kupferman et al., 1978)

Radionuclide	Periods of Data Availability	Cumulative kCi
H-3	1967-1972	160
Sr-90	1957-1976	92
Cs-137	1957-1976	525
Total Alpha	1957-1974	27
Plutonium	1967-1974	9
Am-241	1968-1974	11

Table 6. Average Concentrations of Radionuclides Near the Windscale Outfall, 1968 (Based on data from Woodhead et al., 1976)

Units	Cs-135	Cs-137	Ce-144	Ru-106	Zr-95
Water pCi/ℓ	-	60	30	90	400
Sediment pCi/g	-	14	400	700	2000
Porphyra pCi/g	-	-	20	200	100
Fucus pCi/g	-	7	20	40	100
Plaice pCi/g	0.4	1	-	-	-

Table 7. Range of Dose Rates (μrad/h) to Marine Organisms from Windscale Outfall* (Based on data from Woodhead et al., 1976)

	Cs-134	Cs-137	Ce-144	Ru-106	Zr-95**
Phytoplankton	-	2-20 x 10^{-2}††	40-200	100-1000	20-500
Zooplankton	-	2-20 x 10^{-2}††	10-40	400-4000	100-3000
Mollusca	-	2-100 x 10^{-2}††	20-60	0.2-2	0.04-1
Crustacea	-	2-100 x 10^{-2}††	10-30 x 10†	7-70	8-200 x 10^{-2}
Fish	0.1-0.5	0.4-1	-	1-10 x 10^{-2}††	8-200 x 10^{-2}††

* Based on wet weight
**In equilibrium with Nb-95
† Muscle
††The dose rates are from internal exposure except for those based on external exposure.

Table 8. Average Surface Water Concentrations of SR-90 and CS-137 in the North Sea and the Minch in 1975-1976 (pCi/ℓ) (Based on data from Kupferman et al., 1978)

	Sr-90	Cs-137	Pu-239+240	Am-241
North Sea	0.5	1.3	0.002	0.0002
Minch	1.0	6.0	---	---

3.1.3 Other human sources

Other human sources of radioactivity to the marine environment include widespread pharmaceutical and industrial uses of radionuclides. As a general observation, however, it may be stated that these other sources contribute only small fractions of the total concentrations and doses. Studies of the impact of catastrophic events such as nuclear wars (National Academy of Sciences, 1975) indicate that marine systems would recover in 20 years with no observable effects to individuals or populations of aquatic organisms.

Two nuclear accidents affecting the marine environment have been studied. A nuclear weapons-carrying bomber crashed near Thule, Greenland, depositing plutonium isotopes in the water. Study of the area showed that 99% of the Pu went to the sediment; the Pu remaining in the water was largely particulate (Aarkrog, 1971). In 1964 a radioisotope thermogenerator (RIG) carried by an unmanned satellite disintegrated upon re-entry into the atmosphere. The particles behaved like global fallout and ultimately about 1×10^4 curies of ^{238}Pu were deposited in the world oceans (Hardy et al., 1973). Although this is a little more than all ^{238}Pu produced by all weapons tests, it is only about 6% of the total weapons plutonium. The Pacific Test Site (N. Marshall Islands) is also a source of radioactivity, especially the transuranics, to the North Pacific Equatorial Current.

3.2 Potential Sources

3.2.1 Sub-Seabed emplacement of high-level radioactive wastes

A prime requirement for an acceptable nuclear power program is a safe method for the ultimate storage of high-level radioactive wastes. At present the United States and several other countries are concentrating their efforts on defining the requirements for repositories safe from human and geologic disturbance. The principal efforts are concentrated on geologic formations--salt, shale, basalt, granite--within the terrestrial land mass. However, alternatives being examined include the use of the deep seabed.

Although dumping of low-level wastes on the seabed can be conducted without significant dose commitment to humans or the ecosystem, it is unlikely that the same methods could be used for high-level wastes. It has been proposed that sub-marine geologic formations may be able to contain these radioactive wastes in isolation long enough for them to decay to inconsequential levels. The advantages of this approach are that a multiple barrier could be provided starting with a waste form of slow dissolution rate, inside a canister, buried in a sediment with high retention and low permeability characteristics, before the radionuclides could enter the ocean system.

The primary goal of the present Sub-Seabed Program is to assess the technical and environmental feasibility of the disposal of high-level nuclear wastes or spent fuel in the impermeable geologic formations covered by the world's oceans (Anderson et al., 1975). The reference sub-seabed disposal system selected for study purposes is the emplacement of appropriately treated waste or spent reactor fuel in a specially designed container into the red clay sediments in the middle of a North Pacific tectonic plate, under the hub of a surface circular water mass called a gyre.

The potential advantages of seabed disposal include remoteness from human activities, the potentially high isolation capability of ocean sediments, the high heat sink capability of the ocean, the large areas available, and the possibility of avoiding the problems of finding and gaining access to adequate terrestrial sites. Some of the potential disadvantages are the difficulty of monitoring and retrievability, the requirement for transport to ports and ocean transport, special port and ship facilities, and the need for national and international acceptance of the use of the deep seabed for such purposes.

This three-phase Sub-Seabed Emplacement Program is being sponsored by the Department of Energy and managed by Sandia, with extensive international cooperation and scientific interchange. Phase I will determine environmental feasibility and is scheduled for completion by 1983. If environmental feasibility is established, phase II will assess engineering feasibility by 1990. If engineering feasibility is established, the concept could be demonstrated by 1995, assuming no delays because of international political considerations. Greater allocation of resources could shorten this schedule by, at most, 2 or 3 years.

Criteria for selection of study areas and specific disposal sites

Deep ocean floor areas for radioactive waste disposal should have certain characteristics:

- Tectonic stability. They should have low earthquake or volcanic activity, with minimum evidence of faulting, and slow, continuous depositional processes.

- Climatic stability. Combined movements of air and water, including changes in climate (e.g., ice ages), should have minimal effect on the underlying geological formation.

- Absence of resources. There should be low biological activity, both present and past, and few or no mineral resources of possible use to humanity now or in the next million years.

- Remoteness. The areas should be as inaccessible as possible to humans. The ocean floors are among the most remote regions on Earth. To intrude upon these areas requires technical sophistication and a large, planned effort. The risks of sabotage or of intentional intrusion upon a sub-seabed disposal site would be quite low.

- Predictability. A geological medium, to be suitable for emplacement of long-lived toxic materials, must be predictable. It must be possible to anticipate changes in its properties with time, and to apply the results of a few measurements, on both horizontal and vertical planes to the larger area under study. The more predictable and uniform the geologic environment, the less detailed specific site studies need be to define the geologic formation. Oceanic areas where processes are slow and continuously depositional, and where tectonic processes have been and are predicted to be at a minimum for millions of years, are the most uniform and predictable on the globe.

At present, the abyssal hills appear to be the most promising for seabed disposal. The abyssal hills, which occasionally form broad low swells (midocean rises), lie seaward of the abyssal plains and are old ocean crust originally formed by extrusions and faulting of basalt from the midocean ridge spreading centers. These vast abyssal-hill provinces (areas of gently sloping hills make up most of the deep sea floor of the North Pacific) are generally covered with 50 to 100 m of red clay. The abyssal hills and rises in the middle of the subocean tectonic plates are seismically passive. Where they also occur below the centers of wind-driven, surface-current gyres (large circular water flow systems), they are stable and relatively unproductive biologically. Bottom currents in the mid-Pacific gyre (MPG) areas of the North Pacific are generally weak and variable.

The multi-barrier concept of radionuclide containment

Seabed nuclear waste disposal is treated as a multiple-barrier assessment problem. A concept based on a set of sequential barriers to the release of radioactive nuclides has been adopted to balance the rates of decay of waste constituents against the rates of migration of the nuclides toward humans. These barriers are the waste form, the waste canister, the sub-seafloor emplacement medium and controlled modification of the medium, the benthic boundary layer, and the water column.

The major task of these studies is to determine whether any submarine geologic formation can contain radioactive waste long enough for it to decay to low levels. Attention is now focused on the waste form and the canister for containment during the period of heat release (near-field interactions) and on the sediments for long-term containment (far-field transport).

Since the required waste isolation time is much longer than can be simulated in experiments, the attributes of each component of the system must be known so that barrier system effectiveness can be predicted and judged by suitably substantiated models. These will be used to characterize subsystems and to enable parametric studies and sensitivity analyses to be conducted.

Barrier 1: Near-field interactions. Nuclide movement throughout the sediment is controlled by natural or induced pore-water movement, by diffusion due to concentration and/or temperature gradients, and by the natural or modified chemical properties of the sediment. During the first 100 years after emplacement, the fission-product-dominated thermal output may induce much larger pore-water velocities than those naturally present. Performance of the canister and waste form will also be important during that period. In addition any chemical, mechanical, or thermal changes caused by heating of the sediments will be of critical importance to the integrity of the primary sediment barrier and to the predictability of containment. The entire influence of heat on the sediment barrier must be identified, described, and experimentally verified. Also during the first 100 years, the sediments, through plastic flow, will be restoring themselves to nearly their original state of compaction.

Barrier 2: Far-field ion transport. The plastic seabed sediments are considered the primary long-term geologic barrier to the migration of radionuclides back to humans. These sediments typically consist of fine-grained (2 microns in size) water-saturated clays with low permeabilities ($\leq 10^{-7}$ cm/s for a hydraulic gradient of unit). The only known driving force for pore-water movement within the sediments in the abyssal hill region is sediment compaction, which occurs at rates of 1-3 mm/10 yr. Existing permeability data suggest that this natural pore-water velocity is in the same range as the rate of sediment accumulation (~ 1 m/10^6 yr).

Migration of radionuclides from a point of emplacement in the subseafloor sediments could be a combination of diffusion and advection. Models are needed to predict reliably the rates of nuclide migration from the point of emplacement toward the biosphere. To develop the necessary models to study ion-transport, the dominant mechanisms for nuclide sorption and migration must be adequately identified, quantitatively described, and experimentally verified.

The effect of sorption properties on long-term radionuclide transport has been calculated based on a transport model. It assumes a pore-water velocity of 10^{-1} m/yr (a factor of 10^5 over the estimated natural pore-water velocity), a 30-m sediment column, and estimated sorption coefficients. The results indicate containment for about a million years for radionuclides with small sorption coefficients. For another set of assumptions, where there is no natural pore-water movement, no interactions between dissolved nuclides and the sediment, a diffusion constant of 3×10^{-6} cm^2/yr, and a burial depth of 100 m, breakthrough time is about a million years. For the same assumption with sorption by the sediment, breakthrough times are 10^8 and 10^{11} years. The dependence of sorptive coefficients on temperature, concentration, and the presence of competing ions is not well known, but preliminary data indicate that, at least for thorium, elevated temperatures and the low nuclide concentrations likely around a waste canister lead to higher sorption coefficients, and hence to longer breakthrough times. Preliminary assessment of the barrier properties of the seabed sediments indicates that the sediments may be an adequate barrier.

Barrier 3: Water column. Another potential barrier to the migration of radionuclides from subsea geologic formations to humans is the water column. Some of the water at the bottom of the ocean basins is believed to have been at those great depths for thousands of years, and is thought to move in a very slow, uniform, plate-like manner. The age of these deep water masses and their horizontal and vertical advection and dispersion characteristics must be known to allow estimates of the barrier properties of the water column, and to allow evaluation of benefits and consequences of dilution and dispersion of any radionuclides inadvertently released. Models must be developed that will allow predictions of transport rates and concentrations for different depository locations and accident possibilities. A recent assessment of the oceanographic situation and the use of a developed simplified model should assist this task (International Atomic Energy Agency, 1978a).

Barrier 4: Deep sea resources and critical pathways. To assess the potential impact of accidentally released radionuclides on humans and the abyssal ecosystem the role of the deep-sea ecosystem must be established. Although there are some data on the existence of fish and invertebrates at these great depths, we have no firm data on population densities, food webs, stability of the system, metabolic rates, or vertical and horizontal migrations from which to assess uptake, accumulation, and transport of radionuclides, and effects of disturbance on the system. We need to determine the direct critical pathways of these radionuclides to humans. The consequences of ocean movements of radionuclides that may result in impacts in other areas used by man must be assessed. Potential dose commitments to human individuals and populations must be determined. Somatic and genetic effects on deep sea biota must also be assessed. In addition radiological assessments will be required for other release or accident situations, e.g., port facilities, transport, and emplacement. A recent radiological assessment for seabed dumping of radioactive wastes provides a technical base for this task. (International Atomic Energy Agency, 1978b).

Barrier 5: Rock. The baseline rock underlying the plastic sediments could be an additional barrier to the migration of radionuclides back to humans. The seabed program now is only monitoring research supported by the National Science Foundation through the International Program of Ocean Drilling and relevant work by the oil companies on the structure and barrier properties of these rocks. If the sediments are found inadequate as barriers, the barrier qualities of the basement rocks will be assessed as part of the seabed program. This assessment will include the thermal, mechanical and chemical responses of the rock to heat, radiation, and intrusion by humans; the behavior of interstitial fluids, both natural and induced; the sorption and ion migration properties of the rock formations; and the selection of sites at which these parameters are optimized.

Current investigations

Specific investigations currently being conducted by the United States DOE program include the following:

- Examination of ocean sediment properties such as vertical and horizontal consistency, heating and heat transfer coefficients, sorptive capacity, and ability to deform elastically to permit penetration.

- Assessment of the problems of heat produced by the waste and the impact of this heat upon the physical and chemical properties of the sediments.

- Sediment-canister waste interaction studies to evaluate potential canister materials.

- Development of analytical and laboratory capabilities to investigate waste canister emplacement techniques.

- Continuation of the characterization and environmental predictability studies of the sediments.

- Characteristics of biological communities in the ocean depth.

- Possible biological transfer and interaction of radionuclides.

- Development of a number of analytical models as part of the overall systems analysis effort.

- Risk assessment.

3.2.2 Alternative nuclear fuel cycles and marine radioactivity

Nuclear reactor fuel cycles now in use have been based on ^{235}U fission. Future systems may use either ^{239}Pu as fuel produced from ^{238}U, or ^{233}U fuel produced from ^{232}Th. Development of these reactor and fuel processing systems is proceeding in several nations, and the demands for energy may lead to their implementation. It seems unlikely that use of alternative fuel cycles will alter significantly the needs for monitoring and research in marine radioactivity. The specific radionuclides to be emphasized may change but the important principles and processes will not change. For example, the ^{235}U cycle and the ^{239}Pu cycle produce a greater total yield of transuranium radionuclides than does the ^{233}U cycle. The ^{233}U cycle, however, will involve increased mining for thorium and presumably will also result in environmental releases of ^{232}U and ^{233}U that are comparable to releases of transuranics from the ^{235}U and ^{239}Pu cycles. Therefore, the cycling, fates, and impacts of radionuclides from any of the fuel cycles are expected to be comparable in the marine environment. Only minor changes in analytical procedures will be required. It will still be appropriate to emphasize the same environmental parameters--source and concentration monitoring, concentration factors, food chain transfer, sedimentation, and remobilization--described in this report.

3.3 Environmental Pathways and Processes

3.3.1 Chemistry of radioelements

The major issues connected with the dissemination of any pollutant in the marine environment are whether it will be concentrated in the aquatic food chain and become a hazard to human health by consumption of seafood, and whether it will damage marine biological populations, communities, or ecosystems. The availability of any pollutant in the biosphere will depend largely on its being in a chemical form that can be accumulated in some manner by organisms.

In terms of radioactive contamination of the marine environment we are largely concerned with the release of radioactivity as a result of the various manufacturing processes involved in the extraction of uranium, fabrication of fuel elements, the release of fission and activation products from the operation of nuclear reactors, and the reprocessing of spent fuel elements and potential releases from the waste management options, including the seabed. The fission process leads to the formation of a wide variety of radioactive chemical elements with different chemical properties. Most of these fission products have relatively short radioactive half-lives and are not of general concern. However ^{90}Sr and ^{137}Cs have half-lives of approximately 30 years and, depending on release rates, may increase in concentration in the marine environment with time. In addition to the fission products, prolonged irradiation of nuclear fuels in power plants results in the formation of the transuranic elements, plutonium, americium and curium isotopes that have half-lives ranging from decades to 25,000 years.

These radionuclides have specific individual chemical properties that affect their behavior in the marine environment and therefore their bioaccumulation. Both ^{137}Cs and ^{90}Sr are typical of groups I and II in the periodic table, and their behaviors can be predicted from those of their stable isotopes and other elements, such as potassium and calcium in the same group. On the other hand, the transuranic elements do not occur naturally, and their behaviors are suggested by those of similar elements in the periodic table. The study of their behaviors is complicated by the fact that they can exist in the environment in several different oxidation states. For example, plutonium may exist in the III, IV, V, or VI oxidation states whose behavior may be compared with the actinides, thorium, protactinium, and uranium. Similarly americium and curium may exist in the III and IV oxidation states.

^{137}Cs and ^{90}Sr have been measured in the marine and freshwater environments for at least 25 years, and their behavior is relatively well understood. It has been found that very little ^{137}Cs and ^{90}Sr has been transferred from the water column of the oceans to the sediments; in the Great Lakes virtually all of the ^{137}Cs, but little of the ^{90}Sr, is incorporated in the sediments.

To a large extent these studies have been based on the release of radioactivity from the detonation of weapons. It was found that ^{90}Sr and ^{137}Cs are soluble in the oceans. It was assumed by many that both plutonium and americium would be unavailable in the environment since such materials could not dissolve in neutral or near-neutral waters. If initially they should do so, insoluble polymeric hydrated oxides would form which would be unavailable for interaction with the biosphere.

Intensive studies of the inventories of plutonium over land and sea have shown that the total amount deposited far exceeds the total exploded in the weapons. The excess arose from the intense neutron irradiation of depleted uranium used in the fabrication of the weapons and the decay of the produced ^{239}Np to ^{239}Pu (with a half-life of 2.35 days). Thus a large proportion of the plutonium now in the environment was formed as single atoms long after the initial explosion.

Studies of plutonium in the oceans and Great Lakes have shown that the fraction remaining in the water column is in true solution apparently as ions, and the concentration is far higher than would be expected if the controlling mechanism were the solubility of Pu (IV) hydroxide. Since Pu (IV) is the most stable oxidation state in process chemical studies, it was again inferred that Pu (IV) would be in the stable state in the environment.

Detailed studies of plutonium in the Great Lakes using ion exchange techniques have led to the conclusion that the Pu is present as an anionic complex and that there is little association with organic complexing agents such as humic acids. More recent studies have indicated that in the Great Lakes and the oceans, plutonium exists predominantly in the VI oxidation state while in solution but is reduced to Pu (IV) when associated with particulate material.

Studies have also shown that from environments as totally unrelated as the tropical lagoons of Eniwetok, the waters of the Irish Sea, and the fresh waters of the Great Lakes, there appears to be an almost constant proportionality (or distribution coefficient) between the concentration of plutonium in the water columns and in the surface of the sediments. The narrow range of values of this distribution coefficient (less than a factor of 10) from areas encompassing a range of concentrations of 10,000 to 1, and sources as diverse as sites of weapon tests, wastes from reprocessing plants, and fallout, suggest that the nature of the process of attachment of plutonium to particulate material in the water column is common to all areas.

The mechanism responsible for this attachment of plutonium (and many other radionuclides) is unknown. The elucidation of this mechanism is important since if the process is a reversible reaction, such as ion exchange or physical absorption, then the sediments can act as a source as well as a sink for radioactive contamination of the oceans. There is some evidence to suggest that in freshwater environments such as the Great Lakes the reaction is reversible and involves a change of oxidation state.

It is clear that the reactions involved are complex and must be evaluated further if we are going to be able to predict realistically the transport, fate, and bioaccumulation of this important pollutant.

While measurements of other transuranic elements such as americium (Am) and curium (Cm) have been made in some of these environments, there are insufficient data to draw any conclusions regarding their overall behavior in the oceans. Just as it has been assumed that plutonium would be in the IV oxidation state, it is now assumed that Am and Cm are in the III oxidation state. However, from thermodynamic considerations it appears that both Am and Cm could occur in the IV oxidation state in the oceans and therefore would behave more like thorium.

Since laboratory study of the chemical behavior of the transuranic elements in neutral or alkaline media has been virtually neglected, there is no data base available to continue theoretical calculations. Therefore, distinctions between the behavior of the transuranic elements in different oxidation states will have to be made on the basis of comparative data for the absorption by sediments and concentration factors in biota for the rare earths, uranium, thorium and the transuranic elements. These relationships may be very different in estuaries when there can be an interaction between seawater and freshwater with widely varying acidities.

3.3.2 Sedimentation of radionuclides

Radionuclides are transferred from seawater to sediments by direct reactions with suspended particles and by biological sedimentation. The rate and completeness of transfer depend on the properties of the specific radionuclide as well as its site of introduction. Isotopes of elements that are abundant in seawater are transferred more slowly than isotopes of rare elements. Zones of high biological activity are sites of more rapid transfer to sediment. Several consequences result from radionuclide sedimentation: 1) biological availability is altered, 2) transport and dilution rates are changed, and 3) the external radiation hazard is changed. In general it appears that sedimentation lowers the availability of radionuclides to organisms consumed by humans. Although filter-feeding organisms may sometimes more readily concentrate radionuclides that are associated with particles, removal of radionuclides from near-surface waters by sedimentation makes it less likely that fish will become contaminated. Since radionuclides in solution are transported by and diluted with water, binding to sediment also decreases the rate of dispersion, and settling to the bottom markedly lowers the rate of movement of particle-bound radionuclides. Rather than being more or less continuously in motion like the water, bottom sediments are transported only intermittently when waves or currents are large enough to cause erosion.

Sedimentation decreases the dose of external radiation (radiation from outside the body) to organisms in the water column and increases the dose to benthic organisms. Sedimentation in the intertidal zone may lead to increased doses to humans since fishermen who work on beaches at low tide may be exposed to radioactivity in the beach sediments. Otherwise, sedimentation lowers dose rates in humans because of shielding by the water.

Sedimentation has sometimes been taken as an eventual and terminal fate for marine radionuclides, i.e., it has been assumed that no remobilization from sediments occurs. This assumption appears to hold surprisingly well in ecosystems that receive continuous inputs because of the greater biological availability of dissolved radionuclides. On the other hand, even slight remobilization can be significant where other inputs are absent. If particles contaminated near the surface sink into deeper, uncontaminated water and release radioactivity there, or if the input of radionuclides into the system is terminated, then remobilization may be the most important source of dissolved radioactivity. For example, fallout from atmospheric nuclear detonations has been transported into the deep sea by particle settling far more rapidly than by water movements (Noshkin and Bowen, 1973), so this route is most significant for deep benthic organisms. Similarly the rate of decline of radioactivity and the levels of contamination of of organisms in the Columbia River estuary following termination of input of radioactivity to the river were controlled by the rate of decline of radioactivity in the sediment (Johnson, 1979). Biological turnover rates and differences between species were much less important during the post-input period than during the period of continuous input. Remobilization appears to be more important in experiments with smaller, closed systems than in very large systems, perhaps because of the more rapid kinetics of smaller systems.

The association of radionuclides with particles and sedimentation occurs by a number of mechanisms. It is important to distinguish among these since the potential for subsequent remobilization or incorporation into food chains depends in part upon how the binding occurs. For example, precipitation of iron and manganese oxides in aerated waters and the coating of mineral particles with these oxides provide highly reactive substrates that bind ions from the water as well as surfaces where hydrophobic organic molecules or colloids are trapped (Jenne, 1968). Thus, the oxide coatings contain not only directly scavenged pollutants but also pollutants associated with organic matter that is scavenged by the oxides. Microbial decomposition of the organic matter after sediment deposition leads to a chemically reducing environment in which manganese and iron oxides dissolve. This may release contaminants bound to the oxides or the organic matter. Reducing chemical environments in the sea also produce sulfide from sulfate in seawater, which may lead to precipitation of iron sulfide and other sulfides. Manganese, however, frequently diffuses into the overlying water. Similarly, the decomposition of fecal material and of remains of organisms either during sinking or on the seabed may release radionuclides bound to these substrates.

Physical disruption of sediments after deposition increases the rate of horizontal transport. It also provides a means for mixing sediments deeper below the sediment/water interface and for accelerating the rate of release of mobilized contaminants into overlying waters. At least three mechanisms of mixing are well known. Disruption by bottom water currents can occur when storms increase the current speeds. Extreme resuspension is visually obvious in the surf zone, but it also appears that storms affect sediment movement even at depths of 100 meters at the edge of the continental shelf. The movement of sediments by burrowing organisms leads to vertical particle exchange that mimics diffusion. Rates and depths of mixing depend upon the activity and abundance of the particular burrowing species. Finally, the production of gaseous decomposition products such as methane may yield bubbles, at least in shallow water sediments, which as they rise through the sediments may cause vertical mixing of the sediments.

3.3.3 Possible pathways

Depending upon human usage of the ocean in an area contaminated with artificial radionuclides, some fraction of these substances can be transferred to people. The number of possible pathways is very large, though in practice it is found that, in any particular situation, one or two pathways are much more important than others. These are called the critical pathways. Associated with these critical pathways are usually a few radionuclides known as the critical radionuclides. It is also possible to identify in the local population the critical group, people who receive a much higher exposure to the contaminants because of their location, age, or eating habits.

Exposure of people to radionuclides is calculated in terms of radiation dose to the human body. Both internal and external pathways of exposure are considered and added together. The mechanics of estimating the dose can be summarized as follows (Foster et al., 1971; Preston and Mitchell, 1973):

- Estimating the concentration of radionuclides that will exist in sea water.
- Estimating the relationships that will exist between concentrations in the water and in critical materials.
- Determining the rates of consumption of particular seafoods by the critical population group and the extent of exposure to contaminated materials that can deliver an external dose.
- Converting the estimated intakes of radionuclides and the intensity of deposited contaminants into estimates of internal and external dose, combining them, and comparing them with recommended limits.

After introduction, dilution of radionuclides occurs by initial mechanical mixing based on the method of discharge and by the natural oceanic processes of turbulent diffusion and advection (International Atomic Energy Agency, Appendix VI, 1961). These latter processes are of great importance in accomplishing the required dilution within a given time and space. Mathematical models are ordinarily used to predict the manner in which the concentrations of radionuclides diminish over distance and time (Pritchard et al., 1971).

Other processes also act to reduce radionuclide concentrations in seawater during dispersion. Interactions with sediments and suspended material are the most important of these. If these processes cause sufficient delay, radionuclides with short half-lives may disappear completely from the system by decay before they reach potentially critical materials. Conversely, these processes may lead to the entry of the radionuclides into pathways of human exposure.

During this initial mixing phase, changes in chemical form of the discharged radionuclides can take place because of the seawater milieu. Such changes affect the subsequent behavior of the contaminant so that it could now show a different environmental behavior from that exhibited near the point of discharge (entry).

The greatest uncertainty in the pathways calculations is associated with the selection of the appropriate factors whereby the concentrations of specific radionuclides in seawater are translated into concentrations that will result in marine organisms. However, much attention has been paid to this subject in recent years, and much better data are now available, particularly for organisms (Patzer, 1976).

Great differences in these factors exist between different radionuclides and different species of organisms, even in the same environment. Because of these differences, careful consideration of the characteristics of each site is required. In dealing with radionuclides with relatively short half-lives, one must remember that accumulation by organisms to a level that is in equilibrium with the environment takes a significant period of time. During this time radioactive decay may reduce the amounts present to levels substantially below those anticipated from the use of unmodified concentration factors (Foster et al., 1971).

Concentration factors for many radionuclides in marine materials other than organisms are not so well established. Few published data are available for concentration factors (distribution coefficients) of many radionuclides in shoreline sediments, or in abyssal organisms.

When radioactivity is discharged to a marine environment, it is necessary to assess the ways in which humans use this environment. The assessment must consider all of the following (Foster et al., 1971, Preston and Mitchell, 1973):

- Use of shore for recreation or living.
- Use of shore or shoreline materials for industrial purposes.
- Use of the seabed that may lead to the contamination of fishing gear or dredges.
- Industrial uses of sea water.
- Use of products, including fish, shell-fish, seaweeds, and salt.
- Other uses of marine life, e.g., for fertilizer.

When an international group recently considered marine pathways of radioactivity, they selected certain pathways (Table 9) as most important (International Atomic Energy Agency, 1978b).

Table 9. Marine Pathways of Radioactivity and Modes of Exposure (data from the International Atomic Energy Agency, 1978b)

Pathway	Mode of Exposure
Fish consumption	Ingestion
Crustacea consumption	Ingestion
Mollusc consumption	Ingestion
Seaweed consumption	Ingestion
Plankton consumption	Ingestion
Exposure from shore sediments	External irradiation
Exposure from fishermen's gear	External irradiation
Suspension of sediments	Inhalation
Evaporation from seawater	Inhalation
Desalinated water consumption	Ingestion
Sea salt consumption	Ingestion
Swimming	External irradiation

It is from this type of assessment that the critical group and critical pathways can be identified. Desired refinements in the estimated seafood consumption by the critical group include not only the true proportion of the diet that is made up of the critical food, but also the proportion of this food that actually originates in the contaminated area (market dilution) (Foster et al., 1971, Preston and Mitchell, 1973).

The intake of radionuclides from consumption of contaminated food and from exposure to contaminated materials is converted into internal and external radiation doses to humans by use of published dose conversion data. Such data (e.g., International Commission on Radiological Protection, 1960) are normally based on "standard man," i.e., a hypothettical adult male of standard weight, habits, and chemical composition. Data for people of different sex, age, size, and habits are now becoming available.

The actual amount of exposure received by people after a waste disposal operation has begun may be substantially different from preoperational predictions. Attention must be directed to actual concentrations of radionuclides that are accumulating in environmental materials. Evaluation should be based on environmental monitoring programs that, if possible, measure radionuclides in materials directly responsible for human exposure. This means analyses of samples of marine species actually consumed by the public, the beaches used by the public, and the gear handled by fishermen. The critical exposure pathways and the critical population groups should be confirmed (Foster et al., 1971; Preston and Mitchell, 1973) and the radiation doses calculated.

There may be instances in which contamination levels in the critical materials are at a very low level or undetectable. Under these circumstances it may be possible to identify some indicator material, preferably sessile (fixed), easily available in quantity, and exhibiting high concentration factors and long biological half-lives for the critical radionuclides (Preston and Wood, 1971). Levels in indicator materials can then be related to discharge rates and used as an indicator of the appearance of these radionuclides in the critical pathway organisms.

A form of environmental monitoring that is becoming more feasible with the development of improved instruments is the direct measurement of critical radionuclides in people by whole body counting (Honstead, 1969; H.M.S.O., 1978). With the technique it is now possible to measure an internal dose for many gamma-emitting radionuclides at levels some orders of magnitude below permissible body burdens. The same technique is also being developed to measure some alpha and beta emitters. When such measurements are available, they should be favored over the estimation of dose from the sampling and analysis of waters and foodstuffs.

3.4. Biological Effects of the Release of Radioactive Materials Into the Marine Environment

The impact on marine ecosystems of radioactivity from close-in fallout or from point sources such as reprocessing plants will be determined in large measure by the radiation dose received from the quantities of radionuclides accumulated by the biota. These quantities depend on the amount of radioactivity the ecosystem receives, on the physicochemical characteristics of each radionuclide, on the chemical and physical properties of the ecosystem, and on the metabolic pathways in the organism. The importance of these factors will differ with the organism, the radionuclide, and the environment.

3.4.1 Dose to the biota

Exposure of living organisms to ionizing radiation is not new because natural radionuclides exist in known abundance in all compartments of marine ecosystems (Table 1). The amount of ionizing radiation emitted and the dose to organisms from natural and artificial sources determine the radionuclide content of the organism and the environment. Potentially, the ionizing radiation may produce effects on the individual organism (somatic effects) and on the progeny of irradiated individuals (genetic effects). For artificial radionuclides, the exposure may be acute or continuous and at high or low levels. Continuous, low-level exposure is important currently because it is the type resulting from fallout, from radioactivity discharged from nuclear facilities, and from waste dumping sites.

Aquatic biota can receive a radiation dose from internal emitters as a result of radionuclides assimilated from food and sorbed from water. External exposure can result from radionuclides adsorbed on the organisms, from the water or from sediments that contain radionuclides. Models have been developed to estimate radiation doses from various sources (International Atomic Energy Agency, 1976). Dose rates from natural radioactivity, fallout, fuel reprocessing plants, and effluent released at nuclear power plants and at uranium mining and milling facilities have been calculated from these models. Estimates of dose rates are variable, and large differences have been determined among organisms in the same ecosystems and for the same organisms from different ecosystems. The estimated dose rates from fallout, initially somewhat higher in the past, are declining and are now in the same range as those from natural background radiation. In total population or global contexts, the dose rates from nuclear facilities are considered negligible compared with natural background radiation. However, in small affected areas, waste disposal has resulted in dose rates much greater than those of background radiation.

Actual measurements of dose to aquatic organisms have been made using miniature dosimeters (Lappenbusch et al., 1971; Woodhead, 1973). These studies have confirmed the calculated dose estimates.

The models used to estimate the dose are conservative, i.e., they overestimate the radiation dose. Conservative assumptions are made on the size of the organisms and the concentration factors used (see section 3.2.3). The results from the dosimeter studies substantiate, in general, the model assumptions.

3.4.2 Radiation effects on aquatic organisms, populations, and ecosystems

The effects of radiation on aquatic organisms have been addressed by Templeton et al. (1971), by Auerbach et al. (1974), Ophel et al. (1976) and most recently by Blaylock and Trabalka (1978). The experimental radiation doses used were acute or chronic and in many cases were orders of magnitude higher than those experienced by natural populations exposed to effluents from nuclear facilities.

A considerable amount of information is available on the survival of adult and young organisms after irradiation with relatively high doses. In general, there is a relationship between radioresistance and the phylogeny and ontogeny of the organisms. Primitive forms are more resistant than the complex vertebrates, and older organisms are more resistant than the young. Bacteria and algae may tolerate tens of thousands of rads, but some fishes were affected by considerably lower doses. The extensive data base on acute exposures may be relevant to assessment of radiological impacts that might exist after a maximum accident at a nuclear power plant (Nuclear Regulatory Commission, 1976), or in the case of nuclear war (National Academy of Sciences, 1975), but not to conditions in current ecosystems.

3.4.3 Effects of chronic exposures on individuals

Comprehensive reviews of the effects of chronic exposure of aquatic organisms to radiation have been written by Ophel et al. (1976) and Blaylock and Trabalka (1978). These authors include discussions of the results from experiments using external gamma- and X-rays and radionuclides in the water. Effects on invertebrates and fishes that were reviewed included effects on fecundity, hatching, malformations, growth rates, survival rates, cytogenetic alterations, and reproductive performance. From the data, the researchers concluded that the radiation dose resulting in a detectable effect differed with the species, that bony fishes were the most sensitive of all groups tested, and that developing young bony fish are more sensitive than adults.

Experimental work with non-aquatic organisms has shown that chronic low-level radiation may result in changes in the hereditary material. It could be expected that increases over background levels of radioactivity would increase the mutation rate and result in new genetic burden in the gene pool. We now know that radiation damage to genetic material depends on both biological and environmental variables and is potentially repairable at the cellular level. Furthermore, the mutation rate does not depend on dose in any simple way if energy deposition rate is fractionated, protracted, or chronic. Thus, the dose-response relationship is the product of the amount and rate of delivery of the dose and the repair mechanisms in the cells.

The genetic effects of radiation in aquatic organisms have been addressed recently by Ophel et al. (1976) and Blaylock and Trabalka (1978). Because only very few investigations consider direct genetic effects it was concluded that our present knowledge on the effects of radiation and/or radioactive contaminants on the hereditary materials of aquatic organisms is not sufficient to draw specific conclusions regarding the impact of chronic low-level exposure on them.

3.4.4 Radiation effects on populations and ecosystems

The effects of ionizing radiation on aquatic populations and ecosystems have been considered by Ophel et al. (1976), Templeton et al. (1976) and Blaylock and Trabalka (1978). Assessment of effects has been hampered by the lack of relevant experimental data. Although both natural and laboratory populations have been exposed to radiation, the dose rates were much in excess of those that exist now or may be expected to exist in ecosystems.

The problems of assessment of effects on populations are complicated by our lack of understanding of the mechanisms by which the number of organisms inhabiting ecosystems is regulated. Furthermore, the same criteria cannot be used to evaluate the effects of radiation on species with high and low fecundity. For the former, reproductive rates are generally very high, selection pressures are strong, and the value of one or even thousands of individual organisms to the population may be insignificant. For the latter, e.g., elasmobranchs and mammals, greater value may be placed on the individual members since reproductive rates are generally low, and in some cases life span is relatively long.

Examination of the data on population exposures shows that radiation effects are unlikely to be demonstrable (see reviews of Ophel et al. 1976; Templeton et al. 1976; Blaylock and Trabalka, 1978). From the information available, Blaylock and Witherspoon (1975) conclude that it would be difficult to detect somatic or reproductive effects on aquatic populations receiving a dose of 1 rad/day or less. The estimated dose rates for existing or potential situations are less than 1 rad/day except for very small localized areas (Blaylock and Trabalka, 1978).

3.5 United States and International Regulations Governing Dumping at Sea

Although the United States had been a major polluter of the marine environment, legislation in the late 1960's and early 1970's provided protection of this important resource. The United States Marine Protection Research and Sanctuaries Act of 1972 bans the transport, for dumping, of high-level waste. Congress would have to amend the act to allow any form of sub-seabed disposal of high-level radioactive wastes. However, under the act EPA has the authority to issue permits for the dumping of low- and medium-level radioactive wastes. (To our knowledge EPA has issued no permits.) Monitoring of these sites has been spasmodic and some have not been examined for fifteen years until recently. Only limited research had been done to predict the impact of dumped radioactive wastes.

Internationally the situation has been quite different. In the early 1970's there were intensive efforts to have an international agreement on ocean dumping of all pollutants. The outcome was the Convention of the Prevention of Marine Pollution by Dumping Wastes and Other Matter in the Oceans (the London Dumping Convention in 1972). The Inter-Governmental Maritime Consultative Organization (IMCO) was designated as the organization responsible for secretarial duties in relation to the convention. The International Atomic Energy Agency (IAEA) was assigned the tasks of defining radioactive materials unsuitable for dumping at sea and providing recommendations to ensure that any dumping of radioactive material into the sea involves no unacceptable degree of hazard to humans and their environment. A Provisional Definition and Recommendations were made by the IAEA to the Second Consultative Meeting of the Contracting Parties to the Convention, and an intensive review was begun in 1975. The Definition specifies radioactive material that may not be dumped under any circumstances, and the Recommendations set forth procedures that should be followed by the appropriate national authorities in issuing a special permit for dumping of acceptable radioactive material.

In 1978 an advisory group composed of experts from 23 countries and the representatives of three international organizations (United Nations Environmental Program, Inter-Governmental Maritime Consultative Organization, and European Nuclear Energy Agency) reached consensus on a revised Definition and Recommendation on the basis of the conclusions and recommendations of oceanographic and radiological consultant groups (International Atomic Energy Agency, 1978a, 1978b). Some major conclusions were that on a purely oceanographic and radiological basis there are no high-level radioactive wastes that would be intrinsically unsuitable for dumping at sea, and that it is the release rates (curies/yr) rather than the concentrations (curies/tonne) which are important. Although these views do not change the operational definition, they do provide the definition with a more rational conceptual basis from a scientific point of view. If waste is contained within a geological formation on the seabed, that repository can accept very much larger quantities than if those wastes were released on the surface of the seabed. The revised (1978) values in the definition are now one order of magnitude lower (more restrictive) for alpha-emitters and the longer-lived (more than 6 months) beta/gamma-emitters; for tritium and short-lived (less than 6 months) beta/gamma-emitters, values are similar to those set forth in the Provisional Definition.

In the revised recommendations, strong emphasis was placed on compliance with recommendations of the International Commission on Radiological Protection by the appropriate national authorities when they issue a permit for dumping. A policy of isolation and containment of waste from the environment was also strongly recommended.

Other important aspects included in the revised Recommendations are the following:

- Prohibition of the dumping of unpacked liquid wastes into the deep ocean.

- The dumping of unpacked solid waste only in such forms that would reach the ocean bed intact.

- New criteria for site selection, including restriction of dumping sites to areas between the latitudes 50°N and 50°S with depths in excess of 5000 m and remote from continental margins, islands, inland seas, or areas with potential seabed resources.

4. PRIORITY RESEARCH

4.1. Deep Ocean Data Base for Sub-Seabed Emplacement of High-Level Radioactive Wastes[1]

The initial results from the Department of Energy Sub-Seabed Program to assess the technical and environmental feasibility of the seabed as a depository for radioactive wastes have been very favorable. The current assessment is that nothing has yet been discovered or is anticipated that raises doubts about the attractiveness of the concept. However the models that have been developed by the United States and others are deliberately conservative since many of the oceanographic transport parameters are only best estimates, and the critical ecological pathways are generic rather than specific. The collection of the important oceanographic and ecological parameters should receive a high priority in the United States National Plan. Serious consideration should be given to an experimental radioactive waste disposal project to validate the critical parameters.

4.2 Monitoring

4.2.1 Long-term monitoring of sources and concentrations

Every input of radionuclides to the marine environment should be considered a natural experiment and to the greatest degree possible should be utilized as such. The dynamics and long time constants involved in many oceanic processes require a long-term monitoring commitment of radionuclide sources and concentration. Without such a commitment verification of the important concepts necessary for the protection of the marine environment (and ultimately the welfare of humanity) may be jeopardized. We strongly recommend that programs of research and monitoring be initiated and continued, as appropriate, for any current radionuclide incursions into the marine environment. These include the following:

- Nuclear weapons tests.
- Global fallout.
- Point sources (Eniwetok, Bikini, etc.).

[1]The panel considered only those aspects of this concept relevant to our need for data in the fields of geology, sedimentology, oceanography, biology, and radiological assessment. We have not addressed engineering aspects such as waste forms, canister design, emplacement techniques, transportation, or the national and international legal aspects, which are discussed elsewhere.

- Outfalls of the nuclear fuel cycle.
- Fuel reprocessing plants (Windscale, UK).
- Individual reactor sites.
- Waste storage and management practices.
- Other controlled releases, such as medical uses of radioisotopes.
- Uncontrolled releases, such as nuclear weapons loss or satellite burnups.

4.2.2 Process studies in monitoring programs

Artifical radioactivity in the marine environment has been successfully managed thus far despite the potential for considerable hazard, as data in hand can demonstrate. Increases in ionizing radiation in the Atomic Age have been only small fractions of the naturally occurring background radiation. Several factors contribute to this situation. Maintenance of release rates well below levels expected to cause harm to humans or to marine ecosystems has been an important factor. Perhaps equally important is the sound program for estimating hazards and for evaluating and correcting practices. When several nations recognized that harm could result from the uncontrolled release of artificial radioactivity into the oceans, they undertook programs to assure that releases should not damage humans or marine ecosystems. These programs have in common the following precepts:

- To understand the impact of pollutants on marine ecosystems, scientists must understand the systems themselves.
- It is necessary to measure accumulation levels directly and to assess impacts in the field in order to assure that protective guidelines are adequate.
- Data from the evaluation of pollutant impacts are useful for the general understanding of marine ecosystems.

The programs have included a component of monitoring. They have also included major emphases assuring that hazardous levels should not be exceeded, and a general understanding of marine processes. The emphasis on processes allows a considerable transfer of knowledge from the area of radioactive pollution to areas of other pollutants such as heavy metals. Furthermore, it provides the means to detect effects of radioactivity and thus assure that safety is continuously maintained.

Control of marine pollution other than radioactive may also be most economically accomplished by adaptation of the basic precepts to the particular pollutant. It is recommended that a balanced approach with both monitoring and process studies be implemented. The process and data acquisition components of a monitoring program must interact. Knowledge of processes is necessary for the design of good data acquisition programs. The resultant data must be analyzed with cognizance of processes. Finally, the monitoring data must be used to detect flaws in and to improve the process models. Only in this way can the effectiveness of control measures and monitoring strategies be known.

4.2.3 Monitoring pollutants in the Great Lakes

Radioactivity is one of many classes of pollutants that we must continue to monitor closely in the Great Lakes. Because these lakes will assume an even greater importance in the future as a resource for potable water (and many other less restrictive uses), it is vital that any trends in pollutant loading be instantly recognized.

The value of this resource has been recognized by the United States and Canadian governments; monitoring and research needs are regularly assessed by an International Joint Commission, which is responsible for the setting of water quality standards in the Great Lakes. Present monitoring programs are largely concerned with compliance with these standards. However, we must also monitor the Great Lakes in order to understand the complex processes that govern the transport, behavior, and fate of pollutants. The data base will provide the information necessary to construct meaningful models to predict trends.

To meet these goals it is recommended that we develop sampling and analytical strategies, particularly analytical methods for heavy metals whose concentration may be as low as or lower than those found in the oceans. It is ironic that more is known about artificial radionuclides in these lakes than about natural radioelements. Since most sources of pollutants to the lakes are controllable and subject to monitoring at the discharge point, the major purpose of additional monitoring programs should be to describe processes within the open lakes and the very important role of deposition of pollutants from the atmosphere.

4.2.4 Monitoring marine sediments for radionuclides

With few exceptions, sediments are the principal environmental reservoir for artificial radionuclides and therefore must be included in radioactivity monitoring programs. It is recommended in sampling and analysis of sediments that key observations/measurements be made so that data from different sites and times can be compared. Data on particle size distribution and sedimentation rate are absolutely essential. In addition, sample sites must be selected for their relationship to known sources and regional transport processes. For example, fine-grained sediments are more likely than large-grained sediments to carry radionuclides (and other pollutants). It is pointless to monitor sediments only at sites of erosion or no deposition; deposition sites are far more sensitive indicators of contamination.

Time series trend analysis for contamination of marine sediments is sensitive to additions of radionuclides. Furthermore, sediments maintain a long-term record of the pollution of a site. Therefore, it can be valuable to compare histories recorded from analysis of surface data and vertical profiles.

4.2.5 Monitoring of existing dump sites

We believe that pertinent data can be obtained from existing national and international radioactive dump sites. However, we are concerned that some past efforts have not been designed and planned to obtain the maximum scientific data in a cost-effective fashion. We recommend that these sites be considered for intensive scientific investigation under interagency guidance to validate our assumption of safety and to improve the technical basis for the evaluation of future operations.

4.3 Ocean Chemistry

The prediction of the behavior of radionuclides, in particular the transuranic elements, in the oceans is essential to our understanding of their fate and effects. The predominant oxidation states and chemical forms of radionuclides, and nonradioactive pollutants as well, need further elucidation.

4.4 Biological Effects

We recommend adoption of the recommendations of a group of experts who met in Vienna in 1974 and identified the research needed to evaluate the effects of ionizing radiation on aquatic organisms and ecosystems. Following is a summary of their recommendations.

- There is a real need for more data on the concentrations of natural and artificial radionuclides, including detailed tissue distributions in representative organisms, in fresh, estuarine, coastal, and open ocean waters and sediments.

- Experimental work to assess the possible effects of irradiation in contamination environments should be performed at the lowest dose rates practicable to minimize the extent of extrapolation from high to low dose rates. Emphasis should be given to organisms and populations from coastal and inland waters.

- Better methods must be developed to permit the recognition of radiation effects in individual organisms, populations, communities, and ecosystems so that sound criteria for the conservation of ecosystems can be established.

- In most cases organisms that are easy to culture but have little ecological significance have been used in laboratory studies on radiation effects. More attention should be paid to species that may have more important ecological roles or may be unexpectedly sensitive to radiation.

- The stability of aquatic communities, as well as other characteristics, should be studied at every trophic level. Comprehensive studies should cover the impact of all pollutants, not just radiation, on populations, communities, and ecosystems. Various institutes could collaborate on such studies. To the extent that it is feasible, studies should be aimed at understanding the role of genetic variation (expressed as discrete polymorphisms and quantitative variations) of individual species in the establishment and maintenance of marine communities.

- Comparative studies of mutation rates induced by radiation and/or conventional pollutants should be undertaken on a wide range of aquatic organisms, including species which possess both high and low reproductive capacities. One such important study would be the genetic effect of low-level radiation, singly or in combination with other stresses, with respect to both genetic damage (gene mutation, chromosomal aberrations, recombinations, etc.) and population damage (population size, biomass, fecundity, fitness components, etc.).

- Surveys should be carried out on the extent of genetic polymorphisms in marine species, e.g., gene-enzyme polymorphisms. To be most useful, the experimental design should be orthogonal with respect to species and enzymes. In order to understand the significance of polymorphisms, their response to varying physical (both mutagenic and nonmutagenic) and biological environments should be studied in both the laboratory and the field. Studies of effects of acute as well as chronic exposure on such systems would be valuable.

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MICROORGANISMS

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1. INTRODUCTION

The microbial flora native to or carried into most coastal and estuarine waters and their underlying sediments generally is extensive in biomass, number of species involved, and diversity of physiological and enzymatic functions they perform. These microorganisms play several roles in marine ecosystems and in human use of the marine environment as a source of food and recreation. They may function as the following:

(1) Agents of human disease that are introduced into the marine waters from human and lower animal wastes and terrestrial environments or that increase in numbers therein because of nutrient or thermal pollution.

(2) Agents of faunal disease.

(3) Sources or mediators of food to higher organisms by the degradation, transformation, and assimilation of nutrients that occur naturally, that are transported into marine waters through terrestrial run-off, or that are introduced by human activities.

(4) Degraders or transformers of pollutants such as pesticides, petroleum products, synthetic organics, and metallic ions like mercury.

The relationship of the pollutant to the microbial flora is different in each of the four functions. (1) With reference to agents of human disease, the microorganism itself is generally the contaminant introduced into the environment (Cabelli, 1978b and 1978c; Levin, 1978), usually by sewage effluents. (2) In faunal disease, an extrinsic pollutant affects a basically intrinsic host-parasite relationship (Anderson and Conroy, 1970; Perkins et al., 1972; Gopalan and Young, 1975), by stressing animals so that their susceptibility to disease increases. (3) The externally introduced organic pollutant is the target for marine organisms that are capable of degrading, transforming or assimilating such materials as petroleum hydrocarbons and pesticides (Atlas and Bartha, 1972; Bourquin and Gibson, 1978; Clesceri et al., 1977; Horwitz et al., 1975; Lee and Ryan, 1978; Pritchard and Bourquin, 1978; Slater, 1978; Walker and Colwell, 1976). (4) Conversely, the microbial flora necessary for nutrient transformations in marine ecosystems may themselves be the targets for these and other organic and inorganic, externally introduced pollutants. Alternatively, the proliferation of heterotrophic microorganisms under nutrient stimulation can have adverse effects such as anoxia.

Association, if not causality, between a form of pollution and some detrimental effect is strong enough in some instances to support criteria, guidelines, and standards as well as monitoring programs. Such is the case with human health effects (Cabelli, 1976, 1978b; USEPA, 1976) and to a lesser extent faunal disease (Young and Pearce, 1975; Ziskowski and Murchelano, 1975). Nevertheless, there is a critical need for additional epidemiological or epizoological data, information associating pollution levels with human and faunal disease and the densities of the etiological agents involved, and research on methodology (especially as related to faunal disease). There is also a critical need for data concerning the roles of microorganisms in marine ecosystems and documenting any effects of pollutants on their activities. Recommendations for research and monitoring related to effects of microorganisms are listed in sections 6 and 7.

2. HUMAN HEALTH EFFECTS

2.1 Identification of Problem

The human population, through its use of potentially polluted coastal and estuarine waters for food, recreation and even drinking water (in the case of the Great Lakes), incurs the risk of infectious disease or biointoxication attributable to etiological agents such as bacteria, viruses, fungi, protozoa, metazoan parasites, and toxic products that they produce (Cabelli, 1978b and 1978c; Craun and McCabe, 1973; Verber, 1977).

Humans are the principal source of these agents; agents such as those causing infectious hepatitis, gastroenteritis, shigellosis, and salmonellosis are carried directly into the marine environment by outfalls for municipal sewage effluents (Clarke et al., 1964; England, 1974), by dumping of sewage sludge (Bias and Bhat, 1965; Palfi, 1972), and by discharge of boat wastes. Some agents come from fecal wastes; others, such as <u>Klebsiella</u>, <u>Aeromonas hydrophila</u>, and <u>Pseudomonas aeruginosa</u> (Dufour, 1976; Mierscier, 1977), appear to multiply in sewage. The infective agents may also enter the marine environment indirectly from rivers that receive such discharges or from translocated dredge spoils.

A less important source of disease is lower animal wastes carried directly into the coastal and estuarine waters by urban and rural stormwater run-off and indirectly by outfalls for sewered stormwater and combined sewer systems. Salmonella, certain metazoan parasites, and enteropathogenic E. coli can be spread from lower animals to humans by these routes (Vanderpoar and Bell, 1975; Faust and Russel, 1956; Smith, 1971).

A third source of infective or toxigenic agents is the marine environment itself since at least three agents, Vibrio parahaemolyticus (Barker and Gangarosa, 1974; Kaneko and Colwell, 1973), Mycobacterium marinum (Jolly and Seabury, 1972), the dinoflagellates responsible for paralytic shellfish poisoning (Fortuine, 1975), and possibly a fourth, Clostridium botulinum (Dolman, 1957), multiply in the water column or in the underlying coastal and estuarine sediments.

To prevent the detrimental effects of marine pollution on humans, public health officials and environmentalists can direct their efforts in the following ways: develop data bases whereby the risk of untoward health effects among "users" can be expressed in terms of some measure of water quality (Cabelli et al., 1975, 1976, 1978a); establish "acceptable risk" levels; apply management and monitoring strategies that will assure that these levels are rarely if ever exceeded.

2.2 Monitoring Objectives

The overall monitoring objective can be stated as follows: continuing examination of waters usable by humans as sources of food, recreation, and potable water for changes that may result in unacceptable risks of infectious disease or biointoxication. So that the monitoring results may be used for prediction, water must be monitored not only at the user areas themselves but also between these areas and potential contributory sources of pollution. This monitoring requirement, coupled with an appropriate sampling regimen, should allow unacceptable changes in water quality to be detected early enough to permit corrective action. Models and the required input data to them are needed to predict the steady state pathogen densities in the water column and the underlying sediments, to relate these equilibrium densities to those at the source of pollution, and to regulate the sources accordingly.

Although the overall objective of a monitoring program can be stated in simple terms, the specific objectives and the monitoring strategies to achieve them are more complex because of the number of potential etiological agents, the many uses of coastal and estuarine waters, and the variety of pollution sources. Furthermore, fecal indicators rather than the enteric pathogens themselves are used to index some of the potential health risks involved (Levin, 1978); this further complicates the development of monitoring strategies and the acquisition of the required data base. Qualitative estimates are generally useless and often misleading in terms of the risks involved. Quantitative estimates of health effects indicators and pathogens in coastal and estuarine waters may be directed toward the following objectives:

(1) To evaluate water quality and changes thereto against existing water quality guidelines for health effects.

(2) To identify and describe pollution sources likely to carry waterborne infectious disease.

(3) To track the movement and fate of any discharges that carry a threat to human health.

(4) To establish the etiology, epidemiology, and ecology of waterborne disease outbreaks.

2.3 Existing Guildelines and Standards; Monitoring Capabilities and Research Needs

Existing health-effects standards for recreational and shellfish-growing waters, with the exception of those for paralytic shellfish poison (American Public Health Association, 1970) and a proposed one for V. parahaemolyticus (Murakami, 1975), relate to those diseases whose source is the fecal wastes of warm-blooded animals. In the United States, guidelines generally set limits for mean densities of total coliforms, fecal coliforms and, less frequently, fecal streptococci (USEPA, 1976). These guidelines and standards serve as the basis for regulatory action despite the meager epidemiological data base that supports them. At present, density measurements for fecal coliforms and/or fecal streptococci should be included in coastal and estuarine monitoring programs. However, neither of these indicator systems is fecal-specific (Dufour, 1976), much less human feces-specific, or as resistant to environmental stress as some enteric viruses (Scarpino, 1975), notably hepatitis A. Recent publications (Dufour, 1976; Cabelli, 1978a) have assessed the strengths and weaknesses of some proposed indicator systems. Improved fecal indicator systems and epidemiological data are needed whereby indicator densities can be related to human health in a dose-response relationship compatible with risk analysis. A volume of data for recreational waters has related swimming-associated gastrointestinal symptomatology to E. coli and enterococcus densities in the water (Cabelli et al., 1976; Cabelli, 1978a). Figure 1 shows the type of data being developed. The regression lines shown are, in fact recreational-water-quality criteria that can be used in the context of risk analysis in terms of health effects. More data are needed for recreational water use, and a similar body of data needs to be collected for shellfish-growing waters.

Although guidelines and standards are not stated in terms of the fecal pathogens themselves, there is a need to establish pathogen-indicator relationships, particularly those affected by wastewater treatment, disinfection, and transport parameters. At present, viral hepatitis and a gastroenteritis, probably caused by the Rotaviruses and Parvo-like viruses, are the most common enteric diseases associated with

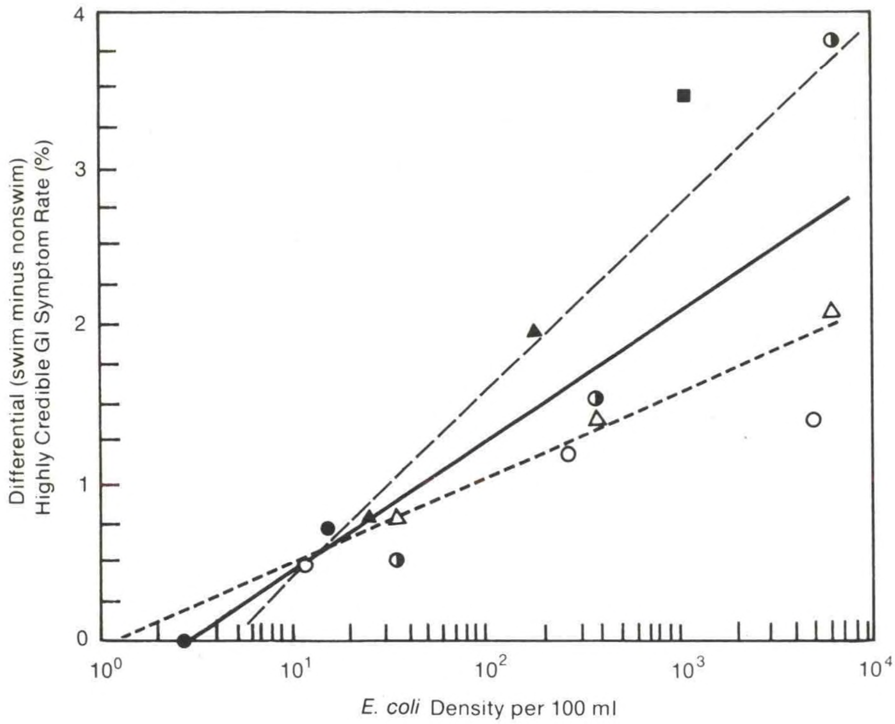

Figure 1. Relationship of mean E. coli density to swimming-associated (swimmer minus nonswimmer) rates of selected gastrointestinal (GI) symptoms at various locations. ● - highly credible GI symptoms, New York City, 1974; ▲ - highly credible GI symptoms, New York City, 1973; ■ - highly credible symptoms, Lake Pontchartrain, 1977; ◑ - vomiting or diarrhea, Cairo tourists at Alexandria, Egypt, beaches, 1977; Δ - vomiting or diarrhea, Alexandria residents at Alexandria beaches, 1977; o - vomiting or diarrhea, Alexandria beaches, 1976. Highly credible GI symptoms include vomiting; diarrhea accompanied by fever or requiring individual to stay home, stay in bed, or seek medical advice; stomachache or nausea accompanied by a fever. —— all data (r = 0.79); – – – – data from NYC + Lake Pontchartrain + Cairo visitor (r = 0.94); ---- Alexandria residents (r = 0.91). (After Cabelli, 1978a).

the use of sewage-polluted coastal and estuarine recreational waters. Two other important research needs are the development of enumerative methods for these agents and the determination of the extent to which the latter two groups of agents are responsible for waterborne gastroenteritis. Several bacterial agents, such as enteropathogenic E. coli, also may be responsible for some of the observed cases of gastroenteritis. The roles of these agents should be determined.

Data obtained during monitoring programs must be evaluated against guidelines for the effluent source as well as those for potentially impacted targets. The development of such guidelines on a case-by-case basis is also important if, through the location of sewage outfalls, we are to balance the need for wastewater treatment and disinfection against the costs of these processes in terms of energy, dollars, and potential ecological and health effects due to chlorinated organics. The translation of target area criteria into effluent guidelines requires information (and practical technology for its acquisition) on the fate of enteric pathogens and fecal indicators in coastal and estuarine waters. This includes realistic decay coefficients for the agents under various meteorological and hydrographic conditions.

Measurements of relevant viral densities in the sources of potable waters (Great Lakes waters) may be necessary as an additional frame of reference to microbiological standards and criteria. These measurements may be needed to determine the effectiveness of a water treatment process in producing finished water with a negligible virus-associated health hazard. A hepatitis A. simulant that is highly resistant to disinfection, can be quantified, and is more prevalent in sewage than the agent, would be useful for this purpose.

Monitoring programs are carried out for only one disease, paralytic shellfish poisoning, in which the source of the etiologic agent is the marine environment (American Public Health Association, 1970). Guidelines and standards supported by dose-response data are available, and monitoring data are examined against them. Anthropogenic pollution may have an impact on the blooms of dinoflagellates that produce these toxin(s); however, more data are needed. Of the other diseases caused by marine microorganisms, "shellfish-borne food poisoning" caused by *V. parahaemolyticus* is the one for which monitoring, along with guidelines and standards, is most likely to be effective. Such monitoring has already been proposed by Japanese workers (Murakami, 1975). However, a better understanding of the epidemiology of the disease and the ecology of the etiologic agent must precede a monitoring program. In addition, the question of the impact of anthropogenic pollution, notably nutrient loading, on the densities of the organism has to be answered. A parallel situation may exist in fresh water for *A. hydrophila* densities, nutrient loading, and *A. hydrophila* wound infections and gastrointestinal disease among swimmers (Hanson et al., 1977; Fritsche, 1975).

2.3.1 Defining the nature and proximity of pollution sources

Microorganisms capable of causing human disease can be introduced into coastal and estuarine waters from a variety of sources, by a number of different routes, and at varying distances from the targets (recreational and faunal growing areas). Furthermore, the discharges may be untreated or treated in a variety of ways before discharge. Each of these factors influences the potential for waterborne disease, but, current indicator systems frequently do not distinguish among them.

Therefore, indicator systems need to be developed that will provide quantitative information on the nature and proximity of effluent discharges with a disease potential. The ultimate requirement is source-specific indicator systems. The development of indicator systems that are specific for human wastes rather than lower animal fecal wastes should receive high priority. Such systems would also be applicable to determine risk of disease from coliform-containing "tarballs" and "greaseballs."

2.3.2 Tracing polluting discharges of health significance

Recent experience with sludge disposal in the New York Bight and effluent disposal in coastal waters and the continuing concern over the dispersion and translocation of dredge spoils point out the need for sensitive and facile methods for tracing and/or monitoring the movement of effluent discharges or sedimented solids that have disease-producing potential. Two microbial indicators have this potential, *Clostridium perfringens* spores and certain bacteriophages. To exploit these indicators, accurate methods for their enumeration in sediments must be developed. These methods must include procedures for extracting the organisms from sediments and concentrating them for analysis. The sensitivity and specificity of the tracers then must be evaluated in field studies.

2.3.3 Systems for establishing the etiology, epidemiology, and ecology of waterborne disease outbreaks

Under specific conditions (notably during an outbreak of waterborne disease or an epidemic of an infectious disease in the population whose wastes are discharges into the water) coastal and estuarine waters need to be examined for the fecal pathogens themselves. In general, methods for studying these pathogens, particularly methods providing sensitive, accurate, and precise density estimates from environmental samples, are difficult to develop and expensive and laborious to perform. Although the enumeration of enteric pathogens will not be required routinely, methodology should be developed for those agents implicated in recreational or shellfish-borne outbreaks of disease. The data obtained thereby could be used to establish the causal relationship of agent densities to the risk of waterborne disease on one hand and the relationship of these pathogen densities to the commonly used microbial indices of fecal pollution on the other (Dudley et al., 1976), although this may not be practical with existing data limitations. Hepatitis A virus, the Rotaviruses, and the Parvo-like viruses are probably the most important etiological agents of marine-associated waterborne disease; methods are needed to isolate and quantify them.

3. FAUNAL DISEASE

3.1 Identification of Problem

Infectious diseases caused by viruses, bacteria, fungi, and protozoa adversely affect the health of marine fishes, crustaceans, and mollusks. Recent studies indicate that the prevalence of some of these diseases is higher in ecologically degraded marine environments. Viral diseases of fishes (Perkins et al., 1972), crustaceans (Couch, 1974a, 1974b; Couch and Nimmo, 1974), and mollusks (Farley et al., 1972), bacterial diseases of fishes (Anderson and Conroy, 1970) and crustaceans (Gopalan and Young, 1975; Young and Pearce, 1975), and neoplastic diseases (of possibly viral etiology) of fishes (Angell et al., 1975; Deys, 1969; Stich, 1976; Wellings et al., 1976) and mollusks (Christensen et al., 1974; Farley, 1969; Yevich and Barszcz, 1976, 1977) are more abundant in animals from polluted environments. Fin rot, a disease of uncertain etiology, is significantly more prevalent in demersal flatfishes from altered environments than in flatfishes from ecologically and hydrographically similar but pristine areas (Mearns and Sherwood, 1974; Wellings et al., 1976; Ziskowski and Murchelano, 1975). Since infectious diseases have potentially serious consequences for the well-being of marine fishes and shellfishes, research is required to assess the impact of environmental change on disease prevalence and to establish criteria for monitoring.

3.2 Priority Research

Unfortunately, most of our knowledge of the diseases of marine fishes, crustaceans, and mollusks is based on observational studies with limited scope and numeric significance. Usually, interest lies in either the infectious agent or the host response, rarely in the role of disease in limiting resource abundance. Also, the majority of the studies unfortunately have involved adult animals and not larvae or juveniles. Although infectious diseases may affect the longevity and reproductive potential of adults, the sensitivity of pre-adult animals is such that survival itself is threatened. The consequences for the resource are obvious.

Research must be initiated to assess the prevalence of infectious diseases of adult and pre-adult fishes and shellfishes from selected, ecologically dissimilar, marine environments. The studies should not be based on morphologic criteria alone but should be augmented by a variety of bio-medical disciplines (biochemistry, immunology, microbiology). Although establishing the etiology of specific diseases is desirable, the iterative process is time-consuming, costly, and demanding in skills. Finding a statistically significant increase in infectious disease prevalence in polluted areas may be adequate without establishing etiology. Once prevalence has been studied, determining etiology, assessing effects of specific pollutants on infectious diseases, and monitoring may all be desirable.

3.3 Monitoring

Monitoring the prevalence of infectious diseases of pre-adult and adult fishes and shellfishes in selected, ecologically dissimilar environments provides the initial evaluation of the impact of environmental pollutants. Laboratory studies to test hypotheses based on field observations logically follow such surveys. Environments selected for monitoring should be characterized by pollution from heat, petroleum hydrocarbons, sewage wastes, and/or industrial by-products. Resident, nonmigratory demersal and pelagic fishes, as well as appropriate species of benthic crustaceans and detritus and filterfeeding mollusks, should be examined at close sampling intervals over an extended time period. Although certain infectious diseases are more abundant during periods of elevated water temperature, seasonal influences on disease prevalence should be evaluated. For most pre-adult fishes and shellfishes, sampling must take place when the animals are available for collection. Although sampling gear is available for retrieving many adult fishes and shellfishes, gear for obtaining most pre-adult animals must be fabricated.

4. PLANT DISEASE

The effect of pollutants on microbial diseases of marine plants has never been defined. Although massive kills of marine plants have rarely been observed, a massive disease of eel grass created ecological havoc in the 1930's along the Atlantic Coast. Research is required on the effect of pollution on infectious diseases of marine plants.

5. IMPACT ON ASSIMILATION AND TRANSFORMATION OF NUTRIENTS

5.1 Identification of Problem

The oceans serve as a disposal system for refractory and nonrefractory wastes such as pesticides, heavy metals, sewage, sewage sludge, crude oil, industrial effluents, and inorganic nutrients, which enter the marine environment as a result of human activities. However, the oceans have a limited capacity to assimilate such wastes and, if this assimilative capacity is exceeded, the marine ecosystem will be drastically altered, perhaps to the detriment of mankind. For example, food production from the oceans may be greatly curtailed, recreational areas may be destroyed, and even the climate may be altered.

The capacity of the oceans for accepting wastes is controlled by the rates and extents to which microorganisms alter or decompose compounds in the waste material. With enough knowledge concerning these microbiological processes, maximum loading rates and limits can be predicted, established, and monitored to prevent drastic alteration of the marine environment. Predictions are complicated since some pollutants may be toxic to those microorganisms that degrade and assimilate other pollutants. Thus, research and monitoring programs must deal with the effect of pollutants on microorganisms and the effect of microorganisms on pollutants. Proposed research should deal specifically with the rates of decomposition or alteration of pollutants, the loading capacity of specified semi-enclosed marine environments, and the effects such pollutants have on mineralization activities carried out by bacteria and other microorganisms. Obviously, the effects on the overall community structure, and particularly that portion significant to the food and recreational resources, must be examined.

Current technology is available to carry out a limited monitoring program. Additional applied and basic research in many areas is needed to improve monitoring technology and to provide criteria against which the findings can be evaluated.

5.2 Research Needs

Microbial processes responsible for the mineralization and recycling of naturally occurring and human-mobilized nutrients in coastal waters may be affected by the level of nutrient input and by toxic pollutants.

5.2.1 Effects of nutrient enrichment and human-mobilized pollutants on microbial processes

Nutrient enrichment in the coastal zone results from many sources: sewage outfalls, sludge dumping, land run-off, river outflows, and natural organic excretions by marine organisms. The increased nutrient level from human-mobilized organic wastes affects the mineralization rates of natural organic compounds, physical and chemical characteristics of the receiving waters, and microbial community structure as it affects the use of microorganisms as food sources for higher trophic levels.

Bacteria mineralize approximately 50% of the carbon fixed by photosynthetic processes (Fogg, 1966; Morita, 1977). Rates of bacterial mineralization determine to a large extent the rates of primary production because of nutrient recycling through this process. Eventually, then, rates of primary production will be affected, and this will in turn determine how much food can be harvested from the sea. Pollutants may significantly alter this important microbial function by overloading the capacity of microorganisms to mineralize. Inhibition of mineralization processes will then lead to an accumulation of organics in the marine biosphere and thus a decrease in the nutrients available to plants. To predict and monitor the effects of pollutants on microbial mineralization processes, additional information concerning the rates and sites at mineralization and the specific organisms involved must be obtained.

Bacteria are primarily responsible for the mineralization and decomposition of human-mobilized organic wastes such as those found in sewage outfalls and sludge. To optimize the use of the ocean as a disposal system without untoward changes in such characteristics of the water as clarity, pH, Eh, and dissolved oxygen, additional information on the fate of organic molecules is needed. Such information can be used to predict how rapidly organic wastes will be destroyed and what environmental factors control the mineralization rates (Pool et al., 1977). Studies should define the load limits, optimize the location of outfalls and dumping areas, and help prevent long term deterioriation of the marine environment (Joris, 1977). This research is needed to establish criteria for sewage outfalls and permit us to monitor the effects of various pollutants on microbial processes.

Bacteria probably serve as food for protozoans, nematodes, and other animals. Results of laboratory investigations tend to support this hypothesis (Bonomi and Frederickson, 1976; Dive, 1975; Hairston et al., 1968; Tietjen and Lee, 1975; Muller, 1975; Hamilton and Preslan, 1967; Gerlach, 1978; Yinst, 1976; Tietjen and Lee, 1977). Nevertheless, to understand the impacts of pollutants on the microbial community and, in turn, the well-being of higher trophic levels, we need (1) in situ demonstrations that the nutrient level affects the level of bacteria grazed and the higher organisms involved in the grazing, and (2) demonstration of selectivity in the food source.

If a group of pollutants is toxic to the primary food source of an animal or to the microorganisms that make nutrients available to the source, the survival of that animal and those higher in the food chain obviously will be affected. Once data have been obtained to satisfy the two needs stated above, we can begin to quantify the effects of various toxic pollutants on nutrient mineralization and the microorganisms involved in the processes. Because this basic information is not available, it is not now possible to establish criteria and monitoring programs to determine the effect of pollutants on the role of bacteria as a food source.

5.2.2 The effect of microorganisms on the biodiminution of refractory and nonrefractory pollutants

The effect of microorganisms on the biodiminution of human-mobilized wastes (pesticides, toxic organics, industrial effluents, crude oil, and heavy metal-organics) depends on their potential and capacity to degrade and transform these pollutants in aquatic ecosystems. Their degrading activities include complete mineralization processes (complete conversion of the pollutant to CO_2 and microbial biomass), detoxification (without complete mineralization), and toxification processes (organic pollutant converted to a more toxic form such as mutagens or carcinogens). The main question in assessing the degradative potential and capacity of marine environments is this: How much of the pollutant can be added to the system before environmental deterioration occurs? The following information is necessary to make this type of assessment:

(1) Qualitative information on whether a pollutant is degraded or transformed (degradation potential) and, if so, by what mechanism (microbiological processes, physicochemical processes) and under what environmental constraints (water type, sediment type, nutrient levels, physical factors, etc.).

(2) Quantitative measurements of the rates and extents by which the pollutant is degraded or transformed, particularly as a function of variations in the environmental parameters.

(3) More complete understanding of the ecology of degradation, transformation, and mineralization processes, particularly as they relate to synergistic, commensal, and other interactive relationships that characterize natural microbial populations. This understanding would indicate those parts of the ecosystem that are "hot spots" and "cold spots" for the degradative potential of a particular pollutant.

At present no comparative information is available about the degradative potential of different parts of aquatic environments. Are pollutants more likely to be degraded in esutarine than in open ocean waters? Will a greater variety of pollutants be destroyed in polluted waters than in unpolluted waters? The continuing generation of rapid, "indicator" answers to such questions contributes valuable information for defining the environmental parameters that regulate degradation and transformation processes, and for determining the assimilatory capacity of aquatic environments.

To determine the assimilatory capacity of an aquatic environment on the basis of degradation potential, the rates and extents of degradation processes (biological and nonbiological) must be quantitatively determined for a variety of experimental conditions. It is equally important to measure the rates and extents of hydrological transport processes, particularly as they relate to absorption/desorption phenomena. Because of the difficulty in performing field studies to describe these rate processes, microcosmic systems will have to be employed. Since such systems are designed to contain most of the major components of an aquatic ecosystem and to simulate natural degradative processes in the laboratory, kinetic analyses can be performed and directly applied to "real life" situations. The data generated from these programs will reflect the numerous ecological relationships that exist in the aquatic environment.

If the assimilatory capacity is to be obtained for a particular aquatic environment, it is important to compare and contrast fate data with the environmental conditions. Such comparisons can best be done by using mathematical models and computer analysis. Such models are being developed and utilized (Clesceri et al., 1977; Falco, 1976). They are capable of predicting pollutants' fates and the assimilatory capacity of aquatic environments. The validity of model predictions depends directly on the accuracy of the measurements of degradation rates and extents. Predictions of water quality criteria generated by these models provide the foundation for continued monitoring of pollutant levels through actual field studies.

Numerous biodegradation studies have revealed that the mechanisms by which pollutants are degraded by microbial populations result from interactions of the bacteria therein, and thus only input/output results can be obtained. Dehalogenation of organohalogens (Bourquin and Gibson, 1978), irreversible binding to sediments (Katin and Lichtenstein, 1977; Hsu and Bartha, 1974; Simsiman and Chesters, 1976), overcoming thermodynamically unfavorable biological reactions (Slater, 1978), sequential transformations of organic materials (Horwitz et al., 1975), toxification processes (Alexander, 1977), and degradation in dilute aqueous environments (Jannasch, 1968; Harder and Veldkamp, 1971) are all now known to be mediated by the cooperative actions of several members of a microbial population. If the assimilatory capacity of an aquatic environment is going to be accurately assessed, extensive basic and applied research efforts must be directed at discovering and characterizing these microbial interactions.

Continued efforts must be directed toward perfecting the design of microcosms used in fate studies (Pritchard and Bourquin, 1978; Giddings and Eddlemon, 1977). Design features of the microcosms should be examined for their effects on degradation rates and adsorption/desorption phenomena. Comparisons should also be made with standard benchmark procedures for assessing fate processes (Falco et al., 1976; Baughman and Lassiter, 1978).

Experimental systems and approaches need to be designed that allow the degradation of pollutants to be studied under the very low nutrient condition typical for aquatic environments. There is evidence that threshold levels (concentrations below which no bacterial metabolism occurs) exist for naturally occurring organics (Falco, 1976), and, depending on chemical structure, pollutants may have considerably higher thresholds.

5.3 Monitoring Objectives

Current technology is available to carry out a limited monitoring program to assess the biodegradation potential of various aquatic environmental situations. Some simple research tools are available that can be used immediately in a monitoring program. These tools will give relative measures of degradative potential. Tests such as the mineralization of the pollutant type to carbon dioxide can easily be employed (Atlas and Bartha, 1972; Lee and Ryan, 1978; Walker and Colwell, 1976; William, et al., 1968). A biodegradation index (based on mineralization) should be established using a standard set of organic compounds as internal standards. This index could be used as a measure of the biodegradability of a particular pollutant as a function of a large variety of environmental conditions and hydrographic parameters. It would also indicate those parts of the aquatic ecosystems that are "hot spots" and "cold spots" for degradative potential of a particular pollutant.

6. SUMMARY OF SPECIFIC RESEARCH NEEDS

The following research needs are not in order of priority; they have been grouped in general areas, then listed in sequence, or related to associated needs.

Health Effects

(1) Health effects criteria for marine and fresh (Great Lakes) recreational waters.

(2) Epidemiological data relating shellfish-associated disease with water quality.

(3) A usable simulant for hepatitis A virus.

(4) Definition of the problem from dissemination, by the discharge of sewage effluents and the dumping of sludge, of plasmids that code for multi-antibiotic resistance.

(5) Good methods to enumerate, especially in sediments, those enteric bacterial pathogens significant in shellfish-borne diseases and certain diseases afflicting swimmers.

(6) Methods for recovery and enumeration of gastrointestinal viruses from shellfish and recreational waters, specifically hepatitis A virus, Norwalk-type agents, and Rotaviruses.

(7) Realistic decay coefficients for health-effect indicators and pathogens and/or technology for obtaining them without using open ocean die-off studies.

(8) Elucidation of the "regrowth" phenomenon in coliforms, and data on the "regrowth" of bacterial pathogens in the marine environment.

(9) Determination of the survival characteristics and fates of health effects indicators and pathogens in sediments.

(10) Better methods for tracing the movement of effluent plumes and deposited sludge and dredge spoils containing infective agents.

(11) A human-specific fecal indicator with "good" survival properties.

(12) Epidemiological data defining the risk of enteric and other marine water-borne disease from stormwater run-off relative to that from sewage wastes.

Faunal Disease

(1) Assessment of the prevalence of disease in adult and pre-adult fishes from selected, ecologically dissimilar, marine environments.

(2) Screening for pathological, histopathological, physiological, immunological, microbiological, behavioral, etc., changes among "ill" and/or moribund animals that might help predict their ultimate fate. This should be done for each "important" infectious disease for which there may be a pollution input.

(3) Development of laboratory data on the effect of pollutants, such as fuel oils, pesticides, "heavy metals", etc., on the dose-response relationship of naturally occurring diseases of finfish and shellfish.

Assimilation and Transformation of Nutrients

(1) Examination of the effects of pollutants on the rates of mineralization and nutrient regeneration in water and sediments.

(2) Investigation of community structure as related to the species that carry out specific processes, the distribution and concentration of these species, and factors controlling their abundance or absence.

(3) Biomass studies in both polluted and unpolluted waters and sediments to determine whether given pollutants enhance or depress growth of bacteria.

(4) Investigation of the effects of pollutants on bacteria used as food sources by higher trophic levels.

(5) Determination of major sites where pollutants affect the microbiological processes.

(6) Determination of the long-term effects of pollutants on microbial processes and ecosystems.

(7) Continuation of the development of computer models for predicting the effect of pollutants on microbial actions and functions in seawater and sediments.

(8) Continued development and application of microcosm technology used in studying mechanisms, rates, and environmental effects of mineralization and transformation processes.

(9) Development of experimental systems and approaches needed for studying the degradation of pollutants under the very low nutrient conditions typical of aquatic environments.

(10) Examination of the microbiology and chemistry of sediment binding phenomena for pollutants.

(11) Investigation of the microbiology and chemistry of surface films.

(12) Research on the recovery and re-examination of viable bacteria from sediments and particles.

7. RECOMMENDED MONITORING PARAMETERS

The monitoring parameters recommended below represent measurements that (a) can be made with available methods which are sensitive, accurate, and precise, (b) provide predictability by identifying long- and short-term trends leading to unacceptable health effects or ecological consequences of pollution, and (c) produce data that can be interpreted and analysed against existing guidelines and standards. The parameters can be placed in three general, somewhat arbitrary groups depending on the type of adverse effect potentially produced by pollution of coastal and estuarine waters. These are (a) human health effects, (b) faunal disease and (c) ecological effects.

Human Health Effects Parameters

Most of the parameters measured index fecal and/or sewage contamination. Enteric pathogens whose sources are exclusively human or lower animal fecal wastes have been omitted. Two parameters, *Vibrio parahaemolyticus* and Paralytic Shellfish Poison (toxins produced by dinoflagellates of the genus *Gonyaulax* and concentrated by shellfish) have geographic and/or seasonal limitations. Although other parameters can be measured, they would not be used in the monitoring context defined in this report. Fullfilling the research needs listed in Appendix A will change and probably increase this list.

(1) Fecal coliforms: This parameter is measured as an index of fecal pollution and the potential for infectious disease associated with it. It replaces "total coliforms," a less fecal-specific group,

and is itself less fecal-specific than E. coli. It should be measured in current monitoring programs because most existing guidelines and standards for shellfish and recreational waters set fecal coliform limits (American Public Health Assoc., 1975).

(2) E. coli: This is a more fecal-specific indicator than the "fecal coliforms." It should be measured for that reason and because recent epidemiological data indicate that its densities in the water correlate best with the rates of swimming-associated gastrointestinal disease (Dufour et al., 1975).

(3) Clostridium perfringens spores: C. perfringens are consistently found in the feces of warm-blooded animals, and no data document their multiplication in the marine environment. Since the spores persist in sediments, they are unsuitable for indexing recreational quality but are useful for monitoring the movement of sewage sludge, detecting distant, intermittent pollution sources, examining shellfish, and tracing the path of sewage effluent plumes (Bisson and Cabelli, 1978).

(4) Klebsiella: Certain biotypes within this genus are included with the fecal coliforms; however, they are infrequently found in feces and only in low numbers. They are routinely found in sewage effluents where they account for about one-third of the total coliform population, and they can be recovered in extremely high densities from certain carbohydrate-rich industrial effluents. Therefore, Klebsiella and the group that includes some of the biotypes, fecal coliforms, are less desirable fecal indicators. They are opportunistic human pathogens; however, no data indicate that they are a real hazard in water. Comparisons of E. coli to Klebsiella densities will, in certain instances, provide information on sources of pollution and changes thereof (Dufour and Lupo, 1977).

(5) Enterococci: Enterococci are an alternative microorganisms, and possibly one supplemental to E. coli in the examination for fecal pollution of marine waters. They are more environmentally resistant than E. coli but are present in lower concentrations in feces and sewage (Levin et al., 1975).

(6) Vibrio parahaemolyticus: V. parahaemolyticus is a major cause of gastroenteritis associated with the consumption of shellfish in the United States. A closely related species has been isolated as the etiologic agent in wounds infected during marine bathing. The source of the agent is the marine environment since the organisms multiply therein, probably in association with zooplankton (Kaneko and Colwell, 1973). V. parahaemolyticus, and much less frequently the toxigenic biotypes responsible for the shellfish-borne outbreaks of disease, have been isolated in high numbers from coastal and estuarine waters of the United States. They disappear from the water column when the temperature falls below 10°C, and an indirect

association appears to exist between the density of V. parahaemolyticus in the water and the proximity of an STP outfall. Methods are available for the enumeration of the organism (Thomas et al., 1976).

(7) Paralytic shellfish poison: Mouse bioassays are used to monitor for the presence of this toxin, usually found in shellfish and dinoflagellates collected during a "red tide" (American Public Health Assoc., 1970). In the United States, monitoring programs for the toxin are usually limited to the northeastern and Pacific coasts from California to Alaska.

Faunal Disease Parameters

Monitoring for faunal disease is not routinely performed; however, it is done during "fish kills." Thus, the incidence of fin rot has been determined in certain local areas (Mearns and Sherwood, 1974; Ziskowski and Murchelano, 1975). Although there are no criteria or guidelines and few experimental data against which the findings can be evaluated, some useful information should be obtained from examining selected species of collected or "live car" animals for the parameters listed in the body of the report.

Ecological Parameters

There are no routine monitoring procedures for microbiological parameters of ecological importance nor are there criteria or guidelines against which the results are evaluated. However, the following parameters have been used at various times.

(1) Microbial biomass; this measurement can be used to monitor changes in total populations in response to pollution. The microbial biomass can be measured in terms of the following:

(a) Adenosine triphosphate (ATP) (Holm-Hansen and Booth, 1966).

(b) Bacterial lipoplysaccharide (LPS), as determined by Limulus amoebocyte lysate test (Watson et al., 1977).

(c) Numbers and sizes of bacteria with the epifluorescent microscope (Hobbie et al., 1977).

(2) Estimation of mineralization and transformation rates by heterotrophic organisms; these processes are used to measure the potential of miroorganisms to degrade materials, and the effects of pollutants on that activity. This can be accomplished by isotopic techniques using water (Wright and Hobbie, 1966), and sediment samples (Harrison et al., 1971).

(3) Isolation of specific physiological groups reflecting community structure and environmental conditions; these groups include organoheterotrophs, sulfate-reducing bacteria, and nitrifying bacteria.

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TRACE METALS

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1. INTRODUCTION

1.1 Problem Identification

Recent advances in sampling and analytical procedures for determining background levels of trace metals in seawater have revealed that natural concentrations of most metals in coastal and oceanic waters are much lower than previously thought (Boyle and Edmond, 1975; Bender and Gagner, 1976; Moore and Burton, 1976; Bender et al., 1977; Boyle et al., 1977; Sugawara, 1978.) For example, recent estimates of natural zinc (Bruland et al., 1978a) and lead (Schaule and Patterson, 1979) concentrations in surface waters of the northeastern Pacific have decreased from 10,000 and 500 ng/liter to 10 and 5 ng/liter, respectively, although there is some question that the analytical procedures used capture 100% of the metals in sea water. These revised estimates and other findings suggest that the anthropogenic input of certain trace metals to coastal waters, which generally are in particulate form, may equal or exceed the natural fluxes to these waters, and that the concentrations of several metals in the mixed layer of entire regions may be elevated significantly as a result of human activities (Hodge et al., 1978). Such elevations have been documented for cadmium in the Southern California Bight (Fig. 1). The natural seawater distributions of trace metals such as zinc (Fig. 2), cadmium (Boyle et al., 1976; Martin et al., 1976; Bruland et al., 1978b), and nickel (Sclater et al., 1976) also are correlated with those of major plant nutrients, implying that these natural metal and nutrient distributions are controlled by similar biological and physical processes.

The ability of humans to elevate trace metal levels in the marine environment causes particular concern with respect to biologically active metals. The problem areas are the following:

- The ultimate toxicity of trace metals to humans if they are accumulated in marine food sources.
- Trace metal toxicity to marine organisms,.
- Possible jeopardy to the vitality of major marine ecosystems through effects on phytoplankton.

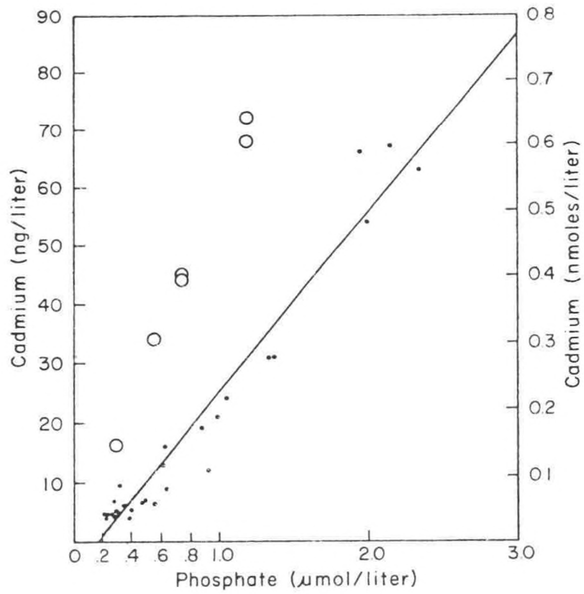

Figure 1. Cadmium-phosphate relationship in seawater. Line shows least-square regression relations for surface samples collected off Baja California, Mexico. Open circles represent data from stations in the Southern California Bight, and were not included in the linear regression calculations. (From Martin et al., 1976).

1.2 Toxicity of Trace Metals to Humans

The methyl mercury poisoning at Minamata, Japan, in the 1950's provides a famous and dramatic example of human poisoning that resulted from metal pollution in coastal waters (Takeuchi, 1972). The oceanographic and sociological conditions that prevailed in Japan, however, are such that similar incidents would not be expected in this country. In a few instances, abnormal levels of mercury in organisms in estuarine waters have been found that exceed present public health guidelines for consumption (Windom et al., 1976; Brown et al., 1977; Gardner, 1978). Nevertheless, the Panel could not identify any instances where trace-metal-contaminated seafood collected from the coastal waters of the United States caused human poisoning. Reported excess contaminations of trace metals in marine organisms generally were localized and occurred near point source inputs. Despite the present lack of evidence, concentration mechanisms for toxic metals in marine organisms may exist, and contamination of seafood by trace metals such as mercury, cadmium, lead, and selenium (which in excess are toxic to humans) (Bremner, 1974; National Research Council, 1976), must be considered.

1.3 Toxicity of Trace Metals to Marine Organisms

Elevated concentrations of certain trace metals in seawater have been shown to be toxic to marine organisms in laboratory experiments (Eisler, 1973; Eisler and Wapner, 1975), even at levels near those

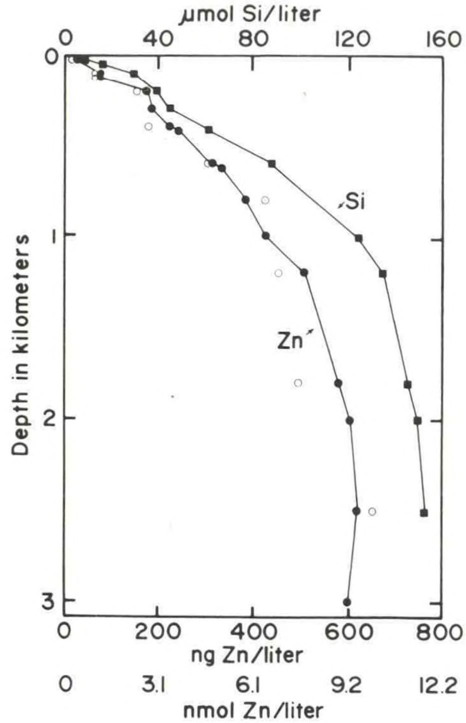

Figure 2. Depth profiles of Zn and Si off the central California coast 37°05'N, 123°22'W). The Zn profile was drawn with data obtained using an organic extraction preconcentration technique. The open circles represent values obtained using a chelex resin preconcentration technique. (After Bruland et al., 1978a).

naturally found (Moore and Stebbing, 1976). However, although elevated levels have been detected in organisms in contaminated areas (Alexander and Young, 1976; Jan et al., 1978; Eganhouse and Young, 1978; Frazier, 1976), only a few documented examples show actual trace metal toxicity to the organisms. One such example is a significant abalone kill attributed to copper pollution from a discharge of sea water that had been held in the copper condensors of a coastal power plant for some time (Martin et al., 1977). The dearth of examples could simply reflect limited scientific investigations or it could indicate that the organisms' natural detoxification processes have not yet been overtaxed (Bremner, 1974; Sternlieb and Goldfischer, 1976; Coombs and George, 1977; Brown and Chatel, 1978a). If the latter is the case, environmental toxicity problems associated with trace metals may become apparent with time. Evidence already indicates that, near one waste disposal site, the detoxification capacity of mussels has been exceeded for certain trace elements (Brown and Chatel, 1978b).

1.4 Impact on Ecosystems

Changes in the species composition of marine ecosystems are difficult to prove given the wide spatial and temporal variability observed. However, metals such as copper and zinc are now strongly suspected of playing a critical role in controlling the assemblage of phytoplankton species in many bodies of water (Barber et al., 1971; Smayda, 1974; Morel et al., 1977; Anderson and Morel, 1978). Subtle changes in the concentration of metals already may be altering some coastal and estuarine ecosystems in unknown ways. The problem is amplified by the fact that the physiochemical state of metals controls their biological effects (Davey et al., 1973; Jackson and Morgan, 1977; Morel et al., 1978; Sunda et al., 1978). For example, the toxicity of copper to aquatic organisms is related to the concentration of the free cupric ion, which can be altered by complexation by natural and anthropogenic organic compounds (Pagenkoff et al., 1974; Andrew et al., 1976; Sundra and Guillard, 1976). Natural and human-induced variations in copper concentrations and in copper complexing agents in coastal waters undoubtedly change copper toxicity to various organisms, particularly phytoplankton (Gurtisen et al., 1977). Similarly, such variations may change the whole ecosystem.

1.5 Trace Metals of Concern

On the basis of measured anthropogenic inputs and environmental contaminations, and laboratory-derived toxicity thresholds, the Panel has classified the following as trace metals of primary concern: cadmium, chromium, copper, lead, mercury, selenium, silver, tin, and zinc. Trace metals of secondary concern are antimony, arsenic, nickel, and vanadium. A number of other trace metals (e.g., beryllium, tellurium, and thallium) are potentially damaging to terrestrial ecosystems because of their increasing use and high toxicity. However, levels in the marine environment and the impact of such metals on marine ecosystems are not known. Another class of metals, which includes cobalt, iron, manganese, and molybdenum (and also copper and zinc under certain circumstances), may cause problems mainly through excessive biostimulation.

2. TECHNIQUE DEVELOPMENT*

We need to measure total metal concentrations accurately and evaluate trace metal speciation (particularly complexation by organic compounds) before we can evaluate existing and potential effects of metals on the marine biota. Therefore, development of reliable measuring techniques should be given high priority.

*This section incorporates many recommendations from Feely and Curl (1978).

2.1 Total Dissolved and Particulate Metals

A significant effort should be directed toward obtaining accurate measurements of metal concentrations in both pristine and contaminated marine waters. The recent advances in sampling and analytical techniques have resulted in data on certain trace metals that are consistently orders of magnitude lower than previously published estimates. When we know the natural levels of metals in marine and Great Lakes waters we will be able to identify those bodies of water that are subject to major anthropogenic inputs. This is especially true for those elements (e.g., Cd, Ni, Zn) whose natural distributions are correlated with nutrients. Martin and his co-workers (Martin et al., 1976) have reported excess cadmium in relation to phosphate and nitrate for waters in the Southern California Bight. Finding such "hot spots" and measuring their chemical levels will enable scientists to use realistic exposure levels in experiments to study effects on organisms.

Considerable information can be gained by analyzing the particulate (filterable) fraction of seawater. Where possible, plankton should be collected and analyzed separately from detrital particulates; however, this often is difficult and requires further technique development. One reason for analysing the particulate fraction is that studies of the biological effects of metals will presumably include assessing the availability of trace elements from that fraction to plankton. Furthermore, the strong tendency of particulates to adsorb trace elements may provide a mechanism to detect significant anthropogenic inputs. In addition, further trace element analyses of plankton may explain the inverse relationship sometimes observed between dissolved and planktonic concentrations of metals such as cadmium (J. Martin, personal communication).

Of special interest is the chemical association between metals and particulates. Techniques are needed to remove metals selectively from different geochemical phases of particulates found in marine, estuarine, and fresh waters.

2.2 Trace Metals Speciation

To determine the potential effects of trace metals on the marine biota, metal speciation including redox state, inorganic complexation, organic complexation, and chelation and formation of stable organometallic compounds must be studied. Unfortunately, few laboratories are competent in analyzing the trace metals in seawater. Determining the several chemical species of each metal is difficult, and contamination problems are extreme. Some sensitive analytical techniques are not applicable to speciation studies because they measure only the total metal concentration, and some methods used to measure metal concentrations may disturb the natural speciation.

Some analytical methods that have been successfully applied to trace metal speciation in aqueous systems may also be applicable in marine waters. The following description of methods is not intended to be complete, and no recommendations of specific techniques are implied.

Thermodynamic calculation methods have been used to estimate equilibrium concentrations of trace metal species by taking into account all known competing equilibria. A main limitation of these methods has been the lack of data on natural organic ligands and associated metal complexes in seawater. Ultrafiltration, dialysis, centrifugation, and molecular size chromatography have been used to identify the relative sizes of materials associated with trace metals. Ion exchange, solvent extraction chelation, and liquid chromatographic techniques have been used in both stable and radio-tracer studies of seawater. Electron-capture gas chromatography has also been used to identify volatile metals.

Several potentially useful spectrosocopic techniques are available, including ESR, Mossbauer resonances, and Raman, UV, and visible spectroscopy. Some electrochemical techniques, including ion selective electrodes, polarography, and voltametric methods, have been used directly in an attempt to differentiate between chemical forms of trace metals in seawater. However, with all these techniques the presence of organic matter can prevent accurate results.

Another approach to chemical speciation uses an organism's response to a metal species to determine the concentration of that species. For example Sunda and Guillard (1976) used glucose uptake rates of bacteria to measure cupric ion activity in seawater. A different approach might use specific enzyme levels in an organism that vary predictably with the concentration of a metal species in seawater.

Analytical schemes are not now available to define all trace metal species in seawater. Therefore, a major effort is needed to develop such schemes so that more meaningful biological studies can be conducted.

2.3 Surface Microlayer

The surface microlayer of seawater contains relatively high concentrations of organic matter, bacteria, phytoplankton, and zooplankton. Elevated levels of certain metals have also been measured in this layer (Duce et al., 1976; Piotrowicz et al., 1972; MacIntyre, 1974; Liss, 1975). Metals such as lead, which have predominantly atmospheric transport paths, fall out on the surface layer and may be concentrated there. Trace metals associated with floatables in wastewater effluents also may accumulate in this layer. Because of the biological processes unique to the surface microlayer, elevated metal concentration there could have significant consequences. To date the evaluation of this problem has been hindered by inadequate sampling techniques and by the microlayer's varying physical status which depends on sea state. Thus, there is need for a device that samples reproducibly just the surface microlayer, and for programs to measure and evaluate metal contamination in the surface microlayer.

2.4 Bottom Sediments

We should expand efforts to describe metal distributions with depth in undisturbed, dated bottom sediments of selected study areas. If metal concentrations are higher in the upper strata of the core than in the bottom strata, unnatural metals inputs are suspected. Thus areas undergoing possible metal pollution can be identified, and further studies can be conducted on inputs and resultant contamination of the water and biota. Metals in sediments are relatively easy to measure, and most laboratories can do so routinely. However, samplers that obtain undisturbed cores are not yet in wide use, and only a few pollution programs include sediment-strata dating. Such dating is important for the following reasons:

(1) Without a time frame it is extremely difficult to know the extent to which a core has been disturbed.

(2) Sedimentation rates are frequently higher in more recently deposited sediments (because of human activities). Therefore metal pollution that is increasing may not be recognizable because of dilution with terrigenous sediments.

(3) Dating is necessary to determine pollutant metal fluxes, which make it possible to compare the extent of metal pollution on a regional basis regardless of sediment type or sedimentation rate.

(4) With a time frame, it is possible to know when a metal concentration started to increase in the sediments. This can be very useful in identifying sources.

Therefore, procedures to sample routinely and to date undisturbed bottom sediments should be further developed and their use encouraged.

3. INPUTS, TRANSPORT, AND FATE

We must describe major sources, routes, and rates of metal input to United States coastal waters so that we can identify anthropogenic sources, determine accumulations of trace metals, and evaluate the metals' ecological impact. Potentially important sources include municipal (domestic and industrial) wastewater outfalls, thermal and other direct industrial discharges, harbor-related activities (vessel paints, sacrifical anodes), solid waste disposal, surface runoff, and aerial deposition.

Some data are already available. For example, Duce et al. (1976) in the NSF-IDOE Pollutant Transport programs are providing information on the fluxes of metals to the world's oceans through atmospheric fallout. Estimates of total input are available for at least three geographical areas. Young and his co-workers (Young and Jan, 1977; Young et al., 1973, 1978a,b) have provided rates of trace metal input by several major routes to the Southern California Bight and some similar information has been obtained for the New York Bight (Mueller et al., 1976), and for northern Chesapeake Bay (Heltz, 1976). Studies are needed in other world population centers that border salt and freshwater environments.

3.1 Estuaries

Estuaries constitute one class of aquatic ecosystems potentially vulnerable to inputs of trace metal and other pollutants. Besides being vital breeding and feeding grounds for many coastal species, these areas of restricted circulation contain other resources important to humans (e.g., shellfish beds, industrial sites, anchorages, transportation paths for ships, recreation, and areas for municipal waste disposal). Many of these uses are in conflict. Because estuaries are mixing zones for fresh and marine waters, chemical reactions take place. These reactions must be understood, particularly those involving metals. Metals introduced to the estuarine area by rivers may be in an ionic, complexed, colloidal, or particulate phase; if associated with colloidal or particulate matter they may be tightly bound or loosely sorbed onto the surface. When they encounter saline waters, metals may change from one chemical state to another. For example, iron and manganese exist in rivers mainly as colloids, probably associated with fulvic and humic colloids which have been shown to contain large quantities of metals (Sholkovitz, 1976); however, once carried into the estuarine environment, these two metals may be deposited in the sediments. If metals are transferred to the sediments (and this has been documented for some metals), estuaries may trap a significant proportion of the metals continuously introduced by the rivers. This process leads to high concentrations of metals in the sediments of these ecosystems. Humans are also adding certain metals directly to the estuaries by way of antifouling and other vessel paints, anticorrosion sacrificial anodes, and dry-dock applications (Young et al., 1979). In time these can accumulate in localized areas, particularly docking and vessel repair facilities.

Edible shellfish, especially oysters, have very high contents of some metals such as zinc (Frazier, 1976). If metal content of the waters and sediments is high, the metal content of the shellfish is usually also high (Young and Jan, 1979). If the metal content becomes too high, the shellfish resource may be endangered.

We need research on the estuarine environment to determine the ultimate fate and biological impact of metals introduced by rivers, outfalls, and vessel-related activities.

3.2 Coastal Ecosystems

Coastal ecosystems adjacent to densely populated or industrialized areas are subjected to potentially damaging inputs of trace metals and other contaminants. Like the estuaries, these regions are often highly productive ecosystems that are subjected to varied and often conflicting uses. The siting of submarine wastewater outfalls or ocean dumping zones near traditional or potential fishing ground is one example.

When metals enter the coastal waters, those remaining in the dissolved phase are redistributed by the currents; those in the particulate phase may be deposited on the ocean bottom. Some metals have a very short residence time in water before they are sequestered by settling particulates or taken up by plants or organisms and either incorporated in their bodies or excreted in fecal pellets and/or molts (Fowler, 1977). Zooplankton fecal pellets containing metals passively sink, and the protective covering of the pellets may be destroyed, releasing certain metals (e.g., Cd, Zn) back into solution. This leads to a characteristic vertical profile, with the surface waters depleted in the metal and the deeper waters enriched. Other elements (e.g., Mn, Pb) remain in the particulate state, and no enrichment in the deep water column occurs. When fecal pellets and other organic matter reach the sediments, a situation can be produced whereby oxygen in the waters may be totally consumed and hydrogen sulfide may be produced. Besides having toxic effects, hydrogen sulfide can react with dissolved metals in seawater and form insoluble sulfides that then become part of the sediments. We need to determine the extent to which sediment-bound metals are available to the benthic biota of coastal ecosystems.

As a further complication, organisms may extract metals from the dissolved, colloidal, or particulate states, and concentrate them to high levels within their bodies. Other organisms can eat them and possibly concentrate certain metals from the first organism. Each successive consuming organism theoretically could have an increased amount of the metal, an example of biomagnification. However, recent studies suggest that such biomagnification of metals through the food web may not occur as generally as once thought, and the reverse process (biodiminution) may be as common or even more so.

Whether a particular metal can be extracted by an organism depends on the metal's state. Thus, for environmental studies the distribution of a metal between the various dissolved, colloidal, and particulate states must be known. A pollutant metal may exhibit behavior similar to its natural counterpart or may have its own behavior pattern. Consequently, it is difficult to predict a pollutant metal's ultimate destination or its threat to humans or their resources.

3.3 Strategy

To obtain accurate descriptions of the complicated input and transport mechanisms of trace metals, as well as their fates in given ecosystems, the Panel suggests the following strategy. A few United States regions that represent the major types of aquatic ecosystems (marine, estuarine, Great Lakes) should be selected for intensive study of the various problems discussed above, as well as certain of the biological effects discussed below. When selecting sites researchers should take advantage of the regional pollution studies already conducted in United States waters.

4. BIOLOGICAL EFFECTS

4.1 Quantification of Availability and Toxicity of Trace Metals to Marine Organisms

We need to assess how long-term changes in the metal chemistry of coastal and estuarine waters, are likely to affect the biota. To do this, we must establish the availability and toxicity of important trace metals to a variety of typical marine species. Two guidelines should be followed in designing the studies: (1) Care must be taken to prevent contamination during collection and preparation of trace metal samples. (2) Chemical speciation of the metals in the culture medium must be an integral part of laboratory and field studies.

The reason for the first guideline is obvious; its implementation is difficult. For example, Patterson and Settle (1976) have pointed out the extreme care needed to prevent metals contamination of tissue samples during dissection. The second guideline stems from the increasing number of studies demonstrating the importance of metal speciation in controlling metal availability and toxicity to microorganisms. As discussed in Sec. 1.4, the toxicity of copper to several phytoplankton species and to some zooplankton and fish larvae has now been shown to be directly related to the cupric ion activity. The availability of Fe is thought to be a function of its complexation by organic chelators. To obtain valid quantitative information on trace metal requirements and tolerances in organisms, it is necessary to determine what metal species actually occur in the natural environment and to use them in toxicity studies.

4.1.1 Acute and Chronic Effects

Acute toxicity testing in the laboratory usually involves exposure to metal levels that greatly exceed even the highest human-induced environmental exposures. These high levels probably overload metal detoxification or storage systems of the organism. The advantage of acute toxicity testing is that it provides a rapid and simple method for comparing trace metal toxicities. Values established by such methods have been used extensively to formulate regulatory guidelines for allowable discharge levels. The disadvantage is that these high levels are unrealistic and do not allow the organism to respond naturally.

Testing toxicity by using chronic exposures is generally considered preferable to acute toxicity testing since the exposure levels of trace metals more closely approach those that occur in the natural environment. Results of laboratory experiments using chronic exposures may have value for predicting the sublethal effects of trace metal pollution in the marine environment. Studies that examine sensitive life stages such as development and reproduction, and especially those that cover entire life cycles or several generations, are particularly instructive. The disadvantage is that such tests take a long time and require careful attention.

4.1.2 Detoxification

Measured concentrations of metals in field-exposed organisms are probably the result of uptake and accumulation over relatively protracted exposures to low levels of contamination, and under certain conditions animals exposed to high levels of trace metals in sediments have developed tolerances to these metals (Bryan and Hummerstone, 1973). Mechanisms for storage, detoxification, and elimination can account for such tolerances. The lysosomal system of cells and the metallothioneins, a class of metal-binding proteins (Brown et al., 1977), are two known systems for such processes in animals (see Sec. 4.2). Toxic responses may occur when detoxification mechanisms become saturated because of excessive uptake of trace metals (Bremner, 1974; Sternlieb and Goldfischer, 1976; Coombs and George, 1977; Brown and Chatel, 1978a).

4.1.3 Phytoplankton Ecology

Not all effects of marine pollution are as tangible as fish kills. Effects such as changes in the species composition of marine ecosystems are difficult to assess, given the wide temporal and spatial variability natural in oceanic waters, and our limited understanding of how ecological processes affect the composition of the aquatic environment.

Recent data suggest that the effect of metal pollution on phytoplankton may be a very important instance of a less tangible effect. Although definite proof cannot be given, circumstances indicate that trace metals are critical in controlling the natural assemblage of phytoplankton species in the oceans, and that metal pollution may be significantly affecting coastal and estuarine ecosystems by changing the natural assemblages. It has been suggested, for example, that toxic dinoflagellate blooms (red tides) may be related to changes in trace-metal chemistry (although some of the most conspicuous and consequential red tides have been of natural origin). Such blooms have obvious detrimental health and economic effects. In many other instances, important effects (both detrimental and beneficial) observed in economically important species may quite possibly be caused by subtle changes at the bottom of the food web (i.e., the phytoplankton).

Besides the complexity of the problem and the gaps in our understanding of oceanographic processes, two specific difficulties account for much of our ignorance of metal-phytoplankton interactions. First, measuring trace metal concentrations in the oceans is not as simple as it appears. Only recently have we realized how extremely low are natural levels (ng/liter) of trace metals in marine waters, and we have extensive and consistent data for only a few trace metals. The implications of low concentrations are still to be explored. Second, the biological effects of the metals are highly dependent on their chemical form, and chemical speciation of metals controls their availability and their toxicity to phytoplankton. We have no direct technique to measure metal speciation in the oceans, except in a very few intances, so we are forced to rely on indirect evidence and on inferences from laboratory data.

Recent laboratory experiments, in which chemical speciation was precisely controlled, have demonstrated that for optimum growth different phytoplankton species require markedly different metal composition in their medium. (F. Morel, personal communication). (At present, data are available mainly for copper and to a lesser extent for zinc and iron). Corroborating these laboratory experiments are the results of various in-situ bioassays. For example, seawater (particularly newly-upwelled seawater) often needs to be conditioned in the laboratory, by modifying its trace metal chemistry, to permit the growth of various phytoplankton species. Added chelators accelerate this conditioning. Experiments with large plastic enclosures have shown that changes in species composition are the major response to increased metal concentration (Grice and Menzel, 1978). Finally, recent experiments using "ultraclean techniques" have shown that profound effects on the measured photosynthetic rate result from small changes in the natural metal concentrations (Feely and Curl, 1978).

Clearly these recent findings imply that the trace metal composition of the water is as important a parameter of the phytoplankton environment as are nutrients, light, temperature, etc.

4.2 Biochemical Markers or Indices of Toxicity

There is evidence that trace metal contents have increased in the environment and in marine animals (as demonstrated in such comprehensive monitoring programs as the Southern California Coastal Water Research Project and the National Mussel Watch). However, there is little direct evidence that either increase has had a detrimental effect on natural marine populations. Little is understood of the actual relationships between metal levels and the biochemical functioning and survival of organisms.

Reductions in survival and growth alterations in specific physiological responses, inhibition of enzymes, and retardation of development have been demonstrated in numerous laboratory studies that exposed organisms to trace metals (Eisler, 1973; Eisler and Wapner, 1975). However, conditions during laboratory exposures have been sufficiently different from natural conditions that useful interpretations have not been possible. Factors such as the chemical form of the metal, the condition of test organisms, the behavior of the test organisms in the laboratory, and exposure duration are believed not to be representative of those in the field. Furthermore, simply analysis of the species assemblage or traditional bioassy studies may be inadquate to determine, in the sea, that natural populations are stressed by excessive or deficient amounts of trace metals. More direct techniques might be developed, based on the biochemical roles of trace metals as necessary nutrients or toxicants. For example, the inactivation of particular enzymatic systems could be measured in natural plankton populations as specific evidence that particular metals are toxic. This possibility is speculative at present but may provide the only practical techniques for field studies.

Two particular biochemical systems already provide potentially usable tools for assessing trace metal stresses in marine animals: lysosomes (Moore and Stebbing, 1976) and metallothionein (Brown et al., 1977). The function of lysosomes in cells includes the uptake and storage of toxic trace metals, such as copper, lead, and mercury, and possibly rendering them nontoxic to the cell (Sternlieb and Goldfischer, 1976). In addition, excessive exposure to certain trace metals can affect the integrity of lysosomes and result in pathological changes in cells and tissue. Appropriate measurements of lysosomal function in animals exposed to trace metal contamination in the field would be useful to assess the possible toxic effects of abnormal metal accumulation in the tissues of marine animals. Also, a preliminary study in mussels indicates good correlation between nonsurvival of environmentally and laboratory exposed mussels and the saturation of the metallothionein pool with metals such as cadmium, copper, mercury, silver, tin, and zinc (Brown and Chatel, 1978a).

Another example of the metallothioneim detoxification mechanism is presented in Fig. 3. As zinc and copper both occur naturally in metal-

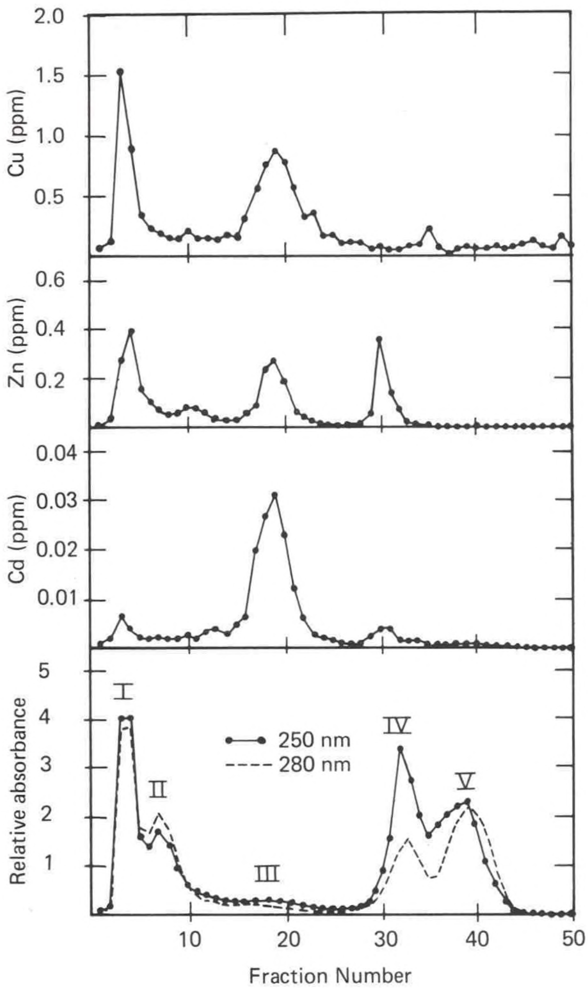

Figure 3. Amounts of copper, zinc, and cadmium in five protein fractions isolated from the liver of a Greater Scaup duck, using a Sephadex column, and absorbances at 250 and 280 nm to identify the position of the main protein peaks. Peak I corresponds to the high molecular weight protein pool which includes enzymes; peak II to haemoglobin; peak III to metallothionein, a protein that can bind and thereby store and/or detoxify trace metals; peaks IV and V correspond to low-molecular-weight cytoplasmic material, such as amino acids, nucleic acids, and ATP. (After Brown et al., 1977)

loenzymes, their relatively high abundance in peak I is to be expected. Excesses of these essential metals are stored on metallothionein (III); Cd, which is a nonessential and toxic trace metal, is bound almost entirely to metallothionein. If the binding capacity of metallothionein is exceeded, as in highly polluted areas, then excesses of Cd may spill over into the enzyme-containing pool (I). Cadmium can displace Cu and Zn from metalloenzymes, disrupting enzyme function, and thereby resulting in toxic effect of Cd to the organism.

4.3 Synergism

The speciation and changes in speciation of trace metals when they enter the marine environment must both be understood. The bioavailability of trace metals is influenced by binding to organic constituents in the marine environment, whether these are natural components of the environment or pollutants (George and Coombs, 1977). These constituents may decrease or increase bioavailability of metals and consequently change the metals' toxic effects, or, in some instances, render some essential metals unavailable for growth.

In particular, methylation of metals appears to increase both uptake and toxicity of trace metals. We must study geochemical and bacterial processes that increase methylation so that highly methylating environments can be avoided as dumping grounds for trace metals. Further studies are needed to clarify which trace elements are methylated and whether or not methylation increases their toxicity.

Organic pollutants may interact similarly to natural organics with naturally occurring or pollutant trace metals. Some organic pollutants may decrease uptake of trace metals or increase their excretion. Others, such as certain organic carcinogens, may increase and influence both uptake and intercellular distribution of metals (Brown, 1977). Evidence indicates that one of the natural detoxifying systems for metals (metallothionein) cannot bind and thereby detoxify methylated metals or metals associated with organic carcinogens (Chen et al., 1973). Thus, release of some organic pollutants containing trace metals may reduce bioavailability of the trace elements, but other organics may have the potential to increase metal uptake and toxic effects of trace metals. Determination of such synergistic effects will permit an evaluation of the potential hazards of releasing certain metals into areas with high concentrations of organic compounds.

Understanding the interactions between trace metals is important for predicting toxic effects. Toxic metals such as cadmium and mercury may displace copper and zinc from metalloenzymes, disrupting the enzymes and causing toxic effects (Brown and Parsons, 1978). If there are deficiencies of copper and zinc, then the toxic effects of mercury and cadmium may occur at lower exposure levels, since the occurrence of metals in the sensitive enzyme pool is partly governed by competitive factors (Brown and Chatel, 1978a). Deficiencies of an essential metal, therefore, may enhance the effects of a toxic metal. For this reason, the ratio of toxic metals to essential metals in effluents may be a major factor governing the survival of organisms in the vicinity of outfalls.

5. MONITORING PROGRAMS

During the past decade numerous monitoring and research programs have generated vast amounts of data on distribution of trace metals in United States coastal marine and estuarine ecosystems. Many of these studies have identified areas of elevated metal concentrations, particularly in surface sediments and certain types of organisms. Although such information has been useful in locating sites or regions of (discrete or diffuse) anthropogenic inputs, and resultant levels of metal contamination in these reservoirs, the data seldom have provided convincing evidence of environmental damage from metal inputs. Future monitoring programs patterned after these earlier studies would probably provide only the same kind of data.

Therefore, the Panel recommends that minimal effort be directed toward monitoring target trace metals in sediments and organisms until adequate research has evaluated the usefulness of such programs in describing the "health" of ecosystems. For example, a number of trace metals have been found to occur at unnaturally high concentrations in the edible tissue (generally muscle) of seafood species around a large municipal outfall in southern California; "contamination factors" (ratio of concentrations in outfall and control zone specimens) range from 2 to 10 in a variety of invertebrates (but not fishes) (Eganhouse and Young, 1976; Jan et al., 1978; Young et al., 1978). Similar concentrations have been measured in other tissues of invertebrates from this region. At present, we do not know whether such contaminations represent damage to these organisms or to their predators (including humans). Rather than continuing to generate more data, we should expend available resources on research into the environmental effects and public health implications of elevated tissue and body burdens of metals now observed in affected coastal areas of the nation.

The Panel recommends that detailed studies of metal inputs, distributions, and states in key phases of the ecosystem (seawater, sediments, biota-trophic levels) be limited to target regions representative of the various United States aquatic ecosystems. Pending the development of additional sensitive and reliable monitoring schemes, comprehensive programs designed to discover and monitor metal contamination over the entire United States coastline should be limited to a few key programs such as the National Mussel Watch. Comprehensive programs should be supported and possibly expanded to include a subtidal benthic species. In general, mollusks appear to best represent (by elevated tissue burdens) anthropogenic inputs of metals, and fishes are among the poorest such bioindicators.

To monitor offshore waters of the continental shelf, a more complicated approach must be employed. The diffuse fluxes of metal pollutants expected in these regions can best be monitored by measuring the amounts of metals that become associated with particles passively sinking through the water column. These particles can be collected in traps suspended in the water column by taut-line buoy systems. Properly designed traps could monitor particle fluxes for extended periods (weeks or months), thus eliminating short-term variability. Relatively few traps would have to be used for adequate coverage of the offshore regions, and costs could be kept at a reasonable level. However, research is needed to establish and improve the accuracy of such systems in quantification of vertical partical flux. In addition, problems with the use of preservatives on the collection and solubilization of elements from particles must also be evaluated.

6. RECOMMENDATIONS

(1) Improved methods of sampling and analyzing seawater for trace metals in the dissolved and particulate states should be developed. Techniques for reliably determining the chemical speciation of metals in both states are also needed.

(2) A procedure should be developed to sample the surface microlayer of the sea cleanly, in a defined and repeatable manner (where and when sea state allows the formation of a microlayer). Techniques also should be developed to isolate detrital particulates from plankton collections for separate trace metal analysis.

(3) From studies of a variety of marine species, threshold values for chronic toxicity and biologically significant sublethal responses should be determined for trace metals of present concern (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, V, Zn). Testing should employ those physicochemical states thought to exist in various major inputs and receiving waters of the coastal United States, including contaminated bottom sediments. Resultant concentration changes in tissues commonly used in monitoring programs (e.g., liver, gonad, muscle, gill) should also be determined to assist in the interpretation of unnatural tissue levels observed in the field.

(4) Particular efforts should be made to describe the dependency of phytoplankton communities on aqueous concentrations and speciation of the trace metals listed in (3), plus Co, Fe, Mn, and Mo.

(5) Reliable and sensitive "indices of toxicity" (e.g., the lysosomal and metallothionein biochemical systems) are needed to evaluate the health of organisms exposed to anthropogenic inputs of metals and other contaminants. These indices should be as specific as possible to a given metal and physicochemical state.

(6) The effect of varying chemical environments on trace metal speciation and resultant bioavailability and toxicity must be determined, especially the following: reactions with natural and synthetic organics; conditions causing methylated and other organometallic compounds; interactions between toxic and essential metals.

(7) A limited number of ecosystems representing major categories of the nation's coastal, estuarine, and fresh waters (e.g., Great Lakes) should be selected for intensive study of the trace metals of concern. This should include determination of the following: natural and anthropogenic routes and rates of input; distributional processes and fates; natural and altered concentrations and states in the surface microlayer, water column, interstitial water, undisturbed dated bottom sediments, and organisms from various positions in the food web; relative health of organisms and communities near major inputs as determined by the most sensitive available indices.

This effort should include a carefully conceived and coordinated quality control program that covers sample collection and preparation as well as analysis.

(8) Until results are available from the research and development activities recommended above, widespread monitoring of trace metals in coastal zones should be limited to a few key programs that accurately document spatial and temporal gradients in metal contamination of useful bioindicators (such as mollusks) and suspended particulates.

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BIOSTIMULANTS

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1. PROBLEM IDENTIFICATION

Vast amounts of public funds are being spent to prevent or mitigate the perceived effects of biostimulants of human origin. Management decisions for beneficial disposal of these compounds depend on knowledge of mass budgets and regional hydrography (Officer and Ryther, 1977). Prevention or mitigation of environmental problems resulting from human activities depend on research and monitoring that directly affect decisions on control and disposal of wastes. Our goal is to provide information necessary to permit the minimum expenditure of funds to control or mitigate problems.

The introduction of a variety of biostimulatory chemicals (nitrogen, phosphorous, silicon, trace elements, dissolved organics) into the coastal ocean and estuarine environment causes increased production of phytoplankton and alterations in species composition. These effects give rise to the following, which can lead to problems: (1) food chain alteration, (2) anoxia, (3) toxic effects, (4) aesthetics, (5) antagonistic and synergistic effects, (6) remote effects, and (7) altered seasonal patterns of production.

1.1 Food Chain Alteration

Phytoplankton are the base of the marine food chain. Consequently, changes in species composition, rate of production, standing stocks, and areal distribution of phytoplankton populations will have profound effects on the biological resources of the coastal ocean.

We can now identify several phytoplankton-based ecosystems that may be altered by human introduction of nutrients and other biostimulatory chemicals into the coastal zone (Glendening and Curl, 1978). One is the ecosystem dominated by diatoms, which are the usual food for filter feeding fishes and zooplankton and which support the large fish populations along the United States shoreline. Diatoms have short lifetimes, are grazed heavily, and are rarely a nuisance. Another is the ecosystem dominated by dinoflagellates, some of which persist for extremely long periods of time, are known to be poor food for most grazers, and can achieve undesirable concentrations because of their ability to swim and actively respond to light. Thus, for example, some dinoflagellate blooms are serious pollution events that must be understood to be predicted and controlled. Recently, it has been suggested that failures of certain fish year classes (e.g., anchovies) are possible when one species of dinoflagellate, rather than another species, is present as the fish larvae's principal food source (Lasker, 1975; 1978).

In the nearshore environment anthropogenic biostimulants may also affect macrophytes (sea grasses and attached algae), leading to enhanced production and expanded range. Shifts from phytoplankton to macrophytes can have profound effects on food chains by reducing food available to usual grazers and increasing the organic detrital load on the environment.

1.2 Anoxia

Biostimulants supplied by domestic sewage outfalls, industrial waste disposal, and agricultural runoff and drainage can make moderately productive coastal waters highly productive. The added biostimulants may cause so-called "runaway" growth, which can lead to oxygen deficiency when particulate matter sinks and subsequently consumes oxygen by degradation reactions. This chain of events can affect entire coastal ocean communities and may lead to alterations of the food chain or directly to fish kills. There is a strong correlation between anoxic conditions and high dinoflagellate concentrations along many coasts (Segar and Berbarian, 1976). This general subject of anoxia is discussed by Gross (1976).

1.3 Toxic Effects

The environmental factors that cause the normally low concentrations of certain toxic phytoplankton species to multiply to bloom proportions at the expense of beneficial species are unknown. Adverse effects are not confined to aquatic ecosystems alone, for people can be poisoned by eating shellfish that have filtered out toxic dinoflagellates even from low concentrations of the organisms.

1.4 Aesthetics

Phytoplankton populations that reach bloom proportions discolor the water and render it unsightly and malodorous, reducing its aesthetic and recreational values. Attached plants occupy the intertidal and subtidal zones of coastal and estuarine waters where they may serve as breeding grounds for some commercially important species or refuges for their young. The introduction of nutrients or other biostimulants can increase the density or expand the range of these plants so that they invade areas where they might not otherwise be present. These alterations can interfere with fisheries, cause unsightly nuisances, and exert excessive oxygen demand.

1.5 Antagonistic and Synergistic Effects

Studies of phytoplankton in the natural environment address other additional priority research areas in pollution research. One of them, evaluation of the effect of more than one pollutant upon the health of a species or community, is of primary importance. Only plants respond to nutrients in the sea. To describe and predict plant populations it is essential to know what pollutant effects are additive, antagonistic, multiplicative, or independent of nutrients.

1.6 Remote Effects

High productivity or marked change in species composition in one coastal area may have profound effects tens to hundreds of kilometers along a coast or along an entire estuarine system. This is a result of continuous undercurrents and subsequent upwelling in the case of coastal systems, or density gradient circulation in the case of estuaries. Thus coastal and estuarine circulation patterns must be taken into account in evaluating the capacity of the coastal ocean to assimilate biostimulants.

1.7 Altered Seasonal Patterns of Production

The normal seasonal sequence of blooms in temperate waters usually includes a summer period of low production due to the exhaustion of nutrients in the upper layer of strongly stratified water. Anthropogenic inputs of biostimulants during the summer period can induce abnormal blooms of organisms (particularly warm water species). These organisms may either be unsuitable food for higher trophic levels or cause anoxia in deeper stable water when the cells sink and decay. Unseasonal introduction of biostimulants may also be responsible for blooms of toxic dinoflagellates.

2. EXAMPLES OF BIOSTIMULATION

Several well-documented examples of biomass increases, anoxia, and changes in community structure resulting from anthropogenic inputs of biostimulants, especially plant nutrients, follow.

2.1 Chesapeake Bay

Chesapeake Bay is the largest estuary in the eastern United States and is a complex system illustrating both the stresses of urban pollution and the controls inherent in a natural system. The bay and its tributaries are bordered by major cities including Baltimore, Md., Washington, D.C., Richmond, Va., and Norfolk, Va. Nitrogen in discharges of treated sewage from the Baltimore and Washington metropolitan areas enters the bay tributaries at rates exceeding 17 metric tons per day. In addition, the upper bay receives input from several rivers whose content of inorganic and organic phosphorus and nitrogen varies seasonally. Most notable among the upper bay tributaries is the Susquehanna River, which supplies 85% of the fresh water to that area (Beaven, 1947) and whose watershed includes extensive agricultural areas and a population exceeding one million.

In 1969 the effects of the Baltimore sewage discharge were not observable in the Chesapeake Bay below Baltimore. However, Bach River, the direct recipient of the Baltimore discharge, was intensely eutrophied, with high chlorophyll concentrations. The absence of a dramatic effect on Chesapeake Bay proper was attributed to dispersion of phytoplankton by the density-driven circulation in the bay, sinking of the excess phytoplankton production, and reactions with iron precipitating phosphate in the discharge. The same phenomenon appears to occur in the Potomac River. The situation is reminiscent of that found in the rivers flowing into the western end of Lake Erie before summer anoxic conditions began in 1958. The lack of dissolved nutrients downstream does not dismiss the eutrophication problem, but merely indicates that the nutrients have been consumed by plants.

Indeed, the presence of methane and low oxygen in the lower layers of the Potomac and the summer anoxic conditions in the deeper central basin of Chesapeake Bay reveal the seriousness of the problem. In addition to surplus organic production, which could conceivably be consumed by grazers and converted to desirable organisms, much of the production is in the form of blue-green algae such as *Microcystis aeruginosa*. This produces unattractive algal mats, which are not grazed, thereby leading to deposition in the sediments and a consequent high oxygen consumption.

2.2 New York Bight

Another East Coast region with a large urban influence is the Middle Atlantic or New York Bight, the continental shelf region stretching from Cape Cod to northern Virginia. Forty-five million people live in the cities and suburbs bordering this region. Their wastes are discharged to the Bight waters through rivers, outfalls, and barged disposal (Simpson et al., 1975). The anthropogenic nitrogen supplied to the Bight apex primarily from the Hudson/Raritan Bay system of New York has been estimated to be as high as 85% of the total nitrogen input (Table 1) (O'Connor, 1976). Sources of oxygen demand in the Bight, based on organic carbon loadings, are summarized in Table 2. It is apparent that decomposition and respiration of phytoplankton are the principal oxygen users throughout the year, and completely dominate the system during the summer months.

Table 1. Nitrogen Loadings to Waters of the New York Bight Inshore of 102 km[1]

Source	Annual Estimate (million tons/day)	June-August Estimate (million tons/day)
River Input		
Wastewater	204	
Runoff	136	
Total	340	136
Ocean Dumping		
Dredge Spoil	63	44
Sewage Sludge	17	12
Atmospheric Fallout	64	71

[1]J. S. O'Connor (1976).

Table 2. Total Potential Oxygen Demand From Major Sources in the New York Bight[1]

Source	Annual Estimate (million tons/day)	June-August Estimate (million tons/day)
River Input[2]	5,000	5,000
Primary Production	5,700	17,000
Ocean Dumping		
Sewage Sludge	1,100	1,100
Dredge Spoils	2,100	2,100

[1]Segar and Berberian (1976).
[2]Considerable uncertainty exists.

The important point from the budgets in these tables is that ocean dumping has little effect on the eutrophication problems of the New York Bight. The increased nutrient supply from urban discharge has dangerously elevated the production rates to a point where a greater than average perturbation of the natural cycle--such as that during the spring of 1976--can cause severe anoxia and fish and shellfish kills throughout the Bight area. Unusual meteorological conditions of 1976 evidently resulted in an early spring river discharge, causing an early and prolonged density stratification within the Bight and reducing the vertical mixing of oxygen. Onshore flow of coastal water during the spring caused restricted flushing of the bottom waters (an estimated 20% of the 1975 rate) and advected great numbers of the dinoflagellate *Ceratium tripos*. The abnormally high oxygen demand from decomposing *Ceratium* resulted in anoxic and near-anoxic conditions over thousands of square kilometers of the Bight. It is conceivable that this particular episode would have occurred on a smaller scale, or even not at all, had the enormous supply of anthropogenic nutrients not been available to the system. Although the New York Bight has always been a naturally productive area, it is the anthropogenic nutrient inputs to an already nutrient-rich system that have caused problems (Gross, 1976; Ryther and Dunstan, 1971; Swanson and Sinderman, 1978).

2.3 California Embayments

On the West Coast of the United States the Los Angeles-Long Beach Harbor area of San Pedro Bay is a seriously polluted body of water demonstrating many of the stresses of urban eutrophication. It is a relatively shallow dredged basin with low tidal flushing and low current velocities. The harbor is surrounded by about 7 million southern California residents and is the third busiest port in the United States.

Heavy organic matter loads caused by fish canneries and other sources reduce visibility in the water to much less than 1 m. Oxygen depletion in the outfall plumes may induce "white tides" of bacteria, colloidal sulfur, and suspended protein-fat complexes. Localized "green-tide" blooms of unidentified euglenoids have also been observed. Recently red tides of the dinoflagellate *Gonyaulax polyedra* have been observed in some parts of the harbor all year round.

2.4 Northern California Waters

Farther to the north, the San Francisco Bay estuary is showing signs of stress, such as altered species composition, from its use by millions of local inhabitants for municipal, industrial, and agricultural waste disposal, recreation, commerce, and fishing. Increasing volumes of nutrient-rich wastes coupled with the proposed sustained reduction of fresh-water inflow resulting from development of the Central Valley water diversion project may accelerate the process of eutrophication. In the southern end of San Francisco Bay the situation is amplified by lack of river inflow and large volume sewage inputs from the San Jose municipal facilities. Higher nutrient loading and lower species diversity are observed in these waters.

2.5 The Baltic Sea

The Baltic Sea region is the largest brackish water basin in the world. It is a heavily traveled waterway, a greatly utilized recreational resource, and an important fisheries center. The Baltic is the receptacle of the sewage of 17½ million people as well as the industrial waste products of seven bordering nations. Its pollution problem is strongly influenced by complicated physical oceanographic processes.

The Baltic is a large, fjord-like body of water, separated from the North Sea by narrow, shallow entrances (maximum sill depth = 18 m). Since freshwater input from river runoff and precipitation greatly exceeds that lost by evaporation, there is a large net outflow of relatively fresh water at the surface and a smaller inflow of more saline water at depth. A marked stratification limits vertical exchange, and tidal mixing is weak; hence, high salinity water occasionally becomes trapped in deep basins.

During recent decades oxygen content of Baltic deep water has decreased (Fig. 1). This oxygen decrease has been accompanied by an increase in phosphate concentration. Heavy organic loads, causing reduced oxygen concentrations, have been reported from local fjords. Where oxygen is reduced to zero, hydrogen sulfide has appeared. Even in areas where no oxygen decrease is documented, thick sediment deposits from sewage pollution have affected the structure of benthic and fish communities.

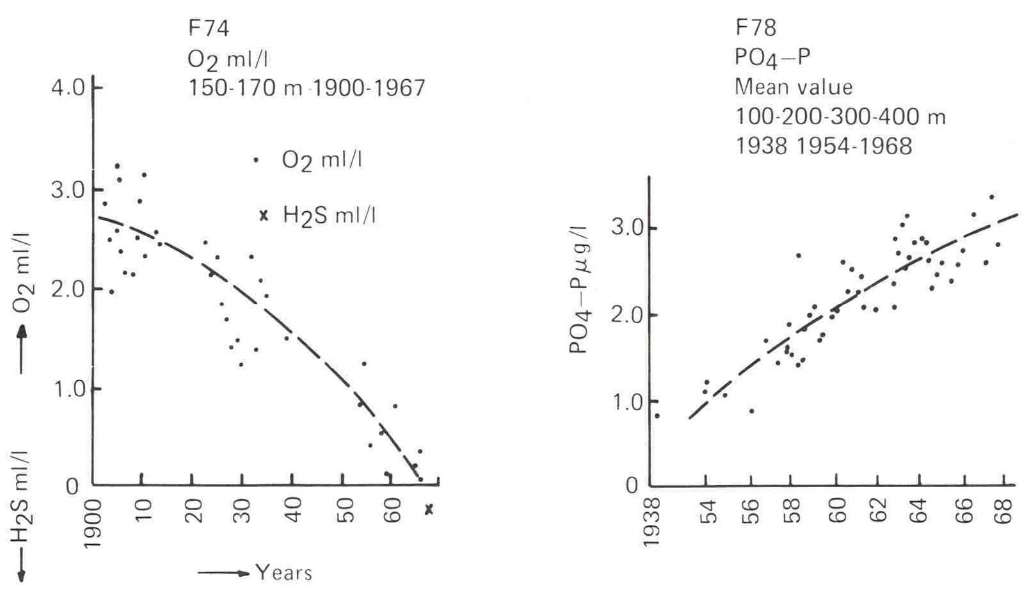

Figure 1. Oxygen and phosphorus in different deep parts of the Baltic (after Lundholm, 1970).

2.6 Kaneohe Bay, Hawaii

Kaneohe Bay on the northeastern coast of Oahu is a classic and well-documented example of urban eutrophication resulting from biostimulation. The bay is approximately 12.8 km long and 4.3 km wide. Its circulation is restricted by a barrier reef that separates most of the bay from the open ocean. The southern sector of the bay has the most limited circulation and is the location of a large municipal sewage treatment plant which adds an estimated 9.5×10^6 liters of secondarily treated sewage daily.

Added nutrients from the urban sewage and stream runoff from surrounding lands during heavy seasonal rains have increased the plant biomass and organic detritus, affecting the underwater light regime in a region once characterized by clear water. A 4½-year data set has been used to refine a planktonic ecosystem model describing the organic nitrogen budget at various nutrient input rates. A surprising feature of the bay system is the importance of regenerated nitrogen as the primary nutrient source maintaining the large plankton biomass and high rate of production.

The effects of nutrient enrichment have gone beyond bulk changes in phytoplankton population parameters. Although total zooplankton biomass has remained nearly constant, there has been a shift toward more microzooplankton organisms relative to larger forms. The abundant Hawaiian endemic fish, *Chaetodon miliaris*, became smaller in Kaneohe Bay than elsewhere and appeared to be reproductively inactive. The decrease in numbers of large zooplankton, the primary food of healthy fish, has been suggested as the chief cause of physiological stress.

Kaneohe Bay also provides the best-studied example of the effects of sewage on coral reef communities. The area was characterized by lush growth of many shallow water coral species before the introduction of sewage effluent. More than 99% of the corals in the southern basin of the bay are now dead, and living species transplanted there die within a few weeks. Mortality has been correlated with sewage-related variables such as turbidity and phosphate concentration, but it is believed that hydrogen sulfide released from anoxic sediments may be responsible. In addition, *Dictyosphaeria cavernosa*, a normally unimportant reef alga, has become the major benthic organism associated with increased sewage discharge. This alga spreads over and kills coral colonies by physically isolating them from light, oxygen, and food.

2.7 Aegean Sea

The effects of nutrient loading are documented for a region of the Aegean Sea at the northern apex of the Saronikos Gulf, Greece (Dugdale et al., 1970). The effects of nutrient addition are observed easily in the Saronikos Gulf since the background nutrient levels of the eastern

Mediterranean Sea are extremely low. A region of decreased transparency and increased primary production occur in a plume pattern as a result of a persistent cyclonic circulation pattern. The phytoplankton populations are composed primarily of diatoms and some dinoflagellates. The most deleterious effects of the outfall are reduced transparency, presence of floatables, and destruction of the benthos by the sludge field. The effects of restricted circulation are demonstrated in the adjacent Elefsis Bay, communicating with the Saronikos Gulf through two narrow passages with shallow sills. Elefsis Bay receives Keratsini effluent under some wind conditions and receives a mix of industrial and domestic sewage from a series of outfalls. Large populations, primarily dinoflagellates and some diatoms, occur along with a greatly reduced diversity in the zooplankton population. Summer stratification results in rapid deoxygenation of the water below the thermocline, and large fish kills now are reported annually. Hydrogen sulfide can be detected in the deeper waters during this period. The large industrial and domestic sewage outfall of Athens enters Keratsini Bay there.

2.8 Adriatic Sea

The Adriatic Sea is an oblong gulf of the Mediterranean situated between Italy and Yugoslavia, partitioned into northern, central, and southern basins. It is primarily the shallow northern basin in which eutrophication has become a problem. Pollution results from intensive urban, recreational, agricultural, and industrial development. Several heavily polluted rivers, the largest being the Po, discharge into the northern Adriatic basin. The Gulf of Muggia near Trieste is the recipient of effluents from a large complex of refineries and industrial plants. Dinoflagellate blooms along the Italian coast are adversely affecting the tourist industry as well as reducing the attractiveness of beaches for the local residents. Presumably the food chains are altered also by the dominance of dinoflagellates.

2.9 Oslo Fjord

The narrow Oslo Fjord is situated in the southeastern part of Norway and stretches 100 km from the island Ferder to Oslo, a city with a population of 500,000. The seaward portion of the fjord has a depth greater than 100 meters in most places, but the sill at Drøbak, 30 km south of Oslo, is only 19.5 m deep. Circulation and mixing within the inner fjord are seriously restricted by small amounts of fresh water inflow, small tidal amplitude, and marked stratification during summer months.

A considerable amount of wastewater is discharged directly or indirectly to the Oslo Fjord from industries, agriculture, and urban areas surrounding the fjord. The discharge from rivers and sewers amounts to 1.25 metric tons of phosphorus and 6 metric tons of nitrogen

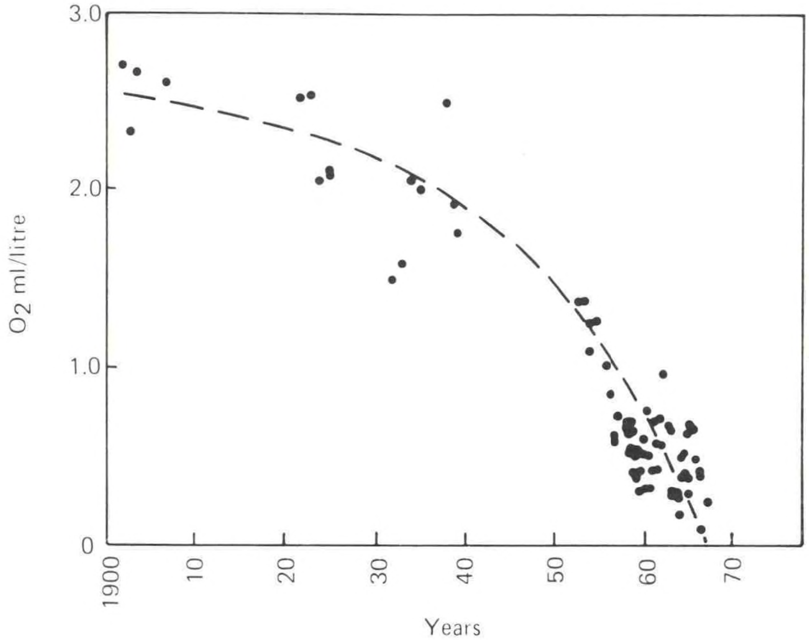

Figure 2. Mean values of O_2 (ml/litre) below the halocline in Landsort Deep 1902-67. (after Perkins, (1974)

per day into the inner fjord. Signs of pollution and increasing eutrophication due to slow exchange of water masses in the inner Oslo Fjord have been observed since the early 1930's. There are numerous indications that the undesirable effects of increasing pollution are caused by biostimulation.

The surface layers, down to about 10-m depth, are affected by a considerable increase of drifting and attached algae, which increase turbidity and often strongly discolor the water. The total organic load in the fjord is largely determined by the areas of concentrated algal growth in the surface layers. Oxygen consumption by sinking organic particles has left the deeper water masses oxygen-deficient and in some basins void of oxygen (Fig. 2).

2.10 Lake Washington

In 1933 Lake Washington was classified as oligotrophic, poorly nourished. As a result of the introduction of nutrients from sewage treatment plants the lake became eutrophic. In spring of 1963 standing stocks of phosphate and nitrate had increased by six times, and chlorophyll concentrations during summer blooms by ten times. In 1963 2.45

million cubic meters of secondary effluent entered the lake each day. Sewage effluent was diverted from the lake to the West Point outfall on Puget Sound beginning in 1963, and the diversion is now essentially complete. Although in 1963 oxygen in deep water had declined to only 60% of its 1933 value, it is clear that, had the effluent not been diverted, the bottom waters of the lake would have gone anoxic. Indeed, by 1957 oxygen concentrations at the bottom were approaching zero (Edmondson, 1972, 1977). Because Puget Sound is well mixed by tidal action there has been no evidence of eutrophication there from the diversion.

2.11 Lake Erie

Although most of the water entering Lake Erie comes from Lake Huron, which is distinctly oligotrophic, Lake Erie was showing signs of stress in the western basin in 1950. A combination of agricultural runoff and phosphate from human wastes and detergents caused the lake to change its character. In 1958, nearly 70% of the deepest water in the central basin was oxygen-deficient; blue-green algae replaced diatoms and green algae; mayflies whose larvae were the most valuable food for fish were replaced by worms, clams, snails, and midges that were more tolerant of low oxygen levels and higher organic matter concentrations. Salmonids were replaced with coarse fish starting in the 1920's as a result of both increased turbidity from soil erosion and increased and changed production from eutrophication. Although it has been recently decreed that cities bordering the Great Lakes may not use phosphate detergents, soil erosion and sewage effluents will continue to influence productivity (Burns and Ross, 1972; Larsen and Mercier, 1976).

2.12 Great South Bay and Moriches Bay, Long Island

In the 1950's, changes occurred in these two bays that eliminated a once-famous oyster industry of the region. Although the bays were obviously highly productive, a study showed that the phytoplankton were dominated by two species of coccoid green algae, Nannochloris atomus and Stichococcus sp. and not by the usual community of diatoms and flagellates that customarily occurred in other bays and estuaries of the Long Island region. It was determined that the unusual algae blooms resulted from the combined effects of enrichment of the bay waters from numerous duck farms located along their tributaries, and from reduced salinity and high summer temperatures due to reduced flushing of the bays. The green algae were found to be a poor food for the filter feeding oysters, which were completely replaced by other benthic organisms of no commercial value.

2.13 Omura Bay, Japan

Omura Bay is a constricted basin with weak tidal movement, an anoxic central basin, and nutrient-depleted surface waters. Blooms of the dinoflagellate Gymnodinium sp. cause red tides to occur there particularly in spring and early fall, often accompanied by mass mortalities of fishes. The spring blooms originate in the tributaries to the bay and apparently result from runoff from the surrounding agricultural land. The fall bloom, on the other hand, originates in the central portion of the bay and appears to be related to the onset of anoxic conditions in the deep waters of the basin. It has been postulated that nutrients, low pH, and perhaps sulfide associated with the anoxic bottom tides stimulate the production of the toxic dinoflagellates.

2.14 Hiroshima Bay, Japan

Hiroshima Bay and the adjacent region of the Inland Sea receive fresh water from three rivers and large amounts of industrial pollution and municipal raw sewage from three and four cities, respectively. Nutrient loads from these sources are responsible for colored water, so called Akashiwo in Japan, which is caused by blooms of flagellates and diatoms. The species composition of the bloom has changed significantly since 1956 and at present is predominantly flagellates (Rhodomonas lacustris, Heterosigma inlandica, and Hemieutreptia antiqua). Fishery resources in the region have been severely damaged by these blooms, especially by Hemieutreptia blooms, which are avoided by fish. Heavy rains, bringing high nutrient loads (250 mg N m^{-3} d^{-1}) from swollen rivers, combined with high temperatures and subsequent water column stability give rise to bloom conditions.

2.15 Tokyo Bay, Japan

Tokyo Bay is seriously polluted by municipal waste discharges. Hydrographic observations reveal two major gyres. One is composed of stagnant coastal water in the inner bay; the other is derived from ocean water and circulates counterclockwise in the middle of the bay before exiting on the western side. The most severely polluted waters are those of the inner bay. Eutrophication of Tokyo Bay results in frequent "red-tide" blooms of photosynthetic flagellates during summer. Observed red-tide organisms include Eutreptilla sp., Gyrodinium sp., and Exuviella sp. The formation of a bottom layer of oxygen-depleted water is attributed to these repeated red-tide episodes. The layer occurs in association with microbial decomposition of organic matter originating from, or provided by, red-tide organisms.

3. PRIORITY RESEARCH

A successful research program should lead to the formulation of general conclusions as well as to specific answers to regional problems. One of the most difficult general problems is to distinguish between natural events and human impacts on coastal ecosystems and to assess the magnitude of each. This task is difficult because of the complex interactions between biostimulants, toxic pollutants, food chains, and physical parameters.

For an understanding of these interactions, a combination of modeling and analysis and both field and laboratory studies is needed. The modeling activities should be used in formulating hypotheses, planning research, and analyzing data. Modeling may then continue throughout the life of the program in a support role. Field and laboratory studies should be used to determine and understand processes and interactions and to establish the quantitative data base of rates, reactions, functions, and interrelations needed for the subsequent refinements to numerical modeling efforts.

3.1 Modeling

One of the first modeling activities should be work with general, conceptual systems models for coastal and estuarine eutrophication based upon existing knowledge and available data. As warranted, conceptual models then may be used that either have been converted into a numerical model form or readily lend themselves to such conversion.

Variables and boundary conditions will differ from site to site, but the general models should be constructed to have wide applicability. As specific sites are selected, the general models should be applied to them. The conceptual models in the form of flow charts can be used to organize existing information and data and to identify data gaps. Simulations should be made using existing data to test assumptions; sensitivity analyses may then be used to reduce the number and kinds of experimental and observational studies. As the data set for each site or experimental procedure improves, the models may be altered and optimized.

The second phase of modeling should be the construction of applied engineering models on a regional, watershed, or coastal system basis, to provide system specifications in terms of inputs, outputs, and recycling of biostimulants.

3.2 Field and Laboratory Studies

Laboratory studies should be used to understand and quantify interactions among phytoplankton, biostimulants, and physical forcing functions, to provide model parameters, and to interpret field observations.

The field studies may provide physical oceanographic data and descriptive chemical and biological information such as biostimulant concentrations, species, and densities of organisms for each site. Field and laboratory studies should proceed concurrently, and both are necessary precursors to the ultimate numerical modeling efforts.

3.2.1 Physical process studies

Two types of physical process studies are required: studies of processes contributing to stability and multilayered flow, and studies of processes of advection and diffusion. The former are required because stability and layering direct the field of flow, limit organisms to particular depths, and act as barriers to mixing. Advection and diffusion studies are needed to estimate flushing rates and advective and circulation transports and to provide information on dilution rates and concentrations of nutrients and organisms.

Diffusion in the natural environment is affected by tidal and turbulent fluctuations in the mean flow field. Because of the spatially variable velocities, many with a tidal signature, it is necessary to sample on short spatial and temporal scales. In shallow water, bottom boundary layer problems and the alteration of apparent basin geometry with changing sea level are sometimes significant. The presence of features such as sills and natural phenomena such as storm surges, upwelling, and wind-induced effects are important. For these reasons maximum use should be made of historical data and analyses before site-specific studies are defined.

3.2.2 Chemical studies

Nutrient budgets and cycling

In the study of coastal or estuarine eutrophication, the elucidation of nutrient dynamics and the identification of the sources and sinks of these nutrients are essential. Through laboratory and field studies and through modeling, chemical budgets of important nutrients in selected areas should be derived as typical examples of coastal and estuarine habitats. Rates of chemical and biological transformations as well as the changes in concentrations should be included in these budgets.

Biostimulants, under the broadest classification, include not only the major nutrients, nitrogen, phosphorus, and silicon, but also certain trace metals that serve as integral components of electron transport systems and essential enzyme systems. A definitive identification must first be made of points of entry of biostimulants (natural and anthropogenic) and the transport mechanisms by which nutrients are lost from the system. Only then can the significance of anthropogenic eutrophication be assessed. Generally, the sources of nutrients in a coastal or estuarine system include exchange with open ocean water, terrestrial runoff, municipal input, benthic regeneration, and atmospheric fallout.

Nutrients are lost from the system through advection, incorporation into sediments, and to some degree, through air-sea exchange. (An example of the last process is the reduction of nitrate to nitrogen gas, subsequently lost to the atmosphere.) Once nutrient budgets are defined, and circulation and biological dynamics estimated, a general model may be developed to predict the symptomatic response of the system to increased anthropogenic stress.

Trace constituent studies

Several trace elements and organic compounds are known to be required for growth of phytoplankton. Some of these, including Fe, Mn, Zn, Cu, Mo, Co, and vitamins, have been studied under laboratory conditions, and in a few cases growth-limiting levels have been established for selected species of phytoplankton. Although the natural abundances of most trace constituents do not limit production, they may limit production where levels of major nutrients have been increased by human activities. Furthermore, very little is known about the processes by which these substances are incorporated into marine phytoplankton (Jenne and Luoma, 1977). It is possible that some trace-element/organic complexes are incorporated more easily than others and, thus, may have a significant effect on productivity. However, the creation of organic ligands generally decreases the bioavailability of trace metals in the short term and thus may stimulate or fail to stimulate phytoplankton growth, depending on both the absolute and relative concentrations of the metals and organic ligands.

Certain selected metal combinations may have synergistic or antagonistic effects on productivity. For example, colloidal iron oxides in natural water may provide a surface for adsorption of other trace metals. This could result in significant increases or decreases in productivity depending on the concentrations of the metals and on the ability of organisms to assimilate and disassociate the trace elements from the colloidal iron particles.

Our understanding of the critical relationships between trace elemtns and primary production is imperfect. Comprehensive laboratory and field experiments are needed to delineate the most significant processes involved in the uptake and release of trace elements by marine plankton.

3.2.3 Primary production

Enhanced primary production of organic matter in the pelagic zone is a principal result of eutrophication. In the absence of other limiting factors, total plant biomass increases rapidly in direct response to biostimulant input rates. The final yields of organic material and of the oxidative capacity of an area or ecosystem are critical indices of the overall condition of the environment. Important proposed studies of primary productivity include the following:

(1) Review and define the seasonal productivity characteristics of biostimulant-stressed marine areas compared with unstressed ones.

(2) Quantify the effects of circulation processes on phytoplankton bloom formation and dispersal, and on biostimulant concentration.

(3) Develop criteria to distinguish natural primary production perturbations from those changes attributable to anthropogenic biostimulation.

(4) Determine oxygen production and consumption rates by aquatic communities with and without anthropogenic inputs.

(5) Determine why estuarine and coastal systems are unable to adjust to "excess production," an inability that leads to anoxia.

The effects of eutrophication extend beyond excess production of organic matter. The structure and functions of biological communities can be significantly altered depending on the species of phytoplankton produced. Documentation of long-term community modifications and resulting ecological consequences is required. These relevant topics need to be considered:

(1) Seasonal composition and diversity of phytoplankton communities under natural conditions.

(2) Effects of biostimulation on phytoplankton community structure and functions.

(3) Ecological implications of induced changes in community structure and function such as alterations of production rate, yield of phytoplankton, sinking rate, size spectrum and nutritional value of organisms, or other characteristics that affect their availability to herbivore populations.

(4) Development of indices, suitable for monitoring community changes, that demonstrate progressing eutrophication and serve to identify potential problem areas.

An understanding of complex feedback mechanisms requires the use of spatially related time-series to investigate the relationship between physical phenomena and the behavior of plankton populations. Such interrelationships have been found in Chesapeake Bay and Narragansett Bay, for example. Spatially related time-series are also needed to study the rate of decay of biostimulants as a function of circulation regimes. Eastern and western boundary current regimes carry effluents parallel to coastlines, and the observed effects may be seen some distance away.

In addition to enhanced plankton production, changes in macroscopic algae and vascular plant abundance and distribution are seen in fresh and marine waters. These changes in production can alter food chains by decreasing food available for filter feeders and increasing food for detritus feeders.

Most studies are conducted on either laboratory or field scales. An intermediate scale approach is possible in which bodies of water are enclosed or confined. Although circulation features are altered and boundary conditions introduce complications, the effects of additions of biostimulants and pollutants can be studied under more controlled conditions with such experimental facilities than are possible in the field.

3.2.4 Secondary production

Zooplankton and benthic organisms are usually regarded as important components of ecosystems because of their considerable biomass, their role in supporting populations of economically valuable species, and their own edibility. However, from the point of view of ocean health and properly functioning ecosystems, their extremely important roles are less obvious. Two of the most important roles are the consumption of "excess" production, so that it does not immediately decay, and the recycling of nutrients. Generation times for zooplankton and larger benthic organisms are relatively long. These animals also are limited by factors other than available food. As a result, these higher trophic-level organisms cannot adjust their population sizes rapidly to accommodate changes in primary production and at some point are unable to cope with excessive amounts of food.

Most of the energy in food consumed by higher trophic levels is respired and most of the nutrients in consumed food are also excreted. Thus, instead of being totally locked up in large organisms, nutrients are made available over and over again. Research is needed to quantify recycling by higher trophic-level organisms. It is clear that certain ratios of one kind of organism to another are desirable. It may be that "nature's balance" is best, but since humans have already changed this balance in some systems, it would be wise to change it in a rational, knowledgeable way instead of haphazardly. Research should be directed toward determining the optimum ratios of organisms in systems affected by anthropogenic biostimulation.

3.2.5 Detritus

Not all suspended particulate matter in coastal systems is living. The nonliving component consists of sand and clay fragments, usually with an organic coating; dead plankton; fragments of dead organisms; and organic gels, all usually coated with a layer of microorganisms. Another large part of the nonliving organic matter in the ocean is that present as dissolved compounds, a reservoir that greatly exceeds the quantity of all other forms of organic matter in the sea. The origin, age, and fate of these nonliving components are assumed to be relevant to studies of biostimulant cycling. However, until recently the tools have not existed for a rigorous examination of the question whether aquatic systems are nourished by detritus or detritus constitutes an energy and nutrient drain that is not repaid in the form of harvestable organisms and a properly functioning system.

We need to characterize dissolved organic matter and detritus, in terms of chemical and physical composition, origin and fate, nutrient value and use, and functional roles in the nutrient budgets of aquatic systems. Sediment traps, deployed when circulation measurements are made, will provide material for characterization studies and measurements of the nutrient value of the particulates.

It is widely assumed that microbes attached to particles carry out significant nutrient remineralization and recycling activities, and that the microbes themselves are the most nutritious part of the particle for filter feeders. These assumptions need to be tested, particularly because, of all parts of marine ecosystems, we know the least concerning the behavior of microbial organisms in the recycling of nutrients (Pomeroy, 1974).

3.2.6 System oxygen demand

Under aerobic conditions, the organic matter fixed by the photosynthetic process forms the basic substrate for a series of biochemical reactions involving bacteria and higher trophic levels. If the oxidative potential of the organic matter formed exceeds the replenishment rate of oxygen, the system is subject to oxygen depletion with subsequent denitrification, hydrogen sulfide formation, and mass mortalities. Oxygen demand is routinely measured in the vicinity of sewage outfalls on the assumption that oxidizable matter in sewage constitutes the principal oxygen sink in the system. However, the decay of organic matter produced photosynthetically from nutrients in sewage constitutes the principal cause of anoxia in estuaries and populated coastal regions. Thus, calculations of biological oxygen demand must include organic matter produced in the system by photosynthesis, as well as organic matter derived from external sources. Analytical chemical and biochemical techniques coupled with circulation studies are needed to calculate the complete biological demand for oxygen. Such techniques could become an important monitoring tool.

4. MONITORING PROGRAM FORMULATION

4.1 Rationale

"Monitoring" has been frequently advocated but seldom conducted because the specific objectives were inadequately developed. A long-term commitment of money and effort for results of unknown usefulness is unacceptable. However, a consideration of biostimulation research leads inevitably to the suggestion of monitoring. The rationale is based on four requirements: the need for data on long-term trends and short-term variability, the need for an early warning system for crisis response, the need for early warning for research mobilization, and the need for time-series observations to improve our understanding of biostimulatory processes.

4.1.1 Long-term trends and short-term variability

Biological processes are notoriously "noisy." Imbedded in the noise are a variety of trends, all of which must be analyzed to allow us to differentiate between "normal" and "abnormal" events and to determine their frequencies. Time-series are difficult to justify in their early stages because their analysis leads to partial and inconclusive results. As the data base lengthens, many interesting trends and cycles unfold that reveal changes that can be "viewed with alarm," ignored, or exploited.

4.1.2 Early warning for crisis response

In the past we have been presented with "crises" which actually were a long time in developing but which appeared as sudden changes as the last stage was reached (e.g., the "death" of Lake Erie, anoxia in the New York Bight). If the proper parameters are chosen, the trends leading to the crisis could be assessed, an early warning given on an appropriate time scale, and possible corrective action taken.

4.1.3 Early warning for research mobilization

Most field efforts are scheduled years ahead, but ecological events cannot be scheduled. The scientist does not have advance information of when or where to make detailed or synoptic observations. The ideal field program would be a modest monitoring program that would keep track of events in order to mobilize, on very short notice, the field experimental stage during periods of particular interest. The monitoring program could detect, for example, a precipitous buildup of a population or decline of a chemical compound, signaling the need to mobilize more intense effort.

4.1.4 Improved understanding of the natural ecosystem

Successful monitoring, e.g., in the California Current and Los Angeles Bight, has delineated the normal, baseline ecological interactions, against which perturbations due to human intervention can be evaluated. Also monitoring data can be used to improve or validate models of ecological processes.

4.2 Implementation

Year-to-year changes in the timing of blooms, in bloom species, and in their fates must be documented in a few well-chosen coastal environments that are representative of a spectrum of environmental types. Three important areas must be understood in this regard: (1) physical circulation and water movement, (2) relative importance of diffuse and point inputs, and (3) the extent to which the environment was/is naturally enriched.

An understanding of the influence of point and diffuse inputs of inorganic and organic forms of nitrogen and phosphorus depends on the degree to which we can quantify these inputs in time and space relative to the natural variability of the system, and on how well we can evaluate the mechanisms that govern the pathways and rates by which different forms of nitrogen and phosphorus are processed by the system. Field experiments should be designed in the context of long-term monitoring programs to provide sufficient time and space resolution to detect long-term chronic effects as well as the effects of short-period events (e.g., storms, fish kills, presence of unusual predators). Experimental studies and modeling should be used to test specific hypotheses generated by these and previous observations and to direct subsequent field observations. Data collected from such monitoring programs could provide information for rational choices of methods for the disposal of anthropogenic biostimulants.

4.3 Techniques and Measurements

The design of any monitoring strategy should be tailored to the type of system under consideration, techniques currently available, funding, and knowledge of the system. Strategies to satisfy the four requirements of monitoring (Sec. 4.1) would include observations from both moored instrument arrays and ships in areas where problems are anticipated.

Moored instrument arrays should include current meters; salinity, temperature, and dissolved-oxygen sensors; and biological monitors such as fluorometers and in-situ particle counters. State-of-the-art biological monitoring systems can be added as they become available. The data obtained should provide information about circulation patterns, phytoplankton and zooplankton abundance and distribution, population size parameters, and trends in oxygen concentration. A few such moored arrays would provide continuous long-term data with minimum effort, as well as indicate where and when more detailed shipboard observations should be taken.

A number of measurements may be made on shipboard to aid in evaluating the physiological state of phytoplankton. Some of these are measurements of rate processes which cannot be measured from moored arrays.

4.3.1 Growth rate of populations

Some techniques, such as ^{14}C production measurements, are available for routine shipboard observations. Laboratory techniques, such as culture systems, could be developed for shipboard monitoring observations. Several innovations such as measurement of in vivo vs. dichloromethylurea (DCMU) fluorescence, and RNA/DNA ratio by microspectrofluorometry may aid in the assessment of specific growth rates, at least on a relative basis. The latter technique is relatively new and especially exciting since estimates of RNA, DNA, and size may be made on individual cells. Although it has not been applied to phytoplankton research so far, the technique's potential for extracting this valuable information from individual cells is great, and the information would provide a breakthrough in this field.

4.3.2 Species composition and nutrient concentrations

Detection of shifts in population composition (e.g., from diatoms to dinoflagellates) could be accomplished by microscopic counts and electronic particle sizing. Measurement of dissolved nutrient concentrations must be made by conventional techniques. The ratio of silicate to nitrate rises dramatically in a dinoflagellate-dominated system and could provide early warning of developing dinoflagellate blooms. On the other hand, a dinoflagellate-dominated system may be the result of a low Si:N ratio (which may be caused by sewage low in silicate but high in N and P).

4.3.3 Nutrient state of a phytoplankton population

The techniques available include ^{14}C and ^{15}N isotope measurements requiring some period of incubation after addition of the isotopes, and perturbation techniques in which a spike of one nutrient is added and the decline of that nutrient and other primary nutrients is observed. From the latter technique information can be derived to determine the identity and maximal uptake rate of the limiting nutrient and the potential for response to additional nutrient loading.

4.3.4 Loss rates

Phytoplankton blooms may be the result of decreasing losses due to herbivores, sinking, or advection even with no concurrent change in growth rate. Such losses are difficult to measure, especially since differential loss rates between various phytoplankton species may be highly significant in the development of blooms. Physical losses through advection could be assessed from the moored current-meter arrays, and techniques are available or under development for measuring loss from sinking. Techniques for measuring loss rates from grazing, especially size- or species-specific grazing, need more development before they can be directly applied to a monitoring strategy, although simple measurement of zooplankton concentrations would provide a first approximation. These developments could include measurements of fecal pellet production, gut content analysis of zooplankton, field measurements of digestive enzymes, and laboratory grazing experiments.

5. DEVELOPMENT OF OCEAN HEALTH INDICES

On the basis of nutrient input measurements and circulation studies made in a monitoring program, a first order approximation might be obtained of the assimilatory capacity of the system for biostimulants. Additional insight could be obtained by monitoring selected ocean health indices which are being developed on the basis of community composition changes or physiological functions of organisms that respond to the eutrophication process.

Laboratory and field research should provide information on the best physiological and other indicators for use as health indices. In general, the following should be considered as part of the strategy:

(1) Field observations to identify apparent cause-effect relationships, boundary conditions, and significant rate processes.

(2) Laboratory studies to validate the tentatively identified cause-effect relationships observed in the field.

(3) Parameterizing of time-series from existing field data.

(4) Testing initially chosen health indices under controlled conditions in the laboratory, semicontrolled conditions in simulated natural environments, and finally under actual field conditions.

(5) Including selected indices in proposed monitoring strategies.

(6) Instituting trial monitoring of promising health indices.

Many possible health indices have been suggested for use in evaluating the progress of eutrophication. Subtle indices include oxygen concentration, species diversity, total nitrogen or phosphorus, and carbon/nitrogen ratios. Gross indices include formation of algal mats and massive fish kills. It is therefore important to establish criteria by which these health indices might be evaluated for use in early warning surveillance programs. Four basic criteria for evaluating health indices have been suggested:

(1) Specificity. A health index should be able to distinguish between changes associated with increases in nutrient levels and those associated with other environmental changes either natural or anthropogenic.

(2) Sensitivity. A health index should have sufficient sensitivity to signal possible detrimental effects of biostimulation before significant damage has occurred.

(3) Ubiquity. A health index should be a property or biological characteristic common to most coastal environments.

(4) Ease of Measurement. A health index should be easy to measure and to interpret. It should be suitable for long-term monitoring in large-scale surveillance programs.

From a practical standpoint, few health indices, if any, will satisfy all the criteria described above. However, the criteria focus attention on what is needed and how to evaluate existing and future health indices. Although many existing chemical and biological indices are sensitive indicators of levels of nutrient enrichment, they are not entirely specific. For example, enriched nutrient levels can be related to seasonal patterns of upwelling and vertical mixing as well as human activities. Biological indices such as species diversity can be related to long-term cycles of animal migrations or seasonal reproductive patterns. More research is needed on the development of human-caused eutrophication and associated biological changes that are separate from natural variations before appropriate health indices with a higher degree of specificity can be identified and evaluated.

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FOSSIL FUEL COMPOUNDS

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1. INTRODUCTION

1.1 Problem Identification

Fossil fuel compounds are here defined as the following: (1) hydrocarbons and other organic compounds of petroleum; gas; coal and oil shale; products of coal and oil shale processing; products of petroleum, gas, and coal combustion; (2) organic compounds that result from chemical, photochemical, microbial, and other metabolic transformations of the preceding materials.

Because of the accelerated demand for energy in industrial societies during the past half century, pollution of the marine environment by fossil fuels and their reaction products has been increasing. Only recently has this form of marine pollution received popular and scientific attention.

Significant progress in determining the sources, fates, and effects of fossil fuel compounds in the marine environment has resulted from the decade of research from 1968 to 1978. Before 1968, investigations focused mainly on visible slicks, the aesthetic problem of tar on beaches, and the acute effects of oil spills on birds. By the early 1970's, as a result of several oil spill investigations, it was recognized that the lack of a visible slick did not mean that oil had been removed from the environment (NAS, 1975). After slicks had disappeared, measurable amounts of oil in water, biota, and sediments of coastal ecosystems could persist for periods ranging from days to years.

Fates and effects of spilled oil have been shown to be a function of the type of oil spilled, environmental conditions at the time of the spill (e.g., water temperature and wind speed), and the organisms or ecosystems involved. The time required for ecosystems to recover from the effects of spilled oil can vary from weeks to 5 to 10 years (Krebs and Burns, 1977; Southward and Southward, 1978; Sanders, 1978; Gilfillan and Vandermeulen, 1978). Thus, marine populations may be lost to human use for 5 to 10 years or longer. However, an ecosystem may recover from an oil spill without irretrievable loss of marine populations. Research on effects of fossil fuel compounds has changed from acute toxicity studies to the more difficult studies of chronic effects on whole ecosystems, using careful field observations and controlled ecosystem experiments (Mann and Clark, 1978; Lee and Anderson, 1977; Lee et al., 1977b). Biochemical research, including sophisticated analytical measurements and biological effects studies, has shown that minor components of petroleum (such as thiophenes and toluidines), some products of microbial and animal metabolism of oil compounds, and products of chemical and photochemical reactions, can have significant short- and long-term effects on organisms (Dowty et al., 1974). The implications of this cannot be overemphasized. Reactions that alter fossil fuel compounds to cleanse the environment of fossil fuel pollutants cannot be viewed as a panacea. The products of these reactions can be much more toxic than the original oil components.

To summarize, the key aspects of pollution by fossil fuel compounds have been identified, and in many instances significant progress has been made toward a better understanding of them. A large body of data has been accumulated that describes fossil fuel compounds in coastal and continental shelf ecosystems, and these data are now being, or can be, subjected to interpretation and evaluation. Thus, we are in a good position to formulate a research, development, and monitoring program.

Careful consideration of all possible sources of fossil fuel compounds and a few key measurements have led to the realization that oil spilled as a result of tanker and offshore drilling and production accidents represents only a small part of the total input of fossil fuel hydrocarbons to the marine environment. For example, sewage and industrial effluents, river and urban runoff, atmospheric rainout and fallout, and routine tanker operations have all been identified as real or potentially significant sources of such compounds.

Although petroleum consumption in the industralized world is predicted to decrease substantially between 1990 and 2010, use of coal and oil shale as energy sources and petrochemical feedstock is expected to increase for a century or more. Coal gasification and liquefaction, shale processing, transport, and combustion release many of the same fossil fuel compounds into the environment as do oil combustion, oil spills, and effluent discharge. Thus, preventing significant adverse impact on humans and the environment will require substantial knowledge of the biogeochemistry and effects of fossil fuel compounds and their reaction products. The following sections describe the main problems that must be investigated to obtain that knowledge.

1.2 Sources of Fossil Fuel Compounds

The data in Table 1 provide a summary of several estimates of worldwide petroleum sources and inputs to the marine environment. The totals range from about 2 to 11 million metric tons per year. The most accurate estimate is probably that by the National Academy of Sciences (NAS, 1975), 6.11 million metric tons per year. United States inputs into the marine environment amount to 1.51 million metric tons per year

Table 1. Listing of Estimated Petroleum Inputs to the Marine Environment (in million metric tons per annum)

SOURCE	SCEP	Jeffrey	Porricelli et al.	USCG	Brummage	Charter et al.	Duce and Quinn	Feuerstein	Storrs	Wilson	NAS	Grossling	Koons and Monaghan	Smith
Marine Operation Losses														
LOT tankers	0.03	0.10	-		0.25	0.26	-	-	-	-	0.31		-	1.00
Non-LOT tankers	0.50	0.60	-		0.75	0.46	-	-	-	-	0.77	0.41	-	
Bilges, Bunkering, and other normal ship operations (all ships)	0.50	0.05	-	1.72	0.50	0.61[a]	-	-	-	-	0.50		-	0.30
Offshore accidental discharges														
Tanker accidents	0.10		-		0.12	0.21	-	-	-	-	0.20	0.22	-	
Accidents, other ships		0.20	-		0.02	0.14	-	-	-	-	0.10	-	-	0.35
Pipeline accidents	-		-	-	-	-	-	-	-	-	-	<0.01	-	
Offshore oil production	0.10	0.15	-	0.12	0.10	0.12	-	-	-	0.08	0.08	<0.38	-	0.15
Natural marine oil seeps	-		-	-	-	-	-	-	-	0.2-6.0	0.60	0.24-7.00	0.60	0.60
Atmospheric deposition	(9.0)[b]	-	-	-	-	-	1.5	0.4-0.8	-	-	0.60	-	-	-
Land based discharges														
Refineries	0.30	0.30	-	-	0.30	0.20	-	-	-	-	0.20	<0.62[c]	-	
Terminal transfer operations	0.10[d]	-	-	e	0.01	0.03	-	-	-	-	0.25[f]		-	
Pipeline accidents	-	-	-	-		0.03	-	-	-	-	-	<0.01	-	
Runoff (urban and river)		-		-		-	-	-	-	-	1.90	-	-	1.30
Industrial wastes	0.45			1.98	0.50	0.72	-	-	0.08	-	0.30	1.64	-	
Automotive wastes		0.50	4.4	-		1.03	-	-	-	-	-	1.03	-	
Aviation wastes	-			-		-	-	-	-	-	-	0.05	-	
Municipal wastes	-			-		(11.8)[b,g]	-	-	0.20	-	0.30	-	-	
TOTAL	2.08	1.90	≤9.50	-	2.55	3.81	-	2.4-3.8	-	-	6.11	3.6-11.4	-	3.70

*Data from Van Vleet and Quinn (1978).
[a]Includes product tankers, ore and bulk-oil carriers, disposal prior to dry-docking, and tanker barges and bilges.
[b]Not included in total.
[c]Includes onshore oil production accidents.
[d]Includes all nonship accidental spills.
[e]Included in 1.72 million tons above.
[f]Includes dry-docking operational spills.
[g]Based on Philadelphia average of 0.0177 tons/(person*yr) extrapolated to a world population of 4 x 10^9 and corrected for 30% of total world oil usage by United States.

Table 2. Estimates of World and United States Inputs of Petroleum to the Marine Environment (in million metric tons per annum)

	1975 World[a]	1975 United States[b]	Early 1980's World[a]
Marine transportation/operations and offshore production	2.21	0.35	1.0
Atmospheric deposition	0.6	0.18	0.6
Natural seeps	0.6	0.12	0.6
Land-based discharges:			
River runoff	1.6	0.53	1.6
Urban runoff	0.3	0.10	0.3
Industrial wastes	0.3	0.10	0.15
Municipal wastes	0.3	0.10	0.3
Refineries	0.2	0.03	0.02
Subtotal	2.7	0.86	2.37
Total	6.11	1.51	4.57
Land-based discharges/Total	44%	57%	52%

[a]NAS (1975).

[b]J. W. Farrington (1975).

(Table 2); this means that 25% of the total marine pollution from petroleum is being contributed by about 5% of the world's population.

The sources can be grouped into five categories: (1) marine transportation/operations and offshore production; (2) atmospheric deposition; (3) natural seeps; (4) land-based discharges; (5) dumping. The first four are represented in Table 2.

1.2.1 Marine transportation/operations and offshore production

The values for pollution input from marine operations are estimated with relatively high confidence and are projected by NAS to decrease substantially in the early 1980's. Dissenting authors (McKenzie, 1978; Mostert, 1974) argue that although routine operations may become cleaner in the future because of rising oil prices, supertanker accidents will increase in frequency, raising the total quantity of spilled oil for some time. The number of tanker accidents occurring between 1976 and 1978 supports this view.

Oil spills resulting from tanker accidents near the coast and from offshore production well blowouts receive a great deal of attention from the media and Congress. In contrast, the routine, operational discharges from tankers, terminals, and production facilities receive much less attention although they represent a greater source of pollution (see Table 1).

1.2.2 Atmospheric deposition

Inputs from atmospheric deposition are estimated with low confidence, and quantity projections for the 1980's are the same as for 1975. In a recent paper, Duce (1978) focused on the confusion surrounding sources of organic matter, including hydrocarbons, and their reactivity in the troposphere and eventual deposition on land or sea. The primary sources of hydrocarbons in the atmosphere appear to be fossil fuel and wood combustion, crustal weathering, forest and grass fires, and vapor and particle emissions from vegetation. Only the first is anthropogenic, and in many instances the contributions from various sources cannot be distinguished.

1.2.3 Natural seeps

Even though seeps are found over most of the earth, they tend to cluster in particular areas such as the Gulf of Mexico and Santa Barbara channels. Petroleum from these sources is similar to that from acute spills or other discharges of crude oil, but its impact on communities near natural seep areas cannot be easily separated from that of other natural factors. The introduction of a large amount of petroleum (as in the Santa Barbara blowout of 1969) produces temporary effects but, because the community is already adapted to the presence of petroleum, the effects may endure for less time and appear less obvious than those from a similar discharge in a pristine area.

In their review of natural seeps, Wilson et al. (1974; see also NAS, 1975) included in the meaning of "oil seep" the recycling of sediment material such as shales rich in fossil hydrocarbons. Shale, when weathered, produces sediments with associated hydrocarbons that are transported to the marine environment by fluvial, and probably some eolian, processes.

Authors disagree about the actual magnitude of oil seepage. Wilson et al. (1974) estimated the magnitude of seeps on a global basis from the few actual seeps for which flow figures are available; however, Blumer (1972) did not agree with their estimates and concluded that the input from these sources was 100 times smaller. The seepage condition in the Gulf of Mexico must be among the best known in the world, yet several academic and oil company scientists disagree about the amount of seepage there. Only actual measurements of flow rates and types of material from known seeps can resolve these and other such conflicts.

1.2.4 Land-based discharges

The largest single input for both the United States and the world is from land-based discharges; these account for 44% of the estimated world total in 1975 (projected to be 52% in the early 80's) (Table 2) and 57% of the total for the United States. Inputs from industrial wastes, municipal effluents, and refineries are estimated with high confidence. Those from refineries are projected to decrease by a factor of ten in the early 1980's and those from industrial wastes should decrease by about 50%. River runoff is the major source of land-based discharges and together with urban runoff accounts for about 70% of these discharges. Both are estimated with only moderate confidence. The inputs from runoff are projected to be about the same in the early 1980's. Chronic petroleum inputs have only recently been studied in any detail, and more work is needed to assess their impact on the marine environment.

In the future, land-based discharge of fossil fuel compounds will include those associated with the transportation, processing, and burning of coal and shale as a petroleum substitute. Because of the large U.S. reserves of coal and shale, the amounts of their compounds discharged into U.S. estuaries, coastal waters, and the Great Lakes could be significant.

1.2.5 Dumping

A significant amount of fossil fuel compounds is introduced into coastal and continental margin areas by the dumping of harbor dredge spoils and sewage sludge. The 1976 NAS report states the following: "Dredge spoil is, by weight, the most significant class of material disposed of in the oceans....Control of polluted dredge spoil disposal is made difficult by the unavailability of adequate records of amounts and locations as well as imprecise specifications of which disposal operations are tabulated."

Thus, although amounts of fossil fuel compounds entering the marine environment by dumping of dredge spoils can be estimated, it is difficult to provide accurate numbers for more than a few dredge spoil disposal locations. Fossil fuel compounds in dredged sediments may originate from many sources including industrial and municipal effluents, storm drains, and direct atmospheric fallout and rainout. Furthermore, much dredge spoil disposal represents a redistribution of fossil fuel compounds already recorded in other inputs.

We should restate that some estimates of fossil fuel compound sources are based on a few measurements that used analytical techniques not sensitive enough to measure total hydrocarbons accurately to identify specific components. This is especially evident in studies on atmospheric input and river/urban runoff. More information is required if we are to determine the magnitude and detailed nature of these sources.

1.3 Transport Processes

Physical transport of fossil fuel pollutants can take many paths. The process is complicated by the number of chemically different compounds included. These compounds differ in volatility, solubility, and adsorptive properties, so that even in instances where structural transformation fails to occur, there can be chemical differentiation by partition into the atmosphere, surface microlayer, water column, suspended particulates, and sediment.

1.3.1 Box models

The mechanisms for physical transport of fossil fuel pollutants are conventionally represented by reservoirs of more or less uniform composition (boxes) and processes of transport between them (arrows). Figure 1 is a simple version of such a box diagram. Note that no chemical, spatial, or temporal variation is indicated. Other sources would have different, but qualitatively similar, representations. Such a conceptual model easily lends itself to representation as a set of coupled differential equations; if the contents of each box and the rates of transfer between boxes are known numerically, the dynamics of the system can be calculated, assuming steady-state conditions. Usually, however, all or several of the essential parameters are either missing or poorly known. Thus, this type of model may be a useful guide to planning research, but rarely a satisfactory tool for prediction.

When pollutants are studied on a global scale, box models are frequently used to discover whether sources or sinks are missing and to discover the possible fates of pollutants. For these purposes a box model provides a useful heuristic device. However, too close adherence to the uniform box and the assumption of first-order transfer routes between boxes can lead to false conclusions.

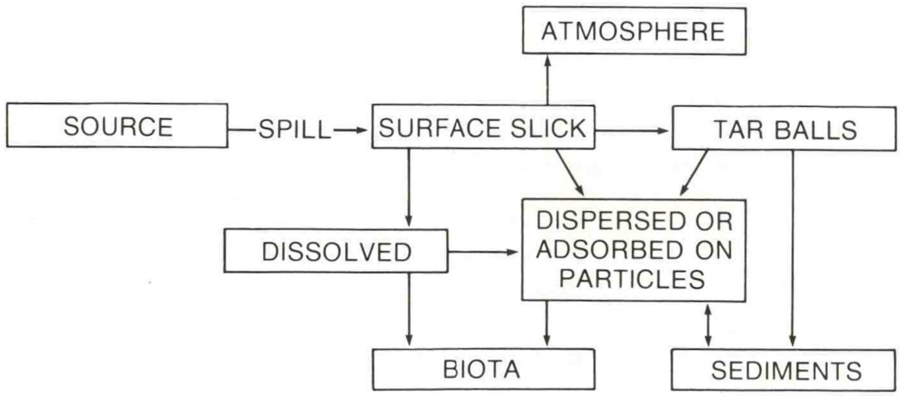

Figure 1. Simple box model of hydrocarbon transport after an oil spill.

Local transport phenomena are complex, and understanding them is often crucial. Examples include the tidal currents in estuaries, sediment transport in coastal waters by rivers, tides, and other currents, wind-driven transport of slicks and floating tar lumps, collection of surface slicks and floating material in downwelling convergences caused by mesoscale circulation, tropospheric transport and fallout, and biologically mediated transport. Examples of the last include benthic deposit feeders mixing different strata of sediment and zooplankton ingesting particulate material that contains hydrocarbon pollutants, followed by excretion of fecal pellets, larger and more coherent than the original particles, and the subsequent rapid sedimentation of these pellets.

Although several transport models have been developed for specific estuaries, they cannot easily be generalized. In addition, the models normally do not include sediment transport, a parameter that becomes increasingly important in studies of toxic industrial effluents that may be incorporated chronically into sediments.

Box models have limited usefulness in considerations of global transport processes because they do not include spatial and temporal characteristics. For example, large oil spills (such as the Amoco Cadiz) introduce into a small area, within a period of weeks, amounts of petroleum pollution (0.2×10^6 metric tons) that are comparable with the annual input from all municipal outfalls in the world (0.2 to 0.3×10^6 metric tons) (Van Vleet and Quinn, 1978).

1.3.2 Spills

The location of a spill, the weather conditions, and the type of oil all affect the subsequent transport and ultimate fate of the spilled oil. For example, oil from the Bravo blowout in the Ekofisk field of the North Sea dispersed rapidly because of its volatility and the violent weather conditions. In addition, the distance from land helped to prevent the fouling of shorelines. Bravo crude hydrocarbons that reached sediments and benthic organisms were low in concentration and relatively few compared with hydrocarbons from other natural and manufactured sources (Johnson et al., 1978). In contrast, the oil spills at West Falmouth in 1969 and in Chedabucto Bay, Nova Scotia, in 1970 occurred under conditions that led to the incorporation of large amounts of oil into coastal sediments. Biological damage resulted and residues of this oil persist today (Teal et al., 1978; Keizer et al., 1978).

1.3.3 Pelagic tar transport

The open ocean of the Sargasso Sea possesses a large standing stock of pelagic tar lumps that appear to be mostly crude oil sludge discharged during operational ballast procedures by tankers off the west coast of Africa. The large lumps found by neuston nets and the particles suspended in the top 100 m of the water column amount to several years' input. The standing stock as measured by neuston nets and beach tar surveys at the Bermuda Biological Station has not changed significantly from 1971 to 1978 (private communication, J. Butler). Thus, the increase in tanker traffic and acute spills seems to have been offset by greater care in ballast handling. Nevertheless, the ultimate fate of this pollutant remains unknown.

1.3.4 Sewage effluents

The areas of Narragansett Bay and Rhode Island Sound provide examples of the transport of fossil fuel hydrocarbons from sewage effluents to the estuarine environment (Van Vleet and Quinn, 1977; 1978). Hydrocarbons, associated with particles, are discharged in the sewage effluent and enter the Providence River. More than 95% of the hydrocarbons in the river are in suspended form, and sewage hydrocarbons account for 40% to 80% of them, on the basis of a flushing rate of 5 to 10 days for the river. Approximately 50% of the suspended hydrocarbons are deposited to the river sediments.

The remaining hydrocarbons are transported down the Narragansett Bay by tidal currents. The concentration of suspended hydrocarbons in the bay decreases with distance from the Providence River to the mouth of the bay and out to about 10 km south of Newport, R.I. These concentrations agree well with those predicted by a hydrodynamic model of the bay that uses the river as the only source of hydrocarbons. Suspended hydrocarbons in the water column eventually settle to the bottom, resulting in a decreasing concentration in sediments from the river to the sound.

1.4 Biological Transformations

Biological processes transform a variety of fossil fuel compounds in the ocean. We discuss separately those transformations that occur in water and those taking place in sediments.

1.4.1 Water

In the water, bacterioplankton, phytoplankton, and zooplankton can take up and metabolize hydrocarbons. Microbes, or bacterioplankton, capable of degrading hydrocarbons, have been isolated in both polluted and pristine waters and appear to be ubiquitous in seawater (Floodgate, 1972; Gunkel, 1973; Walker and Colwell, 1974). It has been demonstrated that input of oil results in large increases in the populations of petroleum-degrading microbes. These microbes attack the various slicks, emulsions, dispersions, and soluble oil components (Atlas and Bartha, 1973; Lee et al., 1978). Using a continuous growth chamber, Gibbs (1975) determined that the microbial degradation rate for Kuwait crude oil was 30 mg/l/year in water from the Irish Sea. Phytoplankton do not seem to metabolize petroleum hydrocarbons but can take up hydrocarbons that are subsequently carried to the sediments (Soto et al., 1975; Lee et al., 1978) or into herbivores.

Zooplankton, including protozoans and copepods, can take up droplets of oil that they then excrete unmodified in the feces (Andrews and Floodgate, 1974; Conover, 1971). For the Arrow oil spill it was estimated that up to 20% of the particulate oil was sedimented to the bottom in zooplankton feces (Conover, 1971). Copepods can also take up dissolved or dispersed hydrocarbons from food or water. The copepods possess enzyme systems that metabolize the hydrocarbons to various hydroxylated metabolites that are later excreted (Corner et al., 1976; Lee, 1975).

Fossil fuel compounds can enter fish through water or food. Uptake is primarily from the water through the gills, but some oil, including tar particles, is ingested. The latter process explains the presence of tar in the stomachs of fish collected in the Mediterranean Sea (Horn et al., 1970). Fish caught in waters near petrochemical industries often have a kerosene-like taint that results from uptake of volatile aromatic hydrocarbons from the water (Ogata and Miyake, 1973). Hydrocarbons that enter through food or water accumulate in the liver and gall bladder as hydrocarbons or metabolites (Lee et al., 1972; Roubal et al., 1977). Buildup of metabolites in the gall bladders of fish is of interest since mammals also excrete lipid-soluble foreign compounds in the bile. Hydrocarbons and their metabolites are discharged in urine or feces.

1.4.2 Sediments

The eventual sinks of the heavier components of petroleum are biodegradation, chemical reaction, and burial in the sediments. Long-term and short-term reactions can take place before, e.g., photochemical reactions or metabolism of 3,4 Benzo-a-pyrene. The degradation of petroleum hydrocarbon in aquatic sediments results from the interaction of microfauna, meiofauna, and macrofauna. In areas of petroleum input populations of hydrocarbon-degrading microbes are large, resulting in a rapid degradation of the alkanes and a slower attack on branched alkanes, cycloalkanes, and aromatic hydrocarbons (Blumer et al., 1973; Zobell, 1969; Walker et al., 1975; Mulkins-Phillips and Steward, 1974). The importance of microbes in degrading sediment hydrocarbons has been well documented whereas the role of benthic animals in the process has been recognized only recently (Gordon et al., 1978).

Many benthic meiofauna and macrofauna species are deposit feeders, important in the oxidation and recycling of sediment organic matter (Tenore et al., 1977). In undisturbed sediments, most microbial activity is restricted to the surface. The feeding processes of benthic animals, however, result in sediment turnover to depths as great as 15 cm (Rhoads, 1967), allowing microbes to degrade organic matter from deeper strata. Polychaete worms can take up hydrocarbons from the sediment. They have an active enzyme system in the lower portion of their intestine that metabolizes these compounds (Lee et al., 1977a, 1978). Certain species of polychaete worms (e.g., Capitella capitata, are associated with areas of high oil input (Reisch, 1971; Sanders et al., 1972).

Tidal flow causes resuspension of fine sediments with their associated hydrocarbons. These resuspended sediments can be taken in by benthic filter feeders, such as clams, mussels, and oysters (Lee, 1976). Bivalves appear to metabolize hydrocarbons slowly, if at all, but the discharge of hydrocarbons in the feces and pseudofeces allows attack by microfauna and meiofauna. Benthic decapods are able to metabolize petroleum hydrocarbons and subsequently excrete metabolites (Burns, 1976; Corner et al., 1973; Lee et al., 1976; Sanborn and Malins, 1977).

The metabolism of polycyclic aromatic hydrocarbons in animals involves hydroxylation and subsequent conjugation reactions, but no ring cleavage, so that the excreted products retain the aromatic ring. Bacteria, using aromatic hydrocarbons as a carbon source, carry out ring cleavage after hydroxylation with eventual degradation of hydrocarbons to carbon dioxide. Bacteria also completely degrade the hydrocarbon metabolites excreted by benthic animals. The metabolic processes are different in that bacteria produce cis-diols whereas animals degrade hydrocarbons to trans-diols. Arene oxides are the first intermediates in the oxidation of aromatic hydrocarbons in animals. Some arene oxides and other metabolites, such as phenols and diols, have necrotic, mutagenic, and carcinogenic properties (Brodie et al., 1971; Levin et al., 1976; Miyata et al., 1976).

1.5 Photochemical Transformations

When non-polar organics and related hydrocarbon residues are introduced into the marine environment, even in small quantities, some tend to accumulate at the air-water interface. Both paraffinic, especially cycloparaffinic, and aromatic hydrocarbons are common at the air-water interface of large bodies of water, and low concentrations may well be ubiquitous (Ledet and Laseter, 1974; Miget et al., 1974; Huang et al., 1978; Wade and Quinn, 1975; Duce et al., 1972).

During spills and chronic releases of petroleum and related types of hydrocarbon sources into the aquatic environment, most components spread into thin films at the air-sea interface. Among the various weathering processes of such materials are evaporation, microbial degradation, dissolution, and chemical and photochemical decomposition. Although marine microorganisms are capable of degrading many types of hydrocarbons, the decomposition rates under natural conditions are not well known (Floodgate, 1972). The photochemical oxidation of aromatic type hydrocarbons can be very rapid (Hansen, 1975; Burwood and Speers, 1974; Frankenfeld, 1973).

Weathering is assumed to reduce the toxicity of spilled oil since low-boiling toxic hydrocarbons (such as benzene) are lost by evaporation and some aromatic hydrocarbons are dissolved. However, laboratory evidence has shown that photooxidation processes, which may occur at the surface of oil films, can result in the formation, during such weathering processes, of water-soluble materials that can be toxic to algae, fish, and other marine animals (Larson et al., 1977). For example, recent reports (Lacaza and de Naide, 1976; Scheier and Gominger, 1976) indicate a marked increase in toxicity of the water soluble fraction after irradiation of crude oils. Similarly, a recent study (Gibson et al., 1978) reveals that irradiated mixtures of polycyclic aromatic hydrocarbons are mutagenic towards Salmonella typhimurium. Thus, photooxidation of petroleum hydrocarbons in the environment seems to increase the toxicity of petroleum and may present a threat to marine organisms and to humans consuming them.

Under simulated environmental conditions, individual compounds such as phenanthrene (which is typical of a class of polycyclic aromatic hydrocarbons common to petroleum, coal, and their respective products) can be converted into a variety of photooxidation products by sunlight. Products isolated so far include arene oxides, epoxy-dihydrodiols, phenols, and dihydrodiols, acids, and aldehydes. Nagata and Kondo (1977) have demonstrated that natural sunlight in the presence of molecular oxygen oxidizes polycyclic aromatic hydrocarbons, similar to phenanthrene, to toxic products. Some of these compounds have potentially necrotic, mutagenic, and/or carcinogenic effects on animal tissues (Brodie et al., 1971; Miyata et al., 1976; Levin et al., 1976).

Samples of spilled oil collected from the 1978 Amoco Cadiz incident along the Brittany coastline have revealed yet another photochemical transformation. In this instance the accumulation of dibenzothiophene oxide was noted (Calder et al., 1978), a significant observation since this compound is reported to be phytotoxic (Schlesinger, 1953). It is interesting to note that dibenzothiophene oxide is metabolized in a manner similar to that of the carcinogenic hydrocarbons (Bhargava et al., 1955). Oxygenated sulfide compounds are even more toxic than the parent sulfides (Arzamastsev and Shadurskii, 1976).

From the study of these model compounds one might predict other photochemical transformations of aromatic hydrocarbons in aquatic environments, but the nature, rate of production, accumulation, and biological properties of the oxidation products are not known.

1.6 Biological Effects

People are concerned about how pollution may affect their health and the quantity and quality of natural resources. Fossil fuel compounds have been identified as important pollutants, and during the past decade considerable effort has been devoted to studying their biological effects. Most research has been directed at the level of individual plant and animal organisms and communities of organisms. Despite their importance, studies at the ecosystem level have been limited because of their greater complexity in execution and interpretation. Research on the direct effects of fossil fuel compounds on humans has also been limited, mainly because the most important effects seem to be indirect. These effects manifest themselves through some alteration of the natural environment on which humans depend.

The most important determinants of biological effects of fossil fuel compounds appear to be the following. All must be considered when biological effects are investigated.

(1) Type of hydrocarbons. The toxicity of different hydrocarbon compounds is extremely variable. For example, low-boiling aromatics, such as naphthalene, are very toxic, whereas n-alkanes have low toxicity.

(2) Environmental conditions. Factors such as temperature, turbulence, wind speed, sediment composition, and sunlight control the availability of toxic materials to organisms.

(3) Biological factors. Species differ in their sensitivity to hydrocarbons, and the sensitivity of one species can change during its life cycle.

Definite biological effects have been observed as the result of both spills and chronic inputs. Effects are usually classified as acute or sublethal. Acute effects are rapid and usually result in death; sublethal effects take a long time to become apparent, perhaps several generations, and do not result directly in death.

Acute effects usually accompany the sudden release of a large amount of fossil fuel compounds into a restricted portion of the environment, i.e., conditions that produce toxic levels. The best examples are oil spills that have resulted in documented kills of seabirds (Bourne et al., 1967) and some intertidal animals (Sanders et al., 1972). Acute effects can also occur near the mouths of outfall pipes, if pollutant concentrations are high. The impacts of acute effects are easy to visualize. Either an important natural resource is killed outright (for example, soft shelled clams, see Dow and Hurst, 1975) or the natural food web is upset so that a commercial fish species loses an important food source and declines in abundance (Sanders, 1978).

Sublethal effects are more important but much more difficult to investigate and quantify. The effects of fossil fuel compounds on specific biological processes on which the survival of organisms depends usually are investigated under laboratory conditions. These biological processes include growth, respiration, reproduction, feeding, and locomotion. A variety of marine organisms have been investigated, including phytoplankton, zooplankton, benthic invertebrates, and fish (Johnson, 1977; Patton, 1977). In most instances, changes in these processes can be seen at petroleum concentration levels that occur in polluted environment. However, the data must be interpreted with caution, because of the problems associated with transferring the results of laboratory experiments to field situations.

At the individual level, impacts caused by sublethal effects include predation and starvation because the weakened animal is unable to escape prey or locate food (Johnson, 1977). The entire population of a species may be severely depressed for several years because of reproductive failures (Gilfillan and Vandermeulan, 1978). At the ecosystem level, the reduction in numbers of one species may alter the composition of the entire ecosystem; new species may become dominant and affect the abundance and nature of harvestable species (Sanders, 1978; Thomas, 1978).

One complicating factor in studying sublethal effects is the inherent variability of natural systems. Ecosystems and their components are constantly changing, even when unaffected by pollutants of any kind, and it is often difficult to determine whether an observed change in a polluted ecosystem is really the result of pollution (Mann and Clark, 1978). Knowledge of the structure, functioning, and variability of natural, unpolluted ecosystems is an essential precursor to understanding the sublethal effects of any pollutant.

The use of control and fossil-fuel-treated enclosures should help determine the sublethal effects of fossil fuel compounds on marine ecosystems. The CEPEX and MERL (University of Rhode Island) projects have determined that changes in the population structure of pelagic and benthic systems have occurred as results of petroleum addition.

The research of the past decade has also shown that the most important biological effects of petroleum hydrocarbons have been experienced by the benthic ecosystems. Lasting damage to pelagic organisms has been difficult to demonstrate conclusively because of the organisms high mobility and variability. The rapid dilution of pollutants, together with the motility and rapid growth rates of pelagic organisms, tends to protect them. In contrast, petroleum hydrocarbons incorporated into sediments are localized, not rapidly diluted, and may last for years. Since some benthic animals are not motile, they cannot escape damage.

2. PRIORITY RESEARCH

2.1 Sources

Determination of the various sources of fossil fuel compounds is essential to describe the present distribution of these compounds in the marine environment more accurately and to predict future inputs from the projected use of coal and oil shale. These sources are discussed in the following sections.

2.1.1 Marine transportation/operations and offshore production

Prevention of pollution by petroleum is preferable by far to any cleanup measures of research on the fate of spilled oil. Because the marine environment (even with the 200-mile limit) is only partly in territorial waters of the United States, any attempt at pollution prevention and control must involve multilateral action by all maritime nations of the world. Such action has been initiated by the Intergovernmental Maritime Consultative Organization (IMCO) and is incorporated in the Law of the Sea negotiations. The regulatory measures required, such as enforcement of maintenance and operation standards, frequent safety inspections, and penalties for violations, are beyond the scope of this report. We recommend detailed, worldwide reporting of oil input from large and small spills and operational discharges to provide accurate data and insights that may lead to more efficient monitoring of petroleum in the marine environment.

Continued support should be given to the program for studying "spills of opportunity" (e.g., *Argo Merchant*, *Bravo*, *Amoco Cadiz*). including both field work and analysis of the results from past spills. Emphasis should be placed on developing quantitative models to describe empirical observations and predict transport and fate of oil in the open ocean and coastal environments, especially from routine operations such as discharge of tankers.

2.1.2 Atmospheric deposition

We recommend studying the role of the atmosphere in transporting hydrocarbons, especially aromatics, through the environment. This is especially important because coal use is projected to increase. The primary sources of atmospheric hydrocarbons appear to be fossil fuel combustion, crustal weathering, forest and grass fires, and vapor and particle emissions from vegetation. Estimates of these inputs are based on few observations and have considerable uncertainty associated with them. Analyses of cores from lakes and near-shore marine depositional environments show an increase in aromatic hydrocarbon concentration between factors of 3 and 10 since about 1900 (Hites et al., 1977; Müller et al., 1977). The primary source of these compounds appears to be combustion, particularly of coal, with transport to the oceans via the atmosphere, or by remobilization of soil or river sediment and fluvial transport to the marine environment.

2.1.3 Natural seeps

The NAS estimate of natural seeps (NAS, 1975) seems to be accepted despite the paucity of substantial data. To distinguish natural from human-induced inputs in seep areas, we recommend research on seepage locations and rates, chemical composition of seep material, and fate of seep material.

2.1.4 Land-based discharges

We recommend studies of the contribution to marine pollution of land-based discharges of fossil fuel compounds. Such discharges are a significant source of fossil fuel compounds in the near-shore marine environment and, with the increased use of coal and oil shale, will continue to be so during the early 1980's. These discharges include river and urban runoff, industrial and municipal wastes, and refinery discharges. They result in chronic, low-level exposures of hydrocarbons, in contrast to spill situations that produce acute exposures.

2.1.5 Dumping

Additional studies of specific dumping sites, such as the New York Bight area, should be conducted to provide information on the fluxes and composition of fossil fuel compounds associated with dredge and sewage sludge inputs.

2.2 Transport Processes

Reliable measurements of fossil fuel compounds should be made for box models, which represent a preliminary stage in the development of more complex and realistic models and provide a structure on which to base a coherent research program. These measurements should be a function of time and space in the various reservoirs of the marine environment, including the following: atmosphere (vapor phase, particulate, dry fallout, rainout), sea surface, water column (dissolved, particulate, colloidally dispersed, adsorbed on other organic or inorganic particles, biota, especially plankton), and sediments (sediment-water exchange, redistribution of contaminated sediment particles, influence of bottom current regimes).

Because of the expense in time, effort, and money the measurements should be limited to a few locations that can be observed in detail during a long time period (5 years or more) to allow for observation of seasonal variations, as well as long-term trends. The choices for study sites should be influenced by such considerations as their validity as models for critical environmental areas, previous data based on hydrology and related subjects, and ease of access.

The rates of transport then can be measured at the same location for the same chemical types of material as were determined in the various reservoirs. Such transportation processes include the following: evaporation, dispersion, dissolution, slick spreading, direct or biologically mediated sedimentation, adsorption on pre-existing particles, and movement of submarine hydrocarbon-bearing sediments. (These sediments may result from erosion of submarine outcrops containing fossil fuel compounds, natural seep formations, sludge dumping, or coastal effluents.)

Study and model construction will be facilitated if the investigation location has few external inputs. Priority may be given, however, to more difficult systems (such as the mouth of a large river with urban development) because their environmental quality is of greater social value.

2.3 Biological Transformations

Research is recommended to determine the rates of microbial degradation of the various classes of fossil fuel compounds. If conducted under field or simulated field conditions, these investigations can evaluate the importance of this process to the final fate of the different components of fossil fuels. Various animals that can metabolize hydrocarbons and bioturbate the sediments (a process that allows an increase in microbial activity) need to be studied and evaluated. While the toxic components of fossil fuel compounds are being investigated, persistence of these components must be measured by determining their biological degradation rates.

So-called detoxification pathways serve to metabolize many foreign organic compounds in animals. The mixed function oxygenase system, which forms arene oxides, phenols, and diols, is responsible for the initial oxidation of these compounds. The presence of this system has been demonstrated in marine fish, crabs, and worms. Exposure of fish to petroleum products, either in the field or laboratory, results in an increase in mixed-function oxygenase activity in the liver, the function of which is to increase the water solubility of the parent compound. This facilitates the excretion of the compounds from the animals. Studies of the kinetics and characterization of the enzyme systems in marine animals will increase understanding of the ability of the marine ecosystem to assimilate fossil fuel compounds without impairment to its integrity.

One aspect of the metabolism of aromatic hydrocarbons is the formation of arene oxides. In mammals some of the arene oxides have been shown to be carcinogenic or mutagenic. The toxic, mutagenic, or carcinogenic properties of these arene oxides and other metabolities in marine animals require further investigation.

2.4 Photochemical Transformations

A series of controlled laboratory experiments should be carried out to help understand photochemical processes. These experiments must simulate actual environmental conditions and utilize both individual and complex mixtures of photosensitive hydrocarbons. They should lead to the development of monitoring techniques to be used in the actual aquatic environment.

The exact nature and rate of formation of most of the complex series of oxygenated products can be obtained by conventional chromatographic methods. Once preliminary chemical characterization has been completed, absolute conformation can be established by direct synthesis. The resulting synthesized products can then be used to study the formation and accumulation of the photo-products in aquatic experiments. Such compounds would become available for testing the toxic properties on aquatic species, tissue cultures, and other bio-assay systems. In addition, it would be valuable to establish the persistence of the more toxic chemical species under typical environmental conditions.

Many photooxidation products are similar or identical to those from biological oxidation processes. The proposed program would make available standards for testing as intermediates and thereby provide a mechanism for achieving an understanding of the biological steps involved in degradation of aromatics by aquatic organisms.

Specific "marker" molecules are necessary to trace complex hydrocarbon mixtures introduced into the environment. After hydrocarbons are released into the environment, a portion rapidly becomes modified into products that no longer resemble the parent hydrocarbons. Some of the chemical transformations resulting from the program may yield useful marker substances.

Accurate and precise methods must be validated to isolate and characterize the chemicals to be monitored in the aquatic environment. Although adequate methods already exist in some instances, new method development should be encouraged for others, particularly the more labile of the oxygen-containing aromatic products.

2.5 Biological Effects

2.5.1 Emphasis on long-term studies of sublethal effects

We recommend long-term interdisciplinary investigations of the sublethal effects of pollution. Short-term, acute investigations are of limited value and should be de-emphasized. More valuable information will be obtained by concentrating effort on long-term studies of sublethal effects. These investigations are more costly and complicated, and require a team approach, using biologists, chemists, physiologists, and biochemists. Attention must be given to the exposure of organisms to chronic and acute inputs and to the organisms' subsequent recovery.

Because of the longer residence time of fossil fuel compounds in sediments than in water (with the possible exception of the open ocean environment where sediment concentrations are very low), benthic organisms are subjected to greater exposure than pelagic organisms. Therefore, they are much more likely to be harmed.

For practical reasons, a limited number of representative fossil fuel compounds should be selected for detailed investigations of their persistence in sediments, availability, and potential toxicity. Attention should also be given to the biological effects of metabolic intermediates, which can be more toxic than the parent compound.

2.5.2 More realistic experimental design

We recommend that the investigations in this program utilize both field and laboratory experiments. Both have their place in the total research program, and they should be conducted simultaneously. Whenever possible, experiments should be performed in the field, under controlled conditions (for example, CEPEX- or MERL-type approach). Laboratory investigations must be conducted under realistic conditions.

2.5.3 Indices of effects

Research into the sublethal effects of pollution should consider three levels of the biota: the individual organism, the population, and, above all, the total community. At the organism level, more attention should be given to the sublethal effects of fossil fuel compounds on behavior, histopathology, and biochemical processes. Further investigation of the sublethal effects of fossil fuel components on larval stages (believed to be especially sensitive) is also needed. At the population level, possible genetic effects demand consideration; at the community or ecosystem level greater attention should be given to the effects on community structure and productivity. More information is also needed on possible food web transfer of fossil fuel compounds, the recovery times of communities exposed to spills or chronic inputs that are terminated, and the capacity of an ecosystem to assimilate toxic hydrocarbons without demonstrating deleterious effects.

2.5.4 Emphasis on ecosystem level

We recommend that research efforts be expanded at the ecosystem level. To date, research on total communities is much more convincing than research on specific organisms. By shifting emphasis to the total community, the variability of individual organisms and populations can be evened out, and the properties of the total system can be seen changing in meaningful and unequivocal ways.

2.5.5 Synergistic effects

Fossil fuel compounds must be studied in their synergistic relations to other pollutants. Investigations, especially those dealing with chronic inputs, must take into account the presence and interaction of pollutants, such as heavy metals and chlorinated hydrocarbons.

2.5.6 Comparison of climatic differences

The importance of climatic differences in different ecosystem types should be examined. One key parameter is temperature, which is known to have a pronounced effect on the persistence of fossil fuel compounds introduced into the environment. Such studies will demonstrate the relative sensitivity of tropical, temperate, and arctic ecosystems.

2.5.7 Need for basic environmental data

We recommend studies of non-polluted natural systems to precede and to provide a basis for investigations of the effects of specific pollutants. Natural systems unaffected by pollutants are inherently variable at all levels. Studies of these systems should be long-term and should consider the variability of individuals, populations, and ecosystems, as well as non-biotic environmental parameters. They would be time-consuming and costly yet necessary if the results of pollutant-specific studies are to be interpreted accurately.

2.5.8 Oil seep investigations

We recommend further research on the biological impact of selected oil seeps. It is important to know whether ecosystems have adapted to chronic oil exposure and if so by what mechanisms. However, since seeps contain only naturally produced hydrocarbons (i.e., produced during oil and gas formation), findings must be applied cautiously to situations involving refined petroleum products, which differ greatly in chemical composition from naturally produced hydrocarbons.

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BIOLOGICAL EFFECTS - A GENERIC VIEW

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1. INTRODUCTION

1.1 Statement of Problem

Our society's concerns with ocean pollution are centered about ourselves. Starting from public health worries about disease transmission from inadequately treated sewage, these concerns have grown to include pollution effects on the marine resources we value. Pollution jeopardizes what resources we can get from the ocean, what services the ocean can or does perform for us, how we can enjoy the ocean, and even how we feel about the ocean.

The exploitation of marine resources has been an important factor in the development of the United States. It is not by accident that so many of this country's largest cities are located in the coastal zone. With careful management the oceans can continue to supply us with fish, shellfish, other food or natural products, petroleum, and minerals. But pollution and inadequate care in preventing potential conflicts among competing resource uses can jeopardize our renewable marine resources and disrupt human societies.

We care about the potential effects of ocean pollution on life. We need to understand these effects so that we may prevent or control them, thus preserving the values inherent in the oceans.

Most properties of the living systems we wish to protect, though we may closely associate them with a particular species, a certain fish or seaweed, depend on the integrity of the ecosystem of which that species is a part. In some instances this dependency is obvious; a commercially valuable shellfish cannot exist if its food source, the phytoplankton, is not available. But many interrelations among animals, plants, and their ocean environment are not obvious. If any part of a system is damaged or destroyed by pollution then the entire system may not perform the service expected.

1.2 Public and Environmental Health

We do not want to be poisoned directly or sickened by ocean pollution. Swimming in polluted waters is dangerous, as is eating fish or shellfish that have accumulated substantial amounts of oil or cadmium. Shellfish can filter and accumulate pathogens from polluted waters, transmitting disease to people who eat them. Pollutants can also be toxic to the marine animals and plants themselves, killing them or disrupting the ecosystem on which they depend. If low levels of pollutants kill fiddler crabs, which are an important food of clapper rails, fewer rails will be available for rail hunters, even though the rails are not harmed directly by the pollutants.

1.3 Renewable Products

Sea fish are one of the world's essential protein sources. The world annual catch of fish is 70 million tons, and 85% comes from the sea (United Nations, 1977). Shellfish are a luxury seafood but can become considerably more available through aquaculture. Algae are used both as food and as a source of chemicals used in foods and other products, including cosmetics, pharmaceuticals, and fertilizers.

Oceans may also contain resources unknown to us. For instance, species of fishes not now commercially important may become so in the future. In addition, chemical resources in marine organisms may yet be undiscovered. Who would have predicted a few years ago that the blood of the horseshoe crab, *Limulus*, would become valuable for diagnosing human disease?

1.4 Economics

Marine food resources are evaluated by the amount of protein they provide and by their monetary and employment value. In 1970 United States fisheries were worth some $500 million to the fishermen themselves (Ketchum, 1972). Socioeconomic values extend even further. The money spent by fishermen provides work for many other people because of the familiar multiplier effect of economists, and fisheries support a way of life in coastal communities.

1.5 Recreation

Recreational uses of the oceans range from sport fishing, through swimming and boating, to the aesthetic pleasures of observation. Sport fishing is a significant part of the total fishing industry, accounting for 20% of the cod and 90% of the mackerel taken in the United States in 1977.

Recreation accounts for the expenditure of perhaps $10 billion per year in U.S. coastal areas. It also supports industries that supply equipment for recreational activities. Even the noneconomic aspects of marine recreational activities can be significant, as witnessed by the Marine Mammal Protection Act and the Endangered Species Act. Much popular support for such laws comes from aesthetic appreciation of ecosystems with all their component parts.

1.6 Mineral Resources

Use of ocean minerals has been limited by our fear of possible pollution during mining, and in some instances, because we want unpolluted minerals, such as clean sand or gravel. If we understand better the consequences of putting various kinds and amounts of pollutants into marine ecosystems, we are better prepared to regulate mining or drilling to prevent pollution from it and to preserve the quality of ocean minerals.

1.7 Life Support

We must consider the value of the oceans, the planet's largest environment, in generally supporting life. Though some aspects of life support may not be seriously affected by ocean pollution (e.g., the way in which water movements moderate climates), many others probably will be. Oceans and their biota play a role in the cycles of biologically essential elements such as carbon, sulphur, nitrogen, and oxygen. For example, coastal areas can be especially important in assimilating sewage effluents. Pollution can damage this ability and detrimentally affect health, economy, and aesthetic attractiveness of coastal areas.

1.8 Acute and Subacute Effects of Pollution

Contamination of the marine environment by human activities has two general biological effects on people and/or on marine organisms: acute or very obvious effects, and subacute or more subtle effects. A well-known instance of acute effects from marine pollution, which had extensive public health implications, was the mercury contamination in Minamata Bay, Japan, in the 1950's. Thousands of persons who consumed mercury-laden fish and shellfish died or suffered permanent injuries. Hepatitis epidemics have resulted from consumption of shellfish contaminated with sewage-derived viruses. Acute effects of pollution on marine organisms have included extensive mortalities of clams, crabs, and sea birds, caused by oil spills. Point-source pollution of natural waters with acutely toxic substances, such as endrin, has also resulted in massive mortalities of fish (Mound, 1962).

The subacute, long-term biological effects of pollution are much more common and potentially more devastating than acute effects. The relationships between long-term effects and specific pollutants are difficult to establish; thus, extensive numbers of marine organisms may be contaminated, and pathological conditions may develop before the need for corrective action is known. If biological effects occur significantly more frequently in newly polluted areas than in the same areas before pollution or in unpolluted control areas, then the effects are suspected to be subacute effects of the pollution. But it is also necessary to show that these biological effects do not result from natural causes independent of human activities.

Some subacute effects have been well documented for individual marine organisms as well as for marine ecosystems and communities. Flatfishes, an important food, inhabit waters polluted by urban areas, such as the New York Bight, the Southern California Bight, and the Duwamish River estuary in Seattle, Wash. As many as 30% of the individuals of some species in these areas have fin erosion disease, a condition that reduces their commercial value and perhaps their abundance. Another condition of flatfish associated with urban/industrial pollution is liver tumors (frequency of 30%) in English sole (Parophrys vetulus) of the Duwamish estuary. These tumors are alarming because humans may be exposed to the same carcinogens as the fish. Another example of a subacute pollutant effect was the reproductive failure of the brown pelican (Pelecanus occidentalis) and other sea birds from the Southern California Bight area caused by DDT discharges from a sewage outfall during the 1960's. Correction of the DDT contamination has resulted in a slow recovery in the numbers of these birds.

Subacute effects on ecosystems are more difficult to document. Pertinent examples have been reported of marine benthic communities that have been drastically modified in abundance and variety of species by sewage effluents and sludge (e.g., Smith and Greene, 1976) or pulp and paper mill wastes (e.g., Pearson and Rosenberg, 1976). Also, major changes of species composition in phytoplankton in the North Sea have recently occurred in conjunction with increases in pollutant levels. Some ramifications of such phytoplankton changes have been demonstrated in the Controlled Ecosystem Population Experiments (CEPEX). When the artificial ecosystems of CEPEX were contaminated with copper or mercury, phytoplankton species that supported the food chain leading to fishes disappeared and were replaced by species that supported commercially worthless, gelatinous zooplankton (Menzel, 1977).

2. KINDS OF EFFECTS

Although we know that human activity can pollute the oceans, we do not know the present or future extent of this pollution or its effect on the health of the oceans. Although some obvious effects can have severe consequences for mankind, the subtle, long-term effects on marine systems deserve careful attention, because the cause-and-effect relationships are so difficult to establish.

Knowledge of the basic physiology and biochemistry of marine organisms and of toxic effects that pollutants have on these organisms is limited. In fact, we know only slightly more about pollutants than their lethal doses. To appreciate the potential importance of pollutants, we can describe the general effects that are possible in the marine environment.

Pollutants, whether hydrocarbons, metals, or radionuclides, can make their way into marine organisms, where they may reside in tissues at varied concentration for varied lengths of time, depending on the pollutant, the species, the individual, and environmental factors. Although many organisms can cleanse themselves of pollutants under proper circumstances, the effects within organisms between uptake and possible discharge are of concern.

The normal functioning of marine animals' organ systems such as assimilative, digestive, nervous, sensory, osmoregulatory, excretory, respiratory, reproductive, and other metabolic processes may be disrupted by pollutants. Metabolic or physiological processes in marine bacteria, phytoplankton, and macroalgae may also be influenced by pollutants. In many instances disturbance of metabolic processes will be accompanied by lesions and other histological changes that may be pathologic. The incidence of infectious and parasitic disease may also be influenced by pollutants, in some instances by damage to host defenses.

Marine pollutants can cause several types of genetic effects. Either the catastrophic elimination of some members of a population or reduction of competitive ability that results from chronic exposure can alter the composition of the gene pool of a population. In individuals, mutagenic, teratogenic, and carcinogenic effects may result. These effects can be related to the metabolic activation of some pollutants, e.g., certain polynuclear aromatic hydrocarbons in hepatic and extrahepatic tissues, although further metabolism may detoxify these bioactivated compounds. Metabolism can also convert some heavy metals to alkylated derivatives, highly toxic to other organisms (Jensen and Jerlöv, 1969).

Behavioral responses to pollutants may include responses of chemosensory and central nervous systems. As a result, changes may occur in the biota's feeding patterns, survival tactics, or mating patterns.

Reproductive success and unaltered productivity are important aspects of a species' survival and utility. Both may be affected directly by the influence of pollutants on early developmental stages. Effects on systems might also affect reproduction, by depriving an organism of energy necessary for gamete production, for example, or by interfering with the processes of gametogenesis or mating.

Although the possible pollutant effects discussed above are conjectural, there is substantial evidence that effects may be extensive. For example, a successful salmon fishery developed in Lake Michigan in the early 1960's. Adult salmon, lake trout, and bloater chubs were found to contain concentrations of DDT, dieldrin, and PCB's that all averaged above the FDA tolerance levels. This stopped the development of an industry using spawning salmon for human and pet food, and the interstate shipment of chubs was banned, with the loss of millions of dollars to the industry. In Lake Ontario fish were found to contain mirex, an insecticide used to control fire ants in the southeastern United States. The insecticide entered the lake from the Niagara River, which had been contaminated by a plant that produced mirex. The concentrations of mirex in the fish were above the FDA tolerance level, and commercial fishing on the lake was stopped.

Our information on extent of pollution effects is based on laboratory and field studies; however, it is inadequate to support even the simplest comment about the impact of marine pollution, particularly low-level contamination. The bulk of toxicologic data obtained for marine organisms is unsuitable for quantitative comparison because of normal variability within species and populations, seasonal and sexual differences, differences in experimental design and conditions, and differences in toxicants, species, and physiological parameters.

An adequate toxicologic assessment involving one marine species and the plethora of pollutants is a formidable task, especially when the effects may appear only in succeeding generations. It is necessary to consider a great diversity of species and all their interactions in even the simplest marine community; such a task is monumental. To understand the effects of pollution on the oceans, both the individual and synergistic effects of pollutants on each species and on the full community in an ecosystem must be studied experimentally.

Although acute effects of one of another pollutant may be specified with precision, the potential synergistic effects of interacting pollutants or of pollutants acting in concert with pathogens are numberless. When one pollutant is added to another, will the second pollutant add to, multiply, or cancel the effects of the first? Will these effects depend on the sequence of exposure to the pollutants? To what degree must the development stage of the organism be taken into account? How will exposure to one or more pollutants influence the probability that a given individual will succumb to disease, and how long will this probability remain altered?

An added complexity that emerges on both the individual and population levels is the mobility of the organism and the population. How can pollution exposure of a migrating organism, such as a yellowfin tuna, be measured? How does a sedentary benthic or passive planktonic organism exposed to several water masses of differing pollutant concentrations react to this sequence of environments?

At the community level, complexities compound even more rapidly. Community composition in any one location varies naturally around one or more characteristic configurations. Does pollution alter the probability that the community will either enter or stay in any one of these natural configurations? How large a pollutant input or how long a chronic pollutant input is required for the community to leave its normal set of configurations entirely? How much larger a push will prevent its return?

At the ecosystem level, feedback loops span not only the species of the community, but also the physical-chemical milieu in which they are set. Organisms, through their decomposition, mixing, sorting, and other activities, can either impede or accelerate the release of pollutants from marine sediments. Bacteria, for example, can both methylate and demethylate mercury, thus altering its toxicity. The sediment-mixing activities of larger organisms can affect the fluxes of resultant mercury compounds across the sediment-water interface. In so doing, organisms alter not only their own, but also other species' and other communities' exposures to pollutants.

We are as yet unable to judge adequately the importance of low-level environmental contamination by organic compounds, and research to date has not provided valid diagnostic or predictive tools to measure the impact of such contamination on individuals of a species, much less on populations of species within a community.

3. PROBLEMS DESERVING PRIORITY ATTENTION

3.1 Introduction

Two major problems are encountered when we evaluate the impacts of pollutants in the field. First, an ecosystem is more than the sum of its parts; important interactions among community members and ecosystem processes cannot be determined by studying these components in isolation. Second, the cause and effect relationship must be demonstrated between pollutant addition and biological response; in other words, the pollution effects must be distinguished from the natural variability inherent in living systems.

Researchers encounter these problems when attempting to determine the threshold levels of pollutant addition that will show biological effects in the field. To what levels of the pollutant should the biota be exposed? The pollutant substance may be diluted, sequestered, or transformed, preventing exposure of some members, or biochemical transformations and food web transfers may add to the exposure levels of other components. For example, would the effects of nutrient loading be mitigated by releasing sewage during the normal period of winter and spring mixing? Would the nutrients in sewage mitigate the polluting effects of petroleum hydrocarbons? Will the threshold of a field population's response depend on its prior exposure to the pollutant or to a related substance? The answers may differ if some species are in critical life stages or if the community has recently experienced a natural (e.g., climatic) stress.

The severity of pollutant impact, in turn, cannot be fully evaluated without resolving the intertwining questions of reversibility and recovery rate. If the pollution assault is stopped, or even if it continues, to what degree will the individual, population, or community recover? If recovery ensues, what paths will be followed and at what rates?

Implicit in the evaluation of both these impacts (degree of alteration and degree to which recovery is incomplete) is the ability to determine at what point the natural variability inherent in living systems has been exceeded and at what point the system has returned to its natural state. Unless the variations in unperturbed systems are known, the impacts of pollutants cannot be recognized and documented. For example, the collapse of the California sardine fishery was generally attributed to overfishing. If such a collapse occurred today it might well be blamed on pollution. But records of sardine populations, consisting of scales preserved in anoxic sediments of the Santa Barbara basin, show that changes in sardine abundance occurred repeatedly before people fished or polluted the California coastal seas.

Individuals, populations, and communities exist and vary on differing temporal and spatial scales. Studies to establish mean reproductive rates of populations and patterns of variations in these rates, for example, require widely differing time periods and sampling frequencies for whales and for phytoplankters. Studies to find mean primary production rates and their year-to-year variations require different spatial sampling networks for Buzzards Bay and for the central North Pacific gyre.

At the individual level, the sources and extent of variability in normal physiological processes must be known for bacteria, algae, or animals. How may differences in sex, reproductive cycle, developmental stages, or environmental parameters contribute to this variability and complicate the effect of pollutants?

At the population level, natural birth rates, death rates, age structures, and spatial dispersion patterns must be known. For example, in the absence of pollution, in what proportion of years is oyster set likely to be successful? Long-term studies spanning numerous generations of a population are necessary to answer such questions. At the community level, how constant is the species list, how stable are the relative abundances of these species, and to what degree does energy flow among them vary from high tide to low, day to night, day to day, season to season, or year to year?

Our biggest problems concern changes known to be associated with pollution. We must decide (1) whether any observed change associated with pollution is really significant, and (2) whether the change was caused by the pollution.

3.2 Long-Term Ecological Studies

To decide whether change is significant we recommend long-term studies of natural variation in marine ecosystems undisturbed by human activity, so that we know what sort of change is normal, i.e., not related to pollution. This need is of highest priority. We suggest that long-term studies be funded at a moderate level at a few selected representative, unpolluted sites on our coasts and in the Great Lakes. The project would continue for decades, though funds probably would be supplied for 3- to 5-year periods. The following kinds of sites should be included:

(1) Intertidal muddy ecosystem, e.g., a salt marsh.

(2) Intertidal rocky coast.

(3) Nearshore (shallow water), mud bottom community.

(4) Nearshore, sand bottom community.

(5) Pelagic-planktonic community in a bay or estuary.

The systems chosen should (1) be reasonably typical or representative; (2) be as unpolluted as possible and unlikely to experience severe human impact (i.e., be protected reserves and sanctuaries); (3) be accessible and close to research centers, so that a variety of scientists could study them.

A species list with species ranked by order of abundance should be prepared for these sites at frequent intervals. The list should be used as a basis for interpreting the importances of the various species in dominating energy flow and determining community structure within the ecosystems. The scientists directing the surveys should actually spend most of the time working on related aspects of the function and structure of the system.

These studies would provide the minimum acceptable amount of time-series measurements of ecosystem properties. The compilation of this body of data would encourage scientists to conduct related studies at these sites, relying on the long-time series to help them interpret their data. In other words the long-term study would encourage establishment and independent funding of a variety of other related studies.

3.3 Experimental Ecosystem Pollution Studies

We propose that interdisciplinary experiments be set up in natural coastal ecosystems to determine how pollutants, singly and in combination, affect ecosystem structure and function. Work should be done on coastal ecosystems because they are accessible to scientists and to pollutants. The type and level of the pollutant and the manner of introducing it should depend on the specific questions asked in a proposed study. Nearby systems could be used for controls. Studies should be interdisciplinary, including ecology, physiology, chemistry, hydrology, etc., depending on the requirements of the specific study.

"Accidental" experiments (e.g., oil spills) should be used when possible, but a pollution experiment with carefully designed controls is preferable for interpreting cause and effect. We are not proposing a correlation study that surveys pollutant concentration and change in ecosystems and suggests causes, though data from such a study would be used for planning experiments outlined here.

We are suggesting here the type of ecosystem experiment now being conducted for forests at Hubbard Brook in New Hampshire (Likens et al., 1970), for salt marshes on Cape Code (Valiela et al., 1976), and for lakes in Manitoba (Schindler, 1974). Some of these studies have included adding pollutants to determine ecosystem effects. Although studies using whole, natural ecosystems are ideal, suitable sites are rare for many types of marine ecosystems. Less ideal are large-scale enclosure studies, such as CEPEX (Menzel, 1977) and MERL (Marine Ecosystem Research Laboratory) (Pilson et al., 1977). Mathematical modeling can often be used in such studies but cannot be substituted for the field experiments.

We are not suggesting which ecosystems or pollutants should be the subjects of these studies. These should be proposed by investigators competing for funds.

Research should be organized around ecosystem manipulation but should also include simpler laboratory experiments. Studies of individual organisms and of selected subgroups of species from the experimental ecosystem should grow out of the systems studies and become an integral part of them. The smaller scale experiments can often be performed in simpler environments, (i.e., in the laboratory) with fewer variables, which can be controlled more readily. Laboratory studies would be designed to examine the parts of the system from its chemistry, biochemistry, and microbiology to the pathology and ecology of individual species and organisms. Such studies of system components then would be compared with the ecosystem experiment, providing a check on their applicability to nature.

Laboratory research to study pollution effects at the sub-ecosystem level and to complement field investigations requires careful selection of the species used for experimental organisms and careful design of the experiment. The optimum species for laboratory experiments should meet the following criteria: (1) the species should be especially sensitive to certain pollutants or essential to the functioning of a well defined ecosystem, as indicated by field investigations; (2) they should be economically important; (3) they should be important organisms that are not found in ecosystems amenable to field studies. The use of experimental organisms merely because they are easy to culture must be discouraged.

The basic design of laboratory experiments should be the same regardless of species or system. Studies must describe dose-response relationships for the action of pollutants on various physiological, biochemical, morphological, or ecological parameters in such a way that physiological and/or temporal relationships can be established.

Like ecosystem experiments, long-term sub-ecosystem investigations must be interdisciplinary. The exposure levels of pollutants and the uptake and disposition of tissue by organisms must be monitored by analytical chemists. The biological properties (life history, nutritional requirements, experimental conditions) needed to maintain the organism must be well known. Organ systems, organs, and tissues to be monitored should be chosen for their importance in homeostasis or reproduction, sensitivity to toxic effects, and pharmacokinetics of pollutants and their metabolites. Metabolic, enzymatic, hematological, and other functions in these tissues can be monitored for change, as can gross morphology, histopathology, and ultrastructure. Effects of pollutants will vary with concentrations and exposure, but as stress and responses decrease there will be greater difficulties in distinguishing between physiological alterations that are ultimately capable of affecting reproductive potential and those that merely represent adaptation to change in another environmental parameter.

Experiments with ecosystems may expose organisms to various concentrations of pollutants. Laboratory studies with defined pollutants can ascertain threshold levels, if any, for observed effects and help elucidate synergistic effects between pollutants and environmental factors that are observed in the field. The length of the experiment will depend on the life span of each organism and the types of possible changes. For example, in fish, neoplasia is detectable after a much longer time period than tissue necrosis is. Population effects can become apparent only in time periods that span several generations.

Harmful effects of low levels of pollution occur when a system's capacity to adapt is exceeded. That stage can be determined only within an appropriate time frame.

4. APPLICATIONS OF RESEARCH

Benefits will result from identifying, quantifying, and better understanding the sensitivity and responses of ecosystems and species to various types of pollutants. Controlling and predicting the effects of pollution are obvious benefits. Such knowledge also will aid regulatory agencies in estimating "safe" levels of pollutants. The immediate economic and health benefits of proper action or inaction based on such knowledge will be substantial.

Studies of toxicology and ecosystems will increase our understanding of how marine biological systems and ecosystems normally function, and how they respond to altered conditions. For example, studies of drug metabolism and effects in animals have led to greater knowledge of cytochrome P-450 systems, offering insight into aspects of steroid hormone metabolism. Analogous insights will let us more safely manipulate biological and ecological systems to our advantage, in aquaculture, for example.

Another benefit of understanding pollutant effects is the ability to develop monitoring techniques useful for accurate assessment and prediction. Describing the patterns of response to pollutants in various species and systems should provide a means to estimate the degree of hazard associated with pollutants, to define the areas affected, and possibly to describe the mechanisms of action of those compounds shown to be hazardous. The ability to adapt to effects of pollution should be determined for each process, organ, organism, and ecosystem with the objective of developing tests for early effects on these systems. This ought to result in a clear index of the physiological and ecological parameters useful as indicators for diagnosis and prognosis of pollution effects.

Several monitoring schemes involving pathological, physiological, behavioral, and ecological parameters exist, with varying potential for detecting pollution-related changes in marine species and ecosystems. However, each of the parameters has definite limitations and none is independent.

Potential monitoring techniques have validity in certain circumstances, but in many instances interpretation of observations is limited. Data obtained through different kinds of monitoring may be extremely valuable in research to explain effects, but the value of the different monitoring techniques must be further defined.

Any adequate monitoring scheme must employ a number of indices; a single index will almost never suffice. A list of such defined indices is not now available for any system. The knowledge derived from research suggested here could be the basis of good monitoring schemes.

4.1 Monitoring at the Level of Individuals

We suggest that physiological and biochemical reactions of individual organisms to pollutants be studied as possible indicators of pollution. Pathological conditions among individuals from marine communities may be useful as pollution indicators if the prevalence of such conditions is significantly higher than in control areas. Principal types of conditions include grossly visible tumors or other lesions, histopathological abnormalities in organs or organ systems, and ultrastructural changes not grossly apparent.

Among the physiological or biochemical features of organisms that could be monitored are some that are normally used in clinical-chemical human medicine. Internal metabolic disturbances are often apparent in blood chemistry. In fish, for example, blood glucose is known to become elevated in animals treated with dieldrin (Silbergeld, 1974). However, other activities, such as handling stress, can also influence blood glucose levels (Hattingh, 1977). Other hematological parameters and serum indices, such as enzymes like LDH, SGOT, lactate, or electrolytes, also vary and are not definitive indicators.

Rates of metabolism or biotransformation of foreign compounds by mixed-function oxygenases (cytochrome P-450) can be induced or elevated by the presence of organic pollutants. This feature could be monitored although the system is extremely complex. Myriad biological and environmental factors can influence biotransformation of indicator substrates, and at times they can reduce activity (Ahokas et al., 1976), but the system may have some use as an indicator under reasonably defined conditions (Stegeman, 1978). Mixed-function oxygenases in marine systems certainly deserve substantial research because of their important and variable role in metabolism and effects of organic compounds.

Many products of biotransformation are more toxic and mutagenic than the parent compounds. Mutagenesis assays, bacterial or otherwise, may thus have some use in evaluating the relative ability of various species or tissues to convert some pollutants to toxic and mutagenic derivatives. Fish, for example, readily activate polynuclear aromatic hydrocarbons to mutagenic form (Stegeman, 1977). Such assays may also describe the mutagenic potential of food organisms contaminated by organics (a public health concern). First-pass screening for mutagenic potential of untested compounds found in the marine environment can also be done. However, the risks of improperly conducting the tests and rashly interpreting the data are great.

4.2 Monitoring at the Community Level

We recommend controlled manipulative field experiments to develop procedures to monitor the effects of pollution at the community level.

Community structure has been monitored much more frequently than has community function. Large segments of the community (e.g., all benthic or all planktonic fauna retained by a given mesh) have been identified to the species level from temporal or spatial series of samples. The resultant data have then been subjected to the analytical and descriptive statistical procedures of classification or ordination to determine whether samples from a possibly polluted place or time differ from the others (e.g., Smith and Greene, 1976). Many statistical subtleties are involved in these procedures, which have therefore been misused and under-used by investigators who are not familiar with their underlying assumptions. Once a statistically significant change in community composition (i.e., one exceeding the naturally expected variability) has been documented, the cause and effect and the implications of the documented shift must be established. By applying ordination and classification methods to controlled ecosystem manipulations, the utility of this approach can be assessed.

Some monitoring programs gather the data needed for such ordination or classification studies but do not measure species diversity. Three problems are encountered when species diversity is tracked through time or space. First there is continuing disagreement over the statistics that should be used to describe species diversity. A simple proof from mathematical statistics shows that one or even two numbers cannot sufficiently describe the distribution of individuals among species, but the arguments continue over which insufficient measures of species diversity are best. Second, the natural variability of a species is difficult to establish. The final problem is that of evaluating the implications of a statistically significant change in species diversity. This can best be done through controlled manipulations.

Another approach to monitoring community structural changes is the use of indicator species. These species fit into one of two categories: species whose presence is taken to be indicative of pollution and species whose disappearance is taken as an early sign of pollution. The usual interpretation of changes in population has recently been questioned by Virnstein (1977). Virnstein showed that at least one opportunistic species in the community studied gained rapidly in abundance when its major predator was absent. Before Virnstein's study, increases of species in the marine benthos were thought to be due largely to release from competing species. Virnstein's study implies that the usefulness of a species as an indicator of pollution depends critically on what other species are in the same environment. Again the usefulness of an indicator species is best evaluated by manipulative, controlled experiments.

Because undocumented interactions are potentially important, the utility of microcosms as community analogs is limited in a monitoring effort. Species that coexist in nature often will not coexist in the laboratory; conversely species often coexist in microcosms because they do not interact there as they do in the field.

Because of the time scales required in systems with larger organisms, monitoring of community functions has been limited largely to microorganisms. The most frequently monitored functions have been microalgal primary production and bacterial heterotrophic uptake. Such monitoring efforts would benefit from controlled manipulations to ascertain the effects of microbial functions, and of alterations in them, on other parts of the ecosystem.

The efficacy of extant procedures for monitoring biological effects at the community level can be seriously questioned, and methods for monitoring community function are especially poorly developed. If theory does not indicate likely parameters for monitoring tools, an effective empirical method of developing such tools can be suggested. One can apply the technique of multivariate discriminant analysis (Goldstein and Dillon, 1978) to identify those parameters or species that best distinguish the control system from the experimentally polluted one.

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