Ocean
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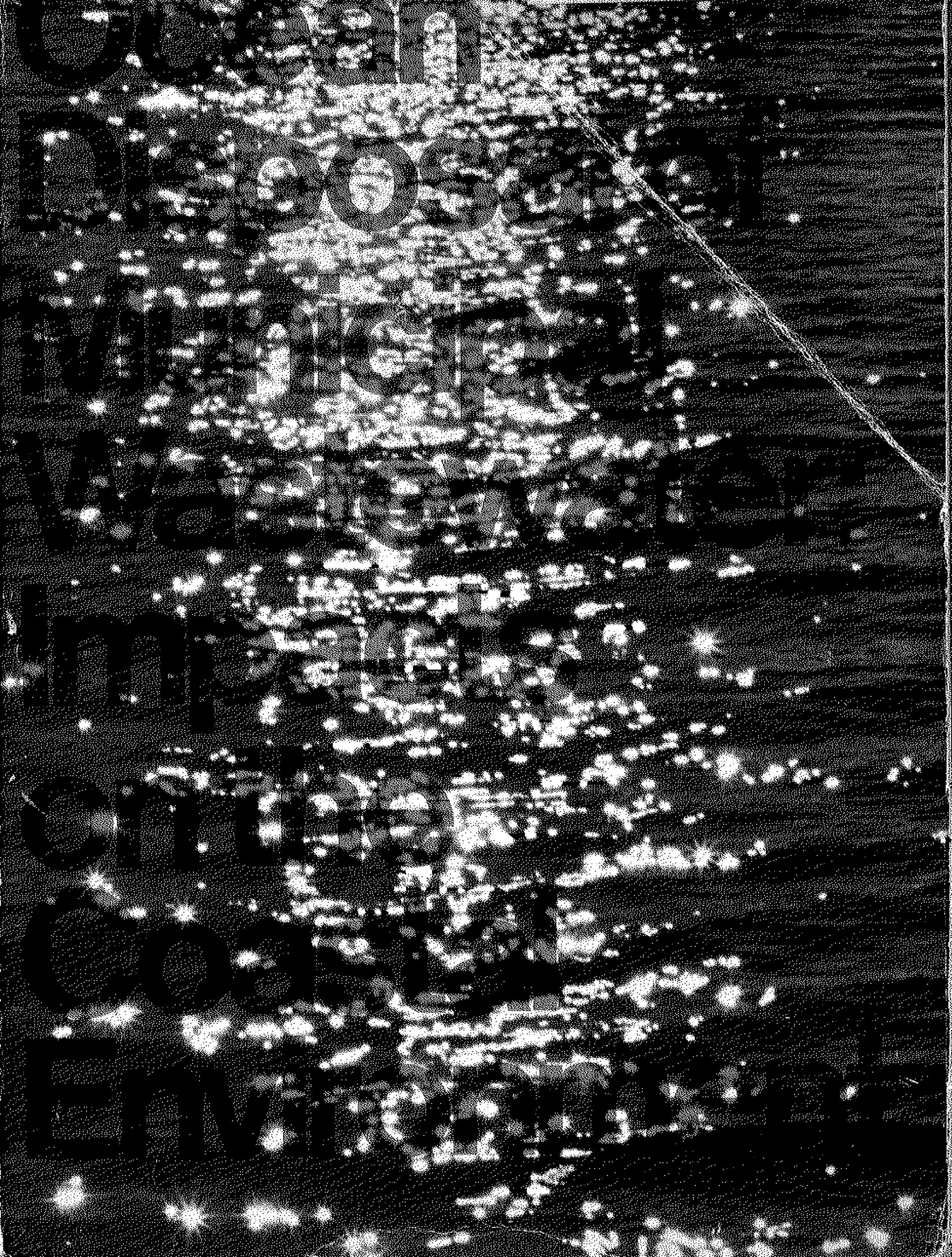
Environment



Ocean Disposal of Municipal Wastewater: Impacts on the Coastal Environment

Volume 1

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Foreword

Municipal wastewater is one of the by-products of our civilization. In the United States, rates of water usage generally vary between 400 and 800 liters per capita per day. Approximately 60 to 70 percent of this water usage results in domestic and industrial wastewater flow. Considering that the U.S. population is now approximately 250 million people, this water usage represents a total wastewater flow of about 40 trillion liters per year, which is about 10 percent of the Mississippi River's average annual flow.

At the present time, most municipal wastestreams are treated and then discharged into inland or coastal waters; furthermore, most of those discharged into inland waters are transported to coastal waters. In times past, major coastal municipalities discharged raw sewage directly to local waters. Currently in these areas, treated municipal wastewaters and their constituents are being discharged from pipes to surface or subsurface coastal waters; or, for the case of the treated sludge, from barges or ships discharging to offshore surface waters. The impacts of such discharges have been varied, depending on the volumes and characteristics of the wastes and receiving waters. In areas where the receiving system has been unable to remove or degrade the kinds and quantities of wastes discharged into it, significant impacts have been observed; in other cases, effects are so small that they are difficult to measure and document.

The purpose of this book is to provide a foundation for future technical and policy decisions on the use of the oceans as a receptacle for municipal wastewater. We have sought to provide insights into two questions: 1) What is the ability of our marine coastal waters to receive municipal wastewaters?; 2) How should alternative ocean disposal schemes and the effects be evaluated?

The idea of synthesizing information on municipal wastewater impacts on coastal waters was originally suggested by J. Frank Hebard, then Director of the National Oceanic and Atmospheric Administration's (NOAA) Marine EcoSystems Analysis (MESA) Program. To initiate the effort, a steering committee was chosen, consisting of:

Norman H. Brooks	California Institute of Technology
Dail W. Brown	National Oceanic and Atmospheric Administration
Herbert Curl, Jr.	National Oceanic and Atmospheric Administration
M. Grant Gross	Chesapeake Bay Institute, Johns Hopkins University (now with National Science Foundation)
J. Frank Hebard	National Oceanic and Atmospheric Administration (now a consultant)
Timothy M. Hennessey	University of Rhode Island
Edward P. Myers	National Oceanic and Atmospheric Administration
P. Kilho Park	National Oceanic and Atmospheric Administration
Harold M. Stanford	National Oceanic and Atmospheric Administration

These individuals were the ones responsible for defining the effort, selecting the topics and authors, and guiding the development of this volume. However, many other individuals assisted. The following acted as reviewers of certain chapters: Frank Dryden (TOUPS Corporation), Felix Favorite (Consultant), Howard Harris (NOAA), Irwin Haydock (Los Angeles County Sanitation Districts), George Jackson (Scripps Institute of Oceanography), Ralph Mitchell (Harvard University), John McGowan (Scripps Institute of Oceanography), James Morgan (California Institute of Technology), Joel O'Connor (NOAA), and Keith Stolzenbach (Massachusetts Institute of Technology).

David Bella (Oregon State University), Wilmot Hess (NOAA; now with the National Center for Atmospheric Research), and Martin Lang (Camp, Dresser, McKee, Inc.) also provided technical advice on the effort. The volume was greatly assisted by the support of Jane Carlson, Jack Ellis, Nate Stiewig, and Joan Myers, all of NOAA. Additionally, Charles N. Ehler, Capt. R. Lawrence Swanson, and Douglas A. Wolfe, all three of NOAA, provided advice and support to see the effort through to completion. The assistance of the MIT Sea Grant Program staff, particularly Elizabeth T. Harding, Madeleine Hall-Arber and Therese Henderson, in assembling all the elements of the final manuscript into this volume was also invaluable. Thanks are extended to all of these individuals or organizations, and particularly to the authors who are identified with each chapter.

A note of special appreciation is extended to Dr. Norman H. Brooks of the California Institute of Technology who, besides being an author and steering committee member, helped with reviewing all of the chapters and suggesting improvements. For a person whose time is in great demand, he provided help above and beyond the call of duty.

Finally, in all fairness to the above individuals, to the authors and NOAA, it must be emphasized that both the statements and conclusions of the individual chapters are solely those of the respective authors. All who were involved in the effort hope that this volume sheds some light on what is both known and unknown regarding municipal wastewater disposal to marine waters.

Edward P. Myers

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1

Introduction

Edward P. Myers

BACKGROUND

The United States and other industrialized countries are facing significant conflicts regarding domestic and industrial activities, environmental impacts including resource depletion, and the associated usage and costs of energy. Concerns over relationships between human activities and their environmental impacts became visible during the late 1960's, reached a high point in the mid-1970's, and have remained strong since. The inclusion of concerns related to energy usage and costs has only recently surfaced and many problems will undoubtedly become more severe in the 1980's.

The resources of the oceans are numerous and include fisheries; sand, gravel, and minerals; transport and commerce; energy; and recreational and aesthetic enjoyment. The oceans have also served as a medium into which certain human-related wastes have been discharged and have been acted upon by natural processes. At one time, the capacity of the oceans to assimilate such wastes was thought to be practically infinite; however, the adverse responses of particular ocean ecosystems to increasing stresses have indicated this belief to be invalid. This is particularly evident in certain coastal regions that border areas of high human activity and are the most subject to stress.

Recent strides to minimize human impacts on coastal ecosystems have focused primarily on the control of municipal and industrial point sources of pollution. The regulatory advances have not been without controversy, however, and the debate continues as some of the alternative wastewater treatment schemes and disposal practices are found to also pose risk, be it due to increased energy usage or other environmental threats.

The purpose of the present volume is to shed some light on only one aspect of this problem, that related to municipal wastewater disposal into coastal waters. Accordingly, the authors have attempted to cover the major aspects of the problem and to integrate them to address management and policy implications. The organization of chapters essentially follows the life history of a contaminant in coastal waters, from the source, through physical dilution and transport and chemical conversion, to effects on marine and human life. To place the technical considerations into a perspective of environmental decision making, the final chapters address some socio-economic, legal and institutional, and management considerations.

PERSPECTIVE ON MARINE POLLUTION

Anthropogenic contaminant inputs to coastal waters, regardless of the source, have resulted in a number of problems for both human and marine life. Especially notable examples include the adverse effects associated with the introduction of mercury and polychlorinated biphenyls (PCBs). Although extreme, events such as the mercury poisoning disaster in Minimata Bay, Japan also come to mind.

Probably more indicative of the complexities of coastal environmental problems, however, was the July 1976 oxygen depletion (anoxia) in marine waters of the middle Atlantic Bight. This lasted months and was characterized by low (less than 1 part per million --ppm) to zero dissolved oxygen levels that extended at the maximum, over an ocean area of about 150 by 60 kilometers (km) beneath the thermocline. The event was attributed to a variety of both natural and human-related (high-nutrient loading) causes, and severly impacted the biological resources of the region (Sharp, 1976; National Marine Fisheries Service, 1977). A mid-September, 1976 survey of the surf clam stocks offshore New Jersey indicated an average mortality of about 50 percent in a 5500 square kilometer (km^2) area. It was estimated that this represented about 25 percent of the offshore surf clam stocks of New Jersey.

Other significant marine pollution events could, but need not be listed; however, it is important to note that they are occurring with an increasing frequency and, for the most part, cannot be related to specific causes. The inability to identify specific cause/effect relationships is largely because contaminant inputs in highly stressed regions are multifarious and the variety of contaminants interact with each other in many ways. While some of these interactions decrease overall toxicity (antagonism), probably most increase toxicity (synergism) (See Chapter 7).

In many instances, severe pollution results from an overloading of organic or inorganic substances that have long been part of the earth's natural systems. Nutrient substances such as nitrate, phosphate, or ammonia, and even metals such as mercury and lead, have been introduced to coastal waters throughout history; however, they are now being introduced in either amounts or forms that are difficult for coastal ecosystems to accommodate, and are thereby causing deleterious effects. The natural assimilative capacities that may exist for such substances are thus being exceeded in certain regions.

Probably the greatest concerns regarding the long-term health of coastal ecosystems are not related to the contaminants that have been part of the evolutionary experience, but to new compounds, particularly the synthetic organic compounds, which are being synthesized at an alarming rate and finding their way into the environment (Chapter 6). Many of these new compounds are known to be very persistent in the environment; consequently, the risks associated with making wrong decisions regarding their application and release to the environment may be quite large (see Chapter 10). The risk is compounded by the long latency periods associated with many of these new compounds. The latency problem, coupled with a wide geographic distribution for some of the compounds, justifies concern and distinguishes such problems from the more historical pollutant concerns (Chapter 10). Furthermore, this concern is intensified when consideration is given to societal time scales, the periods of time required to recognize, respond to, and correct problems.

One example of environmental and societal time scales associated with a marine pollutant event is the much publicized case of mercury poisoning in Minimata Bay, Japan (Goldberg, 1976). In this instance, it was not until 1953 that the first case of a neurological disease was reported, about 15 years after industrial waste, containing mercury, first started entering Minimata Bay. Mercury was not associated with increasing cases of neurological disorders until 1959, and it was not until 1963 that methyl-mercury chloride was identified as the specific active compound.

Finally, in the early 1970's, Sweden, followed by the United States and some other countries, made use of this lesson and adopted upper allowable limits for mercury levels in edible fish. This was some thirty years after the initial introduction of mercury to Minimata Bay.

The time in which marine ecosystems react to, or recover from, contaminant stress is also slow because of the time scales of oceanic processes. Time scales for natural ocean processes are important for waste disposal as shown in Table 1.1, which depicts approximate time and length scales for the ocean discharge of municipal wastewater through an outfall-diffuser system. Approximate scales of time are seen to vary from less than 10^3 seconds for the initial rise and mixing of the buoyant discharge (see Chapter 4), to 10^3 - 10^6 seconds for advection by currents (see Chapter 5) and to greater than 10^6 seconds for large-scale flushing (Fischer et al., 1979). The spatial or length scales are noted to increase in a similar manner.

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Table 1.1 The Effluent Flow from a Sewer Outfall Passes through a Succession of Physical Processes at Scales from Small-to-Large (Fischer et al., 1979)

Phase	Phenomenon	Length scale* (m)	Time scale* (sec)
(1)	Initial jet mixing (rise of buoyant jets over an outfall diffuser in a stratified fluid).	10^2	10^3
(2)	Establishment of sewage field or cloud, travelling with the mean current; lateral gravitational spreading.	10^1 -10^3	10^2 -10^3
(3)	Natural lateral diffusion and/or dispersion	10^2 -10^4	10^3 -10^5
(4)	Advection by currents (including scales of water motion too large compared to sewage plume to be called turbulence).	10^3 -10^5	10^3 -10^6
(5)	Large scale flushing (advection integrated over many tidal cycles); upwelling or downwelling; sedimentation.	10^4 -10^6	10^6 -10^8

*Approximate orders of magnitudes.

The scales of time for cause/effect relationships are also quite variable, ranging from seconds for acute toxicity to years or hundreds of years for chronic toxicity. An example of the latter case is the transmission of genetic defects through several generations before the effects appear. Also, contaminants or stresses themselves have variable time frames that characterize their activity. The oxidation of hydrogen sulfide or the reduction of biochemical oxygen demand (BOD) in aerobic waters is relatively swift, whereas the half-life activity of radionuclides ranges from days to millions of years. A consideration of all of these time and spatial scales is essential to the overall assessment of risk associated with contaminants entering coastal waters. However, such information must be coupled with an understanding of the sources of contaminants, their transport and distributions, and probable effects.

Contaminant Entry

Contaminants enter our coastal waters through four principal modes: direct discharge, direct runoff and riverine inputs, atmospheric inputs, and accidental releases. Generally, those coastal areas bordering highly urbanized regions are most subject to contaminant loads with discharges of contaminants reflecting both the population and industrial activity of the bordering regions (Chapter 2).

An example of an assessment of total contaminant loading in a coastal water body is provided by a study on the New York Bight region (Mueller et al., 1976). This study shows the relative contributions by the four source types to be quite variable and very dependent upon the specific contaminant (See Table C.6). For instance, the relative inputs of total lead are as follows: barging - 44 percent, atmospheric - 9 percent, municipal wastewater - 19 percent, industrial wastewater - 3 percent, and total runoff - 25 percent. For suspended solids, the relative inputs are barging - 63 percent, atmospheric - 5 percent, municipal wastewater - 4 percent, industrial wastewater - 0.2 percent, and total runoff - 28 percent. As indicated in Table A.4, for contaminant entry into the Southern California Bight, source figures vary from region to region.

The National Academy of Sciences (1975a) assessed petroleum hydrocarbon inputs to the world's oceans and found that 35 percent of the input is attributable to losses incident to the marine transportation of petroleum; however, only a small part of this was from tanker accidents, with the majority coming from ballast water and tank washings, the bunkering of bilges, and dry docking activities (Table 1.2). Other sources included river runoff - 26 percent, natural seeps - 10 percent, atmospheric inputs - 10 percent, nonrefining industrial wastes - 5 percent, urban runoff - 5 percent, municipal wastes - 5 percent, coastal refineries - 3 percent, and offshore production - 1 percent.

Table 1.2 Budget of Petroleum Hydrocarbons Introduced into the Oceans (NAS, 1975a)

Source	Input Rate (mta)* Best Estimate	Probable Range	Relative Percentage
Natural seeps	0.6	0.2-1.0	9.8
Offshore production	0.08	0.08-0.15	1.3
Transportation			
LOT tankers**	0.31	0.15-0.4	5.1
Non-LOT tankers	0.77	0.65-1.0	12.6
Dry docking	0.25	0.2-0.3	4.1
Terminal operations	0.003	0.0015-0.005	0.1
Bilges bunkering	0.5	0.4-0.7	8.2
Tanker accidents	0.2	0.12-0.25	3.3
Nontanker accidents	0.1	0.02-0.15	1.6
Coastal refineries	0.2	0.2-0.3	3.3
Atmosphere	0.6	0.4-0.8	9.8
Coastal municipal wastes	0.3	—	4.9
Coastal, Nonrefining, industrial wastes	0.3	—	4.9
Urban runoff	0.3	0.1-0.5	4.9
River runoff	1.6	—	26.0
TOTAL	6.113		100

*million metric tons annually
**LOT refers to Load on Top

Similar contaminant input budgets could be calculated for other pollutants and other regions. Depending on the specific contaminants, these budgets would be influenced by local trends in domestic and industrial activities, precipitation and other weather patterns, treatment or source control practices, and modes of discharge. The concentrations found in the affected environments would furthermore depend upon the regional characteristics of the receiving waters and their biota.

Transport and Distributions

Transport paths of contaminants within marine ecosystems are as varied as the sources; they include advective/diffusive transport of contaminants in solution or in the particulate state (Chapters 3,4,5,6), gaseous transport and exchanges at interfaces (Chapter 6), and biological transport and transfer (Chapters 6,7). Many discharged contaminants enter coastal waters in the particulate state or quickly become associated with this state (Chapter 6). Synthetic organics have a particularly high affinity for particles. This affinity was emphasized in PCB and DDT data of Harvey (1974), which did not show any decreases of concentrations in surface waters with distance from shore, although concentrations in the overlying atmosphere did decrease. The best explanation was that most solid particles in the coastal waters adsorb PCB and DDT from the water while falling to the sediments.

Contaminants that are, or become, associated with particles are transported to the seafloor where they are exposed to an environment with chemistry different from that of the water column (Chapter 6). Sediments can be oxic or anoxic at the sediment-water interface, depending upon the influx of organic matter and the degree of bacterial or other benthic biological activity. Even when surface sediments are aerobic, deeper sediments will be anoxic. These sedimentary chemical changes and gradients result in the mobilization of some metals into interstitial waters where they can diffuse to the sediment-water or oxic interface, and there be reintroduced to the water column or demobilized again (Chapter 6). Complexation of metals with dissolved organic matter, or the bacterial methylation of some metals, can also mobilize metals within the sedimentary environment.

Contaminant transport pathways within estuaries are particularly complex. Being a transition zone where seawater is diluted with fresh water drained from land, the estuarine zone represents an interface between water masses having entirely different characteristics. The density differences between these water masses typically result in the fresher water flowing out and over the underlying saline water. Changes in tidal flows, freshwater flow rate, topography, and winds result in an interface whose characteristics and location are variable with time, resulting in complex and shifting circulation patterns. The hydrodynamic conditions of estuaries result in varied geochemistries for those dissolved and particulate pollutants entering this system.

Salinity, hydrogen ion activity (pH), and electron ion activity (pE), physical-chemical parameters that influence chemical speciation and stability (Chapter 6), all show gradients in concentrations through the transition zone of an estuary. Consequently, strong interactions between dissolved and particulate phases occur, including the precipitation of dissolved materials, the uptake of dissolved materials by solid phases, the mobilization of dissolved substances or ions from solid phases, and the flocculation of particles. Because of precipitation/flocculation occurrences that cause altered particle size distributions and settling velocities, estuaries can become geochemical traps for many substances. These geochemical phenomena within the estuarine zone result in a complex and variable system that is very sensitive to perturbations by humans.

In addition to sediments and water, a major reservoir of contaminants in marine ecosystems is the biota. Biological systems have the ability to accumulate contaminants to levels of concentration many orders of magnitude greater than that to which they are exposed (Chapter 7). The identification of such accumulations of contaminants within certain species is essential in defining critical pathways of contaminants within marine ecosystems, and in identifying those that pose the greatest risk to human or marine biological life.

Effects

The lethal (acute) effects of various contaminants on marine biota are relatively well understood; however, our understanding of the effects on biota of chronic, low level exposure to contaminants is limited (Chapter 7). We do know that such effects can include behavioral perturbations, interference with chemical sensory perception, and genetic effects; however, we do not know to what extent such impacts are being inflicted upon marine ecosystems and what the long-term implications are. One of the major problems has been extrapolating laboratory experiments to actual field conditions; in many cases, this is not entirely valid (Chapter 7).

One other complication in determining the long-term effects of chronic exposure to contaminants is the simultaneous exposure to other contaminants that often results in synergistic or antagonistic effects that are little understood. This lack of understanding relates to the numerous ways, or permutations, by which contaminants can interact with each other. For instance, of thirteen pollutants considered in a proposal for amendments to the Water Quality Control Plan - Ocean Waters of California (California, State of, 1976), there were over 8000 unique combinations, each of which can have its own set of interactions.

A better understanding of both acute and chronic effects to individual species is something that can most likely be achieved in the near term. However, an understanding of the implications of such effects on impacts to marine *ecosystems* is at a stage of infancy and probably will be slow to improve. The problems here are very complex, partly due to difficulty in understanding and modelling *unstressed* ecosystems. For instance, contaminants may impact plankton communities such that overall productivity remains the same but the species composition of communities does change. Since other species that feed on plankton may be very selective in the types of species they find appetizing or suitable, such subtle changes can have a major impact on the rest of the food chain. Another example relates to the role of natural organics in marine ecosysems. It is now recognized that the presence of certain organic substances, by complexing with certain metal ions, can influence total phytoplankton productivity and species composition. Such problems are currently popular research topics in the marine academic community.

THE MUNICIPAL WASTEWATER PROBLEM

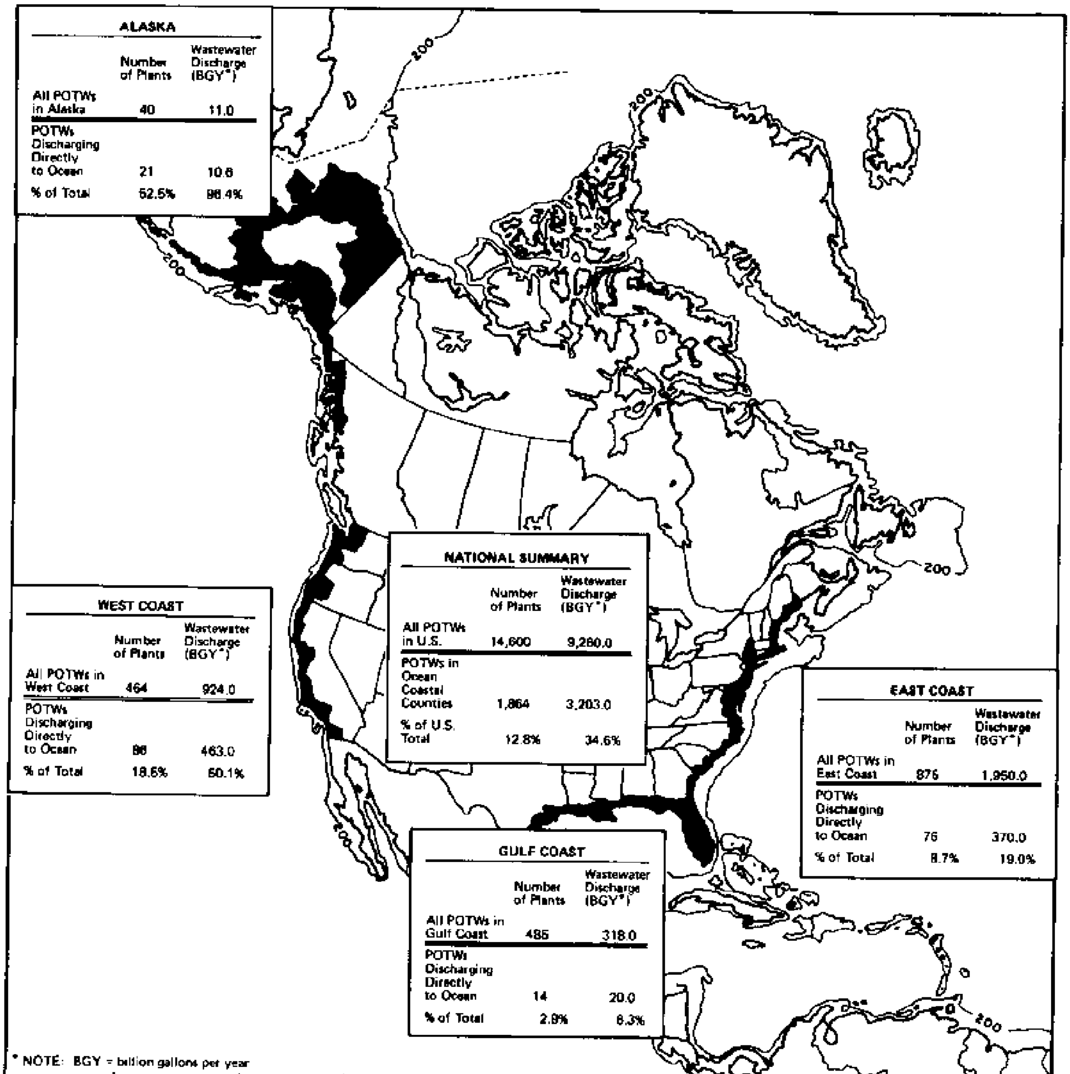
The major sources of municipal wastewaters in the United States are located near the coastal areas where the principal population centers are found. In 1970, 79 million or 40 percent of the population of the 48 adjacent states resided in counties within 80 km of the coastline. The distribution of these people was as follows: Atlantic, 24 percent; Pacific, 11 percent; and Gulf of Mexico, 5 percent. This represents a steady increase since 1940 when 42 million people representing 32 percent of the population were within this coastal band (US Bureau of Census, 1974).

The Office of Ocean Resources Coordination and Assessment (ORCA) of the National Oceanic and Atmospheric Administration (NOAA) has summarized information on the wastewater discharges of US coastal municipalities (Publicly Owned Treatment Works - POTWS), as presented in Figure 1.1. This data, based on a 1978 needs survey (US Environmental Protection Agency (EPA), 1978), indicates the effect of both demographic and industrial trends in the US. Based on the 1978 data, of 9,260 billion gallons (35,000 billion liters) of wastewater discharged each year, 864 billion gallons or 9 percent are estimated to be discharged directly to coastal waters. Of this, the flows are mostly accounted for by the East Coast at 42 percent and the West Coast at 53 percent.

These ocean-discharged municipal wastestreams contain many toxic and other waste constituents; however, they are still more than 99 percent water and thus represent a relatively unused resource. To utilize this resource, certain regions are now using advanced-treated municipal wastewaters to alleviate water shortage problems. For example, the Los Angeles County Sanitation Districts use some wastewater for groundwater recharge, landscape irrigation, and industrial processes. Although the bulk of wastewater in this region is still discharged to the ocean, reuse in southern California will be stimulated in the future as the costs of imported water rise and as the costs of energy continue to climb. Regarding this latter point, it is noteworthy that each million-gallon measure of water that is reused in the Los Angeles region is estimated to be equivalent to a net energy credit of 4500 kilowatt (kw) hours (US Environmental Protection Agency and Sanitation Districts of Los Angeles County, 1976). Los Angeles County also generates methane gas from the anaerobic digestion of the removed sludge, the gas being used to heat the digesters and to power machinery, with some gas also sold to a local refinery.

With municipal waste streams representing both a resource and a problem, it becomes apparent that solutions to their management require a careful evaluation of both technical and policy options. Technical options include the various technologies that are presently available for treating and disposing of wastewaters and their residuals (Chapter 2), as well as the control of contaminant introduction at the source. Source control (also discussed in Chapter 2) requires the control of waste constituents before they ever reach the municipal waste stream. This can be done by pretreatment/recycling for

Figure 1.1 Summary of publicly owned treatment works (POTWs) in ocean coastal counties in 1978. (Office of Ocean Resources Coordination and Assessment, National Oceanic and Atmospheric Administration, 1980).



ALASKA

	Number of Plants	Wastewater Discharge (BGY*)
All POTWs in Alaska	40	11.0
POTWs Discharging Directly to Ocean	21	10.6
% of Total	52.5%	96.4%

WEST COAST

	Number of Plants	Wastewater Discharge (BGY*)
All POTWs in West Coast	464	924.0
POTWs Discharging Directly to Ocean	86	463.0
% of Total	18.5%	50.1%

NATIONAL SUMMARY

	Number of Plants	Wastewater Discharge (BGY*)
All POTWs in U.S.	14,600	9,280.0
POTWs in Ocean Coastal Counties	1,864	3,203.0
% of U.S. Total	12.8%	34.6%

EAST COAST

	Number of Plants	Wastewater Discharge (BGY*)
All POTWs in East Coast	876	1,950.0
POTWs Discharging Directly to Ocean	76	370.0
% of Total	8.7%	19.0%

GULF COAST

	Number of Plants	Wastewater Discharge (BGY*)
All POTWs in Gulf Coast	485	318.0
POTWs Discharging Directly to Ocean	14	20.0
% of Total	2.9%	6.3%

* NOTE: BGY = billion gallons per year

Coastal Region	Total Number of POTWs in Region	% of Total Number of POTWs in U.S.	% of Total Wastewater (WW) Discharge of All POTWs in U.S.	% of Total Discharge in Region Which Is Industrial	% of POTWs in Region with Direct Discharge to Ocean	% of WW in Region Directly Discharged to Ocean	% of Direct WW Discharge to Ocean Which Is Industrial
East Coast	875	6.0%	21.2%	13.7%	8.7%	19.0%	17.5%
Gulf Coast	485	3.3	3.4	6.2	2.9	6.3	1.8
West Coast	464	3.2	9.9	17.3	18.5	50.1	13.2
Alaska	40	0.3	0.1	12.0	52.5	96.4	13.1
Total	1,864	12.8%	34.6%	—	—	—	—

SOURCE: US EPA "1978 Needs Survey Data" as analyzed by the Office of Ocean Resources Coordination and Assessment, Office of Coastal Zone Management, National Oceanic and Atmospheric Administration, January 1980.

industries, and possibly product or product application control. Between waste treatment technologies and source control, almost anything can be done to control these point sources; however, socio-economic considerations are often the limiting factor in applying them.

Economic considerations have particularly motivated the controversy over whether secondary treatment is needed for municipal wastes being discharged to coastal waters. In addition to resulting in increased sludge production, secondary and advanced wastewater treatment systems are expensive to install and then to operate and maintain (Chapter 2). Insights, in addition to those presented in Chapter 2, on the relative magnitude of operation and maintenance costs are offered by information developed by the Los Angles County Sanitation Districts relative to several future wastewater treatment alternatives (US Environmental Protection Agency and Sanitation Districts of Los Angeles County, 1976). The present Joint Outfall System (JOS) for Los Angeles County is composed of two subsystems: 1. five inland water renovation and reclamation plants (WRPs) that have a combined capacity of 5 cubic meters per second (m^3/s) and 2. the 17 m^3/s capacity Joint Water Pollution Control Plant (JWPCP) that discharges its effluent into ocean waters through a submerged outfall system. Total actual flows are expected to increase from the 1975 level of about 18 m^3/s to the 22 m^3/s capacity in the year 2000.

The "no project" alternative (Alternative 1) consists of grant-approved projects that in 1975 were under design or construction, to handle 4.4 m^3/s at the WRPs. The principal difference of Alternative 2 is that the JWPCP is upgraded to full secondary and filtration at the WRPs is further improved. Alternative 3 emphasizes inland treatment, with only 8.8 m^3/s receiving secondary treatment at the JWPCP. To summarize, Alternative 1 is the status quo, Alternative 2 emphasizes coastal treatment and disposal, and Alternative 3 emphasizes inland treatment and maximum reuse potential.

Some of the estimated economic, including operation and maintenance costs, and environmental implications of these three alternatives are indicated in Table 1.3. The costs are based on April 1975 levels and correspond to an Engineering News-Record Construction Cost Index of about 2150. Investments are assumed to be amortized at 7 percent for 20 years, except for diesel trucks needed for sludge hauling,

Table 1.3 Costs and Environmental Effects of Wastewater Treatment Alternatives for the Sanitation Districts of Los Angeles County (US Environmental Protection Agency and Sanitation Districts of Los Angeles County, 1976)

Category	"No Project"[1]	Coastal Treatment[2]	Inland Treatment[3]
Cost Increases (M=millions)			
Capital	$181 M	$368 M	$373.3 M
Annual Capital	17.1 M/yr	34.7 M/yr	35.3 M/yr
Annual O & M	9.5 M/yr	23.4 M/yr	25.5 M/yr
Total Annual	26.6	58.1 M/yr	60.8 M/yr
Energy Summary (millions of kilowatt hours per year, mkhy)			
Gross Energy Use			
Electric Power	198 mkhy	322 mkhy	300 mkhy
Fuel	132 mkhy	162 mkhy	200 mkhy
Total	330 mkhy	484 mkhy	500 mkhy
Energy Recovery			
Recycled Methane	110 mkhy	146 mkhy	146 mkhy
Water Reuse (maximum)	200 mkhy	200 mkhy	250 mkhy
Water Reuse (probable)	125 mkhy	125 mkhy	200 mkhy
Net Energy Use			
w/Max. Water Reuse	20 mkhy	138 mkhy	104 mkhy
w/Prob. Water Reuse	95 mkhy	213 mkhy	154 mkhy
Chlorine Dosage	20 mg/l	10-15 mg/l	10-15 mg/l
Chlorinated Hydrocarbon Emission (w/o further source control)	0.2 gr/sec	0.05-0.06 gr/sec	0.05-0.06 gr/sec
Air Pollutant Emissions (Year 2000)			
Reactive Hydrocarbons	0.9 gr/sec	1.3 gr/sec	1.3 gr/sec
Carbon Monoxide	4.2 gr/sec	5.8 gr/sec	5.8 gr/sec
Oxides of Nitrogen	8.2 gr/sec	14.9 gr/sec	14.9 gr/sec

[1] The "No Project" future alternative would provide advance primary treatment and improved solids removal to full JWPCP flow and also add 100 MGD of secondary treatment.

[2] The coastal alternative would provide full secondary treatment of 400 MGD at JWPCP and no increase in upstream WRPs.

[3] The inland alternative would provide full secondary treatment of 300 MGD at JWPCP and increase capacity of upstream WRPs to accept increased flow for reclamation and reuse.

NOTE: The LACSD Joint Outfall System (JOS) is a regional network of trunk sewers, wastewater treatment and reclamation plants serving an urban area of 615 square miles with a population of almost 4 million and large industrial base presently generating 420 million gallons of wastewater per day (MGD). Since 1960 the JOS has developed into two subsystems: ocean disposal (coastal) at JWPCP designed for 385 MGD primary treatment and all solids handling and "upstream" (inland) disposal at five water reclamation plants (WRPs) providing secondary and tertiary treatment to about 20% of the present flow. None of the alternatives in 1976 considered the possibility of waiver from full secondary treatment (301h program) or energy recovery from sludge per LA/OMA project.

which are amortized at 7 percent for 5 years. Although these interest rates are out of proportion to the present financial situation, the resulting figures provide a relative basis of comparison of the options. The operation and maintenance costs for secondary treatment are emphasized by the more than two-fold increase indicated for annual operation and maintenance, from $9.5 million/year for the "no-project" to $23.4 million/year for Alternative 2, and $25.5 million/year for Alternative 3. Some of the environmental implications are also noteworthy. Net energy usage, accounting for methane recycling and water reuse, increases significantly for Alternatives 2 and 3 while, concommitantly, the discharge of toxics into ocean waters decreases as evidenced by the data on chlorine dosage and chlorinated hydrocarbon emissions. However, air pollutant emissions are estimated to increase with Alternatives 2 and 3, emphasizing the complex trade-offs that are often involved with such environmental problems.

One consequence of better treatment for municipal wastewaters is a greater production of sewage sludge (see Chapter 2). For instance, the secondary treatment requirements mandated under the Federal Water Pollution Control Act Amendments of 1972 are expected to result in an increase in municipal sludge production from a 1975 rate of about 5 million metric tons (dry weight) per year to about 10 in 1990 (National Academy of Sciences, 1977b). Since the management of sewage sludge is already a problem for many communities, the increased volume poses additional concerns.

Presently, there are a variety of alternatives for handling and disposing of sewage sludge, as evidenced in a recent investigation of sludge management alternatives for the Los Angeles/Orange County metropolitan area (LA/OMA Project, 1977). Three major municipal wastewater treatment organizations are responsible for sewage treatment operations in the Los Angeles/Orange County metropolitan area: City of Los Angeles, Los Angeles County Sanitation Districts, and Orange County Sanitation Districts. Together, they received about 900 dry tons per day of sewage sludge solids in 1976; by the year 2000, the volume is expected to double if secondary treatment is implemented. The LA/OMA project investigated eighteen sludge management alternatives in order to develop a long-term sludge management plan and implementation strategy. The most attractive permutations of the alternatives, and their associated monetary and energy costs, are shown in

Table 1.4 along with the estimated effect on air quality, which is also a major environmental concern in this area.

The cost figures in Table 1.4 account for the presence of existing baseline facilities; they also include credits for the value of any energy produced as a part of sludge processing. The required energy data represent the net energy produced or consumed by the candidate system, with energy credits provided by anerobic digestion and certain thermal processes. Based on factors of economic costs, energy consumption, implementability, and reliability, six sludge management options, composed of elements taken from the eighteen listed alternatives, were selected for further study: 1. long distance transport, 2. composting and recycling, 3. thermal processing, 4. ocean disposal, 5. separate secondary sludge processing, and 6. the baseline "no project" alternative. The final recommendation primarily involved combinations of 2. and 3. (LA/OMA Project, 1980).

Obviously, as more thoroughly discussed in Chapter 12, future management strategies for municipal wastewaters must integrate the various environmental, economic, and energy factors that directly or indirectly bear on the problem. As a consequence, optimal strategies are likely to be variable, accounting for the unique characteristics and problems of different regions (see Chapters 11 and 12).

PROBLEM-SOLVING STRATEGIES AND FEDERAL LEGISLATION

Primarily from the standpoint of convenience and economy, coastal communities have historically discharged their municipal wastes into estuarine or marine coastal waters. Furthermore, until relatively recently, such discharges were made through open pipes discharging directly into surface waters or subsurface waters near the seabed. Near the mid-1950s, better engineering practices applied to the mode of discharge allowed for improved water quality and better protection of both public health and marine biological resources. This was exemplified by the ocean outfall diffuser system that discharges an effluent through a perforated pipe section (a diffuser) placed at some depth in the water column, typically on the seabed at a distance from shore (Chapter 4). The discharge of effluent through a multitude of diffuser ports,

Table 1.4 Sludge Management Alternatives for the Los Angeles/Orange County Metropolitan Area (LA/OMA project, 1977)

CANDIDATE SYSTEM NO.	SYSTEM DESCRIPTION	MONETARY COSTS ($/DRY TON)			ENERGY USE[1]	LAND ACQUISITION[2]	NET AIR EMISSIONS (lbs/day)		
		CAPITAL	O & M	TOTAL	10^3MBTU/YR	(ACRES)	PART.	TOTAL NO_x	SO_3
1	INCINERATION	13.82	37.74	51.56	(831)	0	1,600	3,940	2,760
2	PYROLYSIS	12.15	25.80	37.95	(1,436)	0	1,720	4,650	3,400
3	SEPARATE WAS TREATMENT	27.70	41.26	68.96	253	35(C)	1,410	1,410	(1,060)
4	CO-PYROLYSIS	6.33	22.53	28.86	(1,530)	83(C)	810	3,360	830
5	ACTIVE CHAR PRODUCTION	20.79	26.07	46.86	1,504	0	2,120	4,740	900
6	B.E.S.T. DEHYDRATION	15.39	38.28	53.67	781	0	30	5,090	3,040
7	CARVER-GREENFIELD MULTIPLE-EFFECT EVAPORATION	18.07	27.39	45.46	838	0	30	3,560	4,880
8	DEWATERING FOR LANDFILL OR AGRICULTURE	4.31	19.83	24.14	(1,786)	83(C)	60	2,120	120
9	SLUDGE RECYCLE CENTER	4.89	18.64	23.53	(1,719)	113(C)	60	2,200	530
10	EVAPORATION PONDS	12.04	11.22	23.26	(1,356)	3,000(R)	60	2,450	990
11	REMOTE DEWATERING	18.82	28.18	47.00	(704)	100(R)	60	3,080	1,850
12	LIQUID SLUDGE FOR AGRICULTURE	21.15	1.03	22.18	(1,003)	25,900(A_H)	20	2,590	1,530
13	SAN CLEMENTE COMPOST	11.30	30.11	41.41	(1,273)	1,000(R)	320	3,690	740
14	THERMAL CONDITIONING ANAEROBIC DIGESTION	8.42	11.30	19.72	(2,326)	0	120	2,310	(70)
15	OCEAN DISPOSAL	8.26	(4.05)	4.21	(2,044)	0	15	1,120	(380)
16	EXPORTATION	2.77	13.42	16.19	(2,128)	0	0	1,590	50
17	WET AIR OXIDATION	16.15	13.53	29.68	446	0	40	3,870	3,480
18	NEPA-CEQA NO PROJECT	2.28	13.50	15.58	(1,878)	0	60	2,070	290

[1] Energy units are in thousands of million BTUs/YR or 10^9 Btu/Yr.
( ) Indicates a surplus or credit of energy.

[2] (C) Designates lands for composting near the plant,
(A_H) Designates farmland for high rate application,
(R) Designates other lands for sludge disposal remote from the plant sites.

typically 2 to 4 inches in diameter, allowed greater dilutions to be achieved much more quickly than had been achieved by the earlier practices.

Many engineers believed the rapid and high initial dilutions (see Chapter 4), coupled with the further, although slower, natural dispersive processes, would provide sufficient safety to protect public health and marine resources without having to go beyond primary treatment of the effluent (except for disinfection in some cases). A basic tenet was that natural processes within the receiving marine waters would essentially perform secondary treatment on the waste products, and that such use of the ocean resource was both cost effective and logical (Pearson, 1975).

Providing that a certain degree of dilution can be ensured, the philosophy is still generally accepted for the so-called conventional pollutants such as biochemical oxygen demand (BOD), suspended solids (SS), and hydrogen ion activity (pH), as well the basic nutrients. In fact, a workshop on the assimilative capacity of the ocean held by the National Oceanic and Atmospheric Administration (Goldberg, 1979) concluded that "the waste capacity of US coastal waters is not now fully used." However, although this conclusion applies to a number of metropolitan coastal regions, it was also concluded that certain regions, such as the Puget Sound and the New York Bight, provide signs "that the assimilative capacities for some substances or in some areas have been reached or exceeded."

As elaborated upon in Chapter 11, the major framework for handling marine water quality and environmental problems has been cast in the provisions of the Federal Water Pollution Control Act (FWPCA) Amendments of 1972 (P.L. 92-500), the Marine Protection, Research, and Sanctuaries Act (MPRSA) of 1972 (P.L. 92-532), and the Clean Water Act (CWA) of 1977 (P.L. 92-217), which again amended the Federal Water Pollution Control Act. Other legislative acts that also bear significantly on the problem are the Resource Conservation and Recovery Act (RCRA) of 1976 (P.L. 94-580) and the Toxic Substances Control Act (TSCA) of 1976 (P.L. 94-469).

The ultimate goal of the FWPCA amendments of 1972 was to eliminate the discharge of pollutants into navigable waters of the US by 1985; an interim goal was to protect and propagate fish, shellfish, and wildlife, as well as encourage recreation in and on the water. To achieve these goals, the Act mandated specific uniform effluent treatment requirements for point source discharges. For municipal discharges, effluent limitations based on secondary treatment were to be achieved by July 1, 1977. Under Section 208, the Act also provided for the development and implementation of area-wide waste treatment management plans for regions that have substantial water quality control problems. For such regions, Section 208 requires the development and implementation of a comprehensive, cost effective, and institutionally feasible pollution control program for municipal and industrial wastewater, residual waste, storm and combined sewer runoff, nonpoint source pollutants, and land use (Arbuckle and Vandervер, 1978).

As further discussed in Chapter 11 and as alluded to above, the controversy over whether secondary treatment was cost effective or not eventually brought about amendments to the FWPCA, contained in the Clean Water Act of 1977. Section 301(h) amended the secondary treatment requirements for municipal discharges to coastal waters, allowing publicly owned treatment works (POTWs) the opportunity to apply for a waiver from secondary treatment. Such a waiver may be granted if a POTW can demonstrate that it meets certain criteria designed to protect the marine and estuarine environments.

Section 301(h) is probably the first indication that Congress recognized that coastal waters may have a capacity to safely assimilate certain wastes. However, the EPA regulations on 301(h) (US Environmental Protection Agency, 1979) will be tough to meet and, most likely, a number of precedent-setting court battles will follow some of the resulting decisions.

The overall purpose of the MPRSA of 1972 is "to regulate the transportation of material from the United States for dumping into ocean waters." The Act specifically prohibits the transport and dumping of "any radiological, chemical, or biological warfare agent or any high level radioactive waste or except as may be authorized in a permit issued under this title, ...any other material for the purpose of dumping it into ocean waters." Except for the hazardous wastes listed above, and dredged material disposal that is covered by a permit program under Section 103 of the Act, ocean dumping permits may be issued..."where the Administrator (EPA) determines that such dumping will not unreasonably degrade or endanger human health, welfare, or amenities, or the marine environment, ecological systems, or economic potentialities." The Act also mandates that the Secretary of Commerce initiate a comprehensive program of research regarding the effects of dumping and the possible long-term effects of pollution, overfishing, and human-induced changes of ocean ecosystems.

The MPRSA does not specifically prohibit the dumping of municipal sewage sludge into the ocean; however, legislation was signed by President Carter on November 4, 1977, that did prohibit continuation of this practice after December 31, 1981. This legislation was scrutinized by the National Advisory Committee on Oceans and Atmosphere (NACOA) which examined the question of land versus ocean disposal of wastes. In their deliberations, NACOA talked with representatives from the academe, municipalities, and Federal agencies. Their findings are presented in a special report to the President (NACOA, 1981). NACOA recommends that the ocean disposal of municipal (including sludge) and industrial wastes should remain a viable option. More specifically, "wastes should be disposed of in the manner and medium that minimizes the risk to human health and the environment and at a price that this nation is prepared to pay." Also realizing that a return to indiscriminate use of the ocean as a waste disposal medium would be a mistake, NACOA supported additional Federal emphasis on the reuse and recycling of wastes.

Recognizing the real and potential problems associated with the disposal of solid waste, Congress enacted the Resource Conservation and Recovery Act in 1977 "to promote the protection of health and the environment and to conserve valuable material and energy resources." The term disposal "means the discharge, deposit, injection, dumping, spilling, leaking, or placing of any solid waste or hazardous waste into or on any land or water so that such solid waste or hazardous waste or any constituent thereof may enter the environment or be emitted into the air or discharged into any waters, including groundwaters." Although the term solid waste does not include solid or dissolved material in domestic sewage, it does include sludge from a waste treatment plant.

The intent of the Toxic Substances Control Act of 1976 is to provide the authority "to regulate chemical substances and mixtures which present an unreasonable risk of injury to health or the environment, and to take action with respect to chemical substances and mixtures which are imminent hazards." In due course, this Act should be effective in keeping many hazardous chemicals from ever reaching the market and finding routes into the environment.

Obviously, the US approach to solving environmental problems is strongly linked to the legislative mandates that have been passed by Congress. Without doubt, this legislation has had a positive effect on the environment. However, there are concerns that some of the resulting strategies to protect the environment may be costlier in terms of energy, resources, and environmental damage over the long term than are alternative strategies. This concern is particularly acute regarding municipal wastewater input to coastal marine waters.

For the most part, such concerns relate to coherency and consistency of the various pertinent laws. Many feel that the present regulatory framework is based upon a medium-by-medium approach to solving environmental problems, a strategy that does not fully account for the interrelationships among the various environmental compartments. It is also felt that the framework incorporates time schedules that are incompatible with optimal management of the environment (National Academy of Sciences, 1977a). For instance, the National Academy of Sciences notes that the intent to prohibit the ocean dumping of sewage sludge by 1981, coupled with requirements of the Clean Air Act that may restrict the use of sludge incinerators, are protecting specific environmental media while possibly imposing a potentially greater risk on the terrestrial environment.

Although these concerns are moot, it is apparent that strategies for mitigating coastal environmental problems must be part of an overall strategy for protecting the total environment. Using the words from a 1976 National Academy of Science study on sludge management, such strategies should be conducive to an overall minimization of risk and should encourage the concept of "multimedium management" of contaminants (National Academy of Science,1976). A multimedium approach is one that considers the particular characteristics of each environmental medium (ocean, land, and air) and allows for overall environmental protection. Furthermore, such strategies should recognize energy and resource limitations and the interrelationships with waste production, treatment, and disposal methods.

Effective monitoring programs must also become an integral part of such future waste management strategies. Many present monitoring programs are not cost effective; too much of the wrong type of data are being gathered, and these data - both useful and useless - often disappear permanently into storage. Improved monitoring strategies must be responsive to the "right" questions with the type, frequency, and location of data acquisition based upon an understanding of relevant policy questions, potential environmental problems, the regional setting, effective natural processes, and statistical designs that minimize the risk of making wrong decisions (See Chapter 10). Such strategies must also include programs that are designed to give an "early warning" of potential problems before they become either so severe or irreversible that regulatory actions have minimal effect.

One example of the type of early warning program needed is the "mussel watch" initially proposed by Goldberg (1975). Mussels are relatively ubiquitous and are known concentrators of synthetic organics, petroleum hydrocarbons, heavy metals, and radionuclides; they assimilate such contaminants to concentrations that are orders of magnitude greater than in ambient waters, making the mussel an indicator of chronic exposure. Although many inherent problems need to be resolved, this kind of monitoring to check ecosystem "health" or effects should be an essential part of any waste management strategy to minimize risk.

SETTING OF STANDARDS

Risk, more thoroughly discussed in Chapter 10, is common to all living systems. However, concern is warranted when the levels of risk are increased significantly above natural background levels. The degree of concern is related to the level of risk judged to be acceptable; this typically means there is a very low probability of biological effect over some scale of time characteristic of the system. The acceptable level of risk also is a function of the benefit anticipated. For instance, in modern medical practices, a higher level of risk is usually tolerated in the case of life-saving treatment to humans.

Although much progress has been recently achieved in the assessment of risk, the determination of that level considered acceptable is still a subjective process that encompasses social, political, and economic factors. For those responses that can be associated with a "threshold dose", the answer may be at hand; however, experience has proved that it is difficult to apply the threshold dose concept to many chemicals or stresses. Another technique that has been used in risk assessments relates to the "no detectable adverse effect" concept. The problem with this concept is that a level of effect cannot be statistically established with a 100 percent level of confidence, particularly over long time scales. As noted by Lowrance (1976), "many hazards now recognized, such as moderate levels of X-rays or asbestos or vinyl chloride, could at an earlier time have been said to have no detectable adverse effect."

Three basic approaches have been used for assessing human health risks associated with contaminant disposal or leakage into marine waters: critical pathways, specific activities, and mass balances. The critical pathways approach was developed for assessing human health risks associated with the disposal of low-level radiation discharges to marine waters. It was assumed that there are one or two pathways of the numerous possibilities that pose the greatest risk for transporting a pollutant back to humans. In addition, there may be certain populations that experience the greatest risk; these could be those individuals on fish diets, pregnant women, children, etc. The technique accounts for such factors as advective/diffusive transport and associated dilution, bioaccumulation factors, and eventual fates. The most notable example of the application of critical pathways approach is that associated with evaluating risks associated with the discharge of low-level radioactivity into the Irish Sea from the nuclear waste reprocessing plant located at Windscale on Britian's Cumberland coast (Foster et al., 1971).

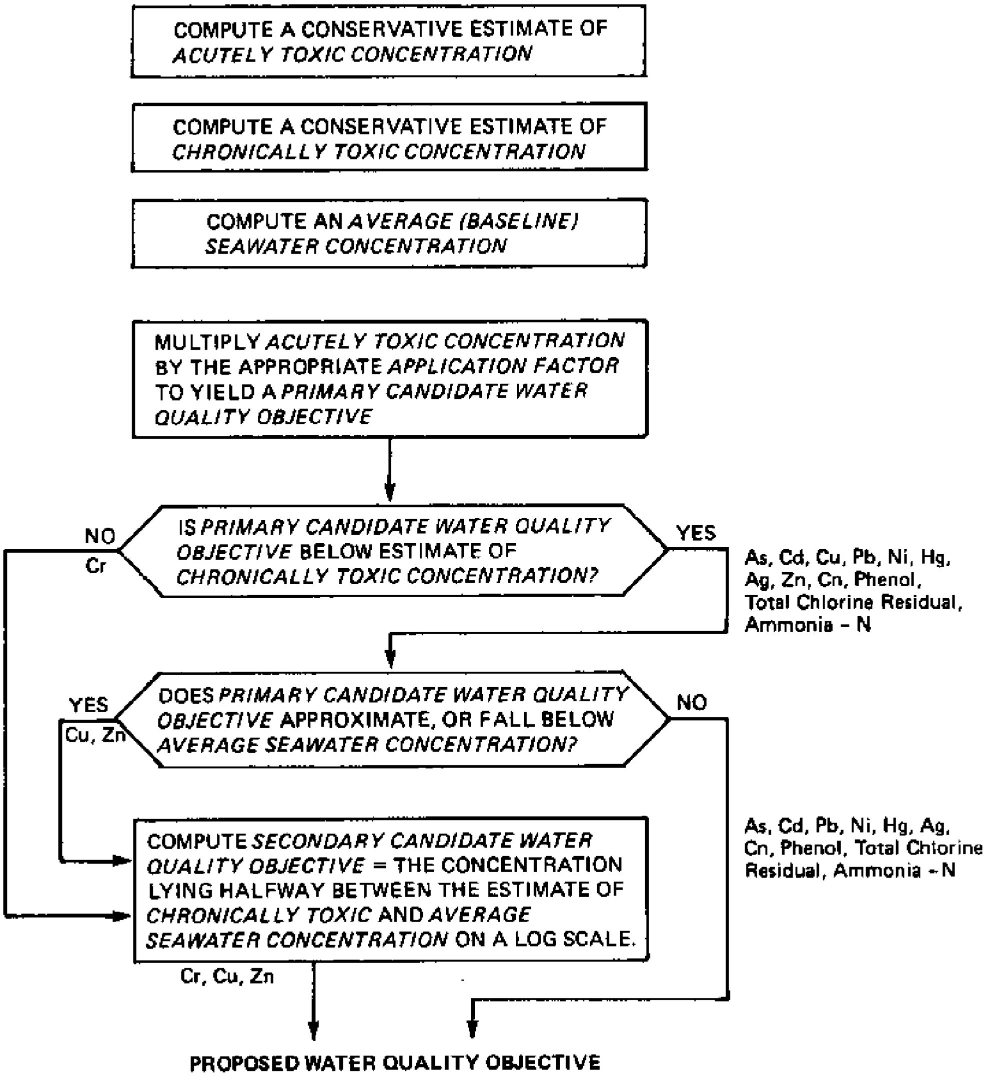
In 1958 the National Research Council's Committee on Oceanography used the specific activity approach to examine the potential public health risk of discharging low-level radioactive wastes into the Pacific Ocean off the North American coast. This approach uses the ratio of the recommended maximum permissible body burdens of individual radionuclides to human body concentrations of the corresponding non-radioactive elements; this ratio is referred to as the specific activity. The advantages of this approach are that it requires neither an evaluation of the bioaccumulation of radionuclides by marine organisms nor an assessment of the human consumption of marine seafoods. The rationale for the approach is that "if the maximum permissible specific activity were not exceeded in the environment where foods were grown, there were no mechanisms by which the specific activities in the foods, or the humans who ate the foods, could exceed the limit" (Foster et al., 1971). The critical concern is thus to ensure that the specific activities or the radionuclides in question do not exceed some reference level in exposed seawater.

The mass balance approach relies upon an understanding of the contaminant inputs and outputs associated with a particular system. Coupled with a knowledge of internal sinks and/or sources, and flushing times within the system, the mathematical formulation of the mass balance estimates the steady-state or transient concentration of the contaminants of concern. As with the other two methods discussed above, knowledge or assumptions regarding dose/response and level of acceptable risk must be known to apply this technique to risk assessment.

The Water Quality Control Plan for Ocean Waters of California (California, State of 1972; revised 1978) is the result of an attempt to determine acceptable risk based on contaminant concentrations relative to natural background concentrations, and upon extrapolation of the "no detectable adverse effect" concept. Many of the effluent quality requirements in the 1972 plan were established by assuming that, following a specified initial dilution, receiving water concentrations would be near those of background values. In contrast, the 1978 amendments to this plan (Appendix E) are based upon the concept of satisfying specific ambient water quality standards. Since effluent standards can encourage pre-dilution of the effluent (versus contaminant control), the 1978 amendments are more conducive to conserving water and reducing total emissions of contaminants to coastal waters. The amendments' basic objective is to keep the concentration level of contaminants in the receiving waters within the long-term tolerances of marine organisms. Criteria were selected on the basis of a statistical evaluation of available acute and chronic toxicity data, and a comparison with background seawater values (Klapow, 1979); the decision process is summarized in Figure 1.2 (California, State of, 1976).

To acknowlege that there is a degree of risk that can be tolerated when discharging contaminants into estuarine and coastal marine water assumes that these waters possess a capacity for assimilating such wastes. The assimilative capacity of a coastal water body might be perceived as the ability of that water body and its associated ecosystem to cope with

Figure 1.2 Decision Paths Followed in the Development of Proposed Water Quality Objectives (California, State of, 1976)



contaminant inputs such that, with all factors taken into account, exposure levels are less than some "acceptable" dose for a particular critical component of the system. Obviously, the human population must be considered as one of these components, for it may be that the marine ecosystem can function under the imposed stress, but that humans who consume certain marine species or venture into the marine environment will be the population most at risk.

The concept of assimilative capacity must be valid for natural substances; however, there are undoubtedly many synthetic substances for which this concept is invalid. It is likely that our terrestrial and freshwater ecosystems also do not possess the ability to assimilate such wastes. For such substances, it may be that the only rational alternatives for protection of the environment are non-production, efficient source control, or total containment. With the possible exception of non-production, these alternatives undoubtedly also have associated risks.

SUMMARY

Contaminants enter our coastal waters from a number of both direct and indirect sources. The issue of whether or not, and to what degree, municipal wastewaters and their constituents can be allowed to enter estuarine and marine coastal waters is thus by no means a simple one. To develop adequate management and regulatory strategies, the problem of municipal waste disposal to coastal waters must be put into perspective with the other involved factors, namely:

1. Other point and diffuse sources that determine "background" concentrations.
2. Regional setting.
3. The socio-economic and political framework
4. The risks posed by alternative strategies

Such a holistic approach to waste management appears to be the rational way to proceed, particularly since our energy and other resources will be more stressed in the future. To provide a basis for future policies that would encourage such approaches, this publication is an assembly of information which bears on the problems of disposal of municipal wastewaters and their constituents to coastal waters.

Chapter 1, Introduction, has tried to provide a perspective of the problem, noting that municipal wastewater is but one source of contaminants to coastal waters. Others include direct industrial discharges, dredge spoil disposal, direct runoff, riverine inputs, atmospheric inputs, and accidental releases. As a result, ameliorating strategies must take into account the relative roles of all factors to minimize overall risk to the total environment in a cost effective way.

Chapter 2, Municipal Sewage Systems, presents information on municipal wastewater generation and characteristics, its treatment, and the resulting effluents that are subject to disposal to estuarine and coastal waters. In particular, waste treatment processes are viewed from the standpoint of the overall functioning of a system into and out of which flow both energy and matter. Inflows include an influent wastestream of certain quality; energy to operate machinery and to heat the biological unit processes; and matter, such as chemicals, for precipitation or disinfection. The outputs, which include effluent, sludge, and gases, from the treatment plant are highly dependent upon the inputs and the degree and types of processes. Discussion focuses on the resultant volumes and qualities of effluents eligible for ocean disposal. Some discussion is also provided of regulatory actions and trends in domestic and industrial activities that may change the variables in the future.

Chapter 3, Coastal Oceans:The Regional Background, discusses the basic characteristics and regional variations of estuarine and coastal waters. Particular attention is focused on those characteristics and processes that play a role in the initial and subsequent fate of discharged waste constituents. This includes density structure and currents in different water types. The chapter basically provides an overview of the types and characteristics of receiving environments.

Chapter 4, Delivery Systems and Initial Dilution, discusses state-of-the-art engineering systems for the delivery of municipal wastes to marine waters, including the controlling variables, limiting factors, and the initial dilutions achieved. The optimum engineering design for discharging a wastestream into marine waters will vary from region to region, dependent upon the volume and characteristics of the waste and the receiving waters. Furthermore, the actual strategy that is chosen should be dependent upon anticipated effects. For instance, is it more advantageous to keep the discharge in surface or subsurface waters, or is it best to place it near the seafloor if possible; is it desirable to contain the waste as much as possible, or to disperse it? This chapter presents methodologies for achieving the desired goal.

Chapter 5, Advection, Diffusion and Particle Settling, discusses the major physical processes that control the subsequent physical transport of wastes discharged to estuarine or coastal waters. The focus is on the advective and dispersive characteristics of these waters and their relationships to dilution achieved as a function of time and distance, and on the physical behavior of particles and floatables. Compared to the process in initial dilution, which may yield initial dilutions of 100 to 1 in minutes, subsequent mixing is a slow process that can take days to reduce the effluent concentration by another order of magnitude. During this time period the particulate phases can interact with one another and settle from the dissolved plume if ambient vertical currents and turbulence are small compared to settling velocities of the particles.

Chapter 6, Chemical Changes, discusses key chemical reactions once municipal effluents or their sludges are discharged to marine waters. The focus is on those species and reactions which play major roles in the health of the marine ecosystem and on those compounds that pose the most risk. Prior to discharge, most municipal effluents have a high sulfide content, zero dissolved oxygen, and negative oxidation-reduction potential. The chemical compounds are thus in reduced states, with many of the metal species tied up as insoluble sulfides. Upon and during dilution of the effluent in receiving waters, a variety of physical-chemical changes takes place including oxidation/reduction, surface adsorption/desorption, and flocculation and precipitation. In addition to affecting the physical state of many compounds - dissolved, colloidal, or particulate - these changes also affect the bioavailability of chemical compounds as well as their toxicity.

Chapter 7, Biological Effects, presents a discussion of biological effects that result from the disposal of municipal wastewater constituents to estuarine and coastal waters. The discussion emphasizes known effects based on information gathered in the vicinity of municipal wastewater discharges and controlled ecosystem experiments. It is apparent that an understanding of the lethal doses of various contaminants on marine biota is relatively well known, and contemporary marine disposal systems can be designed in most cases to ensure concentrations below these levels. However, in regard to the effects of chronic, low level exposure to contaminants, the understanding is minimal.

Chapter 8, Public Health Consequences of Coastal and Estuarine Pollution:Infectious Diseases, and Chapter 9, Public Health Risks of Toxic Substances, both discuss public health issues, concerns, criteria, and associated risks that relate to the discharge of municipal wastes to coastal marine waters. The fact that much concern over the disposal of municipal effluents to marine waters is motivated by the public health concerns is evident by the closing of any polluted beaches and shellfish beds in populated coastal regions, and the setting of standards for certain contaminants such as mercury, PCBs, and bacteria found in edible fish or shellfish. The costs associated with such environmental impacts are relatively well quantified, and in many cases quite large. Furthermore, beyond the potential health risks, the implications are far-reaching, because eventually they affect people's livelihoods and recreation.

Chapter 10, Uncertainty and Policy Formation, serves as a bridge between the earlier chapters, which are science and engineering oriented and subsequent chapters that assess the legal and institutional framework and the management/policy implications. The chapter introduces the normative concepts of equity and efficiency, primarily from an institution-free perspective and further deals with the question, "What is a fair distribution of risk and how can it be imposed on the future?" With an adequate characterization of the burden of risk, in terms of its time profile, severity, and confidence of likelihood, it is possible to formulate policies that bound the risk burden in some ways; for example, by regulating certain toxic chemicals at their source on the grounds of intertemporal fairness. Finally, the chapter asks, "What is the efficient trade-off between the expected present value of the cost of the hazards and the costs of control?" This is the traditional issue in risk-benefit analysis.

Chapter 11, Legal and Institutional Factors, focuses primarily on federal regulation of effluent and sludge discharges from publicly owned treatment works into ocean waters; it also takes account of regulation of waste disposal onto land and into the air. After tracing the history of control efforts, the chapter describes and assesses the present situation. Central shortcomings in the existing regulatory system are poor integration of controls and unnecessarily costly requirements. While recent changes in the law (e.g., secondary treatment waivers) represent important improvements, a good deal remains to be accomplished, and some suggestions for reform are briefly discussed; they are pursued further in Chapter 12.

Chapter 12, Evaluation of Key Issues and Alternative Strategies, presents an integrated summary and evaluation of the problems of ocean disposal of sewage and sludge, and alternative strategies for controlling them. Sections of the chapter address: current disposal practices and risks; key technical issues and their effects on management alternatives (such as source control, treatment levels, outfall design, and sludge disposal procedures); and basic policy and administrative questions. In summary, present policies for discharge of wastewater and sludge need to be revised as they are not properly based on current scientific and engineering knowledge of ocean disposal. Specific conclusions and recommendations are given at the end of the chapter.

Certain aspects of past ocean disposal practices of different regions are relevant in that they provide realistic examples of how various treatment and disposal practices, as well as policies, have affected estuarine and coastal environments. Accordingly, to provide a perspective of current and past regional practices and problems, Appendices A through D present papers dealing with various aspects of disposal in the Southern California Bight, Puget Sound, the New York Bight, and British waters.

Appendix A. Southern California subtropical waters serve as the waste repository for approximately 11 million people. Nearly 4 billion liters of treated municipal wastewater and digested sludge are discharged daily into these coastal waters; of this total flow, approximately 86 percent has received primary treatment only, 13 percent is from secondary treatment, and 0.5 percent is digested sludge or sludge centrate. For the most part, the Southern California waters are well flushed and, with the exception of some specific instances, are not overloaded by these inputs.

Appendix B. The Puget Sound, in contrast to the Southern California Bight, is a large primarily enclosed estuarine system, that is hydrodynamically complex. The Sound is also rich in marine resources and serves slightly over 2 million people. It receives approximately 1 billion liters per day of primary, secondary and tertiary treated municipal wastewaters, half of which comes from the Metropolitan Seattle (METRO) West Point Treatment Plant discharge into the main basin of the Sound. Although the Sound is of generally high water quality, problems do exist that are attributed to municipal and/or industrial discharges into poorly flushed, localized embayments.

Appendix C. The New York Bight, an area extending seaward from Long Island and New Jersey to the edge of the continental shelf and covering an area of about 39,000 square kilometers, is undoubtedly one of the most heavily utilized regions of the world. It is adjacent to the area that includes about 10 percent of the US population. In addition to offering resources of value to recreation, fisheries, commerce and industry, it acts as the eventual receiving waters for large volumes of treated and untreated municipal wastewaters and sewage sludges. The daily municipal wastewater inputs to the Bight from the Hudson-Raritan estuarine system are about 2 billion liters of raw wastewater, 3 billion liters of primary treated wastewater, and 6 billion liters of secondary treated wastewater. To this must be added the smaller direct municipal discharges to the Bight from the Long Island and New Jersey coastal communities which amount to about 0.6 billion liters of primary and secondary treated wastewater. Additionally, approximately 4 billion liters of sewage sludge are barged yearly to the Bight and dumped. The Bight already has severe problems related to municipal and other discharges and to other non-point sources. Furthermore, these problems are only expected to worsen without innovative waste management and resource utilization strategies. This, coupled with the institutional and topographic complexity of the region, gives only an indication of the difficulty in analyzing policy options for this region.

Appendix D. Controls to overcome the resulting pollution problems in the Thames Estuary in England have spanned over a century. The first problems arose in the 1840s when the increasing discharge of raw sewage led to the elimination of much of the commercial fishery and to odor nuisance. Corrective measures started in the 1860s and continued up to the present day have improved the quality of the river markedly.

Currently over 2.5 million cubic meters per day (m^3/d) (550 million gallons per day (gpd)) of sewage effluent are discharged to the river while maintaining a minimum water quality acceptable for the passage of salmon. This improvement has been achieved without recourse to uniform standards of treatment - lower levels of treatment being utilized where the advective and dispersive processes in the receiving waters are greatest.

In addition to sewage discharges, the United Kingdom (UK) dumps at sea 28 percent of the sewage sludge produced. Three areas (off the Thames, in Liverpool Bay and off the Clyde) receive over 8 million tonnes/annum of sludge between them. The effects of dumping are reduced in the first two areas by the high dispersion available from tidal currents. The main problems have arisen from contamination of fish which has been remedied by control of industrial discharges to the sewage works.

The net result of this extensive examination of the problems associated with the disposal of municipal wastewaters and their constituents to coastal waters is that the overall problem is a complex one linked to many other systems. Although there may be uniformity to elements, it is apparent that solutions to associated problems should be somewhat variable, taking maximum advantage of regional differences in waste types, receiving water characteristics, ocean uses, and socioeconomic considerations. In the future, such factors should be evaluated further with respect to the environmental and other implications of alternative strategies, so that cost-effective means of environmental management can be employed.

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2

Municipal Sewage Systems

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Andrew R. Anderson

INTRODUCTION

Municipal waste streams differ in both their rate of generation and their characteristics from region to region, depending upon the population and industrial sector served, regional land uses, precipitation patterns, groundwater levels, and degree of separation between storm water and sewage collection systems. Domestic wastewaters include the typical wastes from the kitchen, bathroom, and laundry, as well as whatever other wastes people may accidentally or intentionally pour down the drain. Commercial and industrial contributions to municipal wastewaters are as varied as the establishments that generate them; they range from sanitary wastes from restaurants, laundries and service stations, to dilute industrial rinse waters, to process wastes containing hazardous chemicals. Storm water runoff contributions in urban regions include pollutants scoured from the land surface as well as those deposited in the wastewater collection system. Even in cities with a separate storm water collection network, some runoff enters the wastewater collection system. As a consequence of these various inputs significant variations occur in the rate of flow and the physical, chemical and biological properties of municipal wastewaters.

The need for treatment of the municipal waste streams was realized by the mid-19th century when many public health problems were associated with sewage contaminated drinking water. By the latter part of the 19th century, engineering innovations treated municipal wastewaters, conveyed them to a logical point for discharge, and collected drinking water from uncontaminated supplies to the extent possible. Since then, advances in wastewater management have been primarily motivated by more definable public health concerns and an awareness of the adverse environmental impacts that can result from improper waste disposal. Today, the degree and type of sewage treatment needed prior to disposal are primarily determined by requirements for: 1. protecting public health; 2. maintaining receiving water quality consistent with its beneficial uses; and 3. preventing a nuisance.

To provide a quantitative basis for evaluating alternative water quality management schemes for the major coastal discharges, this chapter presents

- selected information on municipal wastewater characteristics and the effect of industrial inputs on quality;
- a review of the capabilities of treatment processes to obtain different levels of effluent quality;
- costs, energy requirements, and material balances of selected treatment processes to attain various effluent and sludge qualities for a large coastal (4.4 cubic meters per second (m^3/s), 100 million gallons per day (MGD)) treatment plant.

WASTEWATER CHARACTERISTICS

Besides flow, wastewater characteristics traditionally of concern in the design of treatment facilities are gross solids, floating matter and oxygen-demanding subtances. In some cases, removal of nutrients, such as nitrogen and phosphates, and removal of heavy metals are also of interest. The flow (volume) and physical-chemical characteristics of municipal wastewaters are mainly a function of the type and extent of residential and industrial water use, and the way storm water runoff is collected. Based on a survey of 78 cities by Loehr (1968), it seems that the per capita flow and contaminant load contributions increase with population (Table 2.1). This is primarily due to the greater industrial and commercial contributions in the larger cities.

Typical US per capita water usage is presented in Table 2.2. Per capita use of water for domestic, commercial and public purposes is about 0.42 cubic meters per day (111 gallons). This value, however, is subject to large local and, in some areas, seasonal variations. For example, a survey of 147 California water agencies for the period 1961-1970 showed per capita water uses ranging from 0.37 to 2.33 cubic meters per capita per day (97-615 gallons per capita per day (gpcd) (California Department of Water Resources, 1975). Agencies sampled served a total of over 11 million persons, 56 percent of the state's 1970 population. The average for three large urban areas, Los Angeles, San Diego, and San Francisco, was

Table 2.1 Variation of Per-Capita Daily Waste Loadings with City Population

Population Range	Flow	SS (suspended solids)	BOD_5*	Number of Cities
(1000)	(m^3/cap-d)	(g/cap-d)	(g/cap-d)	
Rural	0.27	51	60	-
<20	0.48	86	72	20
20-50	0.45	77	82	20
50-150	0.57	113	86	20
>150	0.49	113	118	18

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*5-day biochemical oxygen demand

Sources:
Otis et al. (1977), Rural Household Waste Only.
Loehr (1968), 50th Percentile Values of Data from Treatment Plant Operating Records.

Table 2.2 US Per-Capita Water Use (Metcalf and Eddy, Inc., 1972)

Use	Flow	
	(m^3/cap-d)	(g/cap-d)
Domestic	0.23	61
Commercial	0.10	26
Public	0.09	24
Industrial	0.13	34
TOTAL	0.55*	145

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*Units in volume per capita per day.

about 0.68 cubic meters per day (179 gpcd). From 10 to 30 percent of the urban use in these three arid areas was for landscape irrigation, however. Sixty to eighty percent of the total flow typically finds its way into the sewer system (Metcalf and Eddy, Inc., 1972).

Estimates of residential per capita contributions to the municipal waste stream are shown in Table 2.3. The data for solids, oxygen demand, nitrogen and phosphates are based on sampling of rural dwellings and so represent baseline values for purely domestic waste loadings. The metals data were obtained from four cities where predominantly residential areas of sewer systems were sampled to estimate residential loading factors. However, these values may include small additional contributions from commercial sources and runoff. Variation among cities may be due to these effects as well as to differences in metals concentrations in raw water supplies. For instance, the New York City tap water concentrations of 0.06 milligrams per liter (mg/l) and 0.03 mg/l for copper and zinc account for 27 and 13 percent respectively, of the concentrations in residential wastewater.

An example of the industrial inputs to the municipal waste stream is indicated on Figure 2.1 which shows the breakdown of industries in the New York-New Jersey metropolitan area. Apparel, printing, chemical, electrical equipment and food industries predominate. The first four are included in EPA's pretreatment priority list of industries believed to be discharging pollutants of greatest environmental concern. Most of the chemical industries in this area discharge large waste loads to the municipal plants in northern New Jersey. Thus, the concentrations of BOD_5, solids, nutrients and most metals in the large New Jersey municipal plants are about double those for the New York City plants, as seen in Table 2.4. (Note: biochemical oxygen demand (BOD), is a measure of the quantity of organic, oxygen-demanding substances present in wastewater; BOD_5 being the demand exerted during a five-day test.) The southern California wastewater characteristics from the Hyperion and Los Angeles Joint Water Pollution Control Plants (LA/JWPCP) plants, which comprise 66 percent of total wastewater discharges in the area, show the effects of heavy industrialization similar to those seen in northern New Jersey plants. The New York City concentrations are relatively low due in part to the nature of the collection system, a combined sanitary-storm water system.

Table 2.3 Per Capita Residential Waste Loading Factors (Otis et al., 1977)

Parameter	Rural Concentration (mg/l)	Rural Loading (gm pcd)*
SS	189	51
BOD_5	222	60
Total N	24.8	6.7
Total P[1]	15.2	4.1
Flow		0.27 m^3 pcd

	Residential Concentration (mg/l)		Residential Loading (mg/cap-d)			
Metal	New York[2]	Los Angeles Co.[3]	New York[4]	Allegheny Co., PA[5]	Muncie Ind.[5]	Average
As	--	0.014	--	--	--	--
Cd	0.002	0.005	0.9	0.5	2.7	1.4
Cr	0.024	0.02	8.2	8.2	3.2	6.5
Cu	0.22	0.119	77	45	45	56
Pb	--	0.051	--	28	45	37
Hg	--	0.0005	--	--	--	--
Ni	0.073	0.031	5.0	5.4	9.1	6.5
Zn	0.24	0.490	104	77	95	92

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[1] 72 percent contributed by dish washer plus laundry.

[2] Weighted Average Concentrations, Klein et al. (1974)

[3] Eason et al. (1978).

[4] Vigon et al. (1977).

[5] Davis and Jacknow (1975) Residential areas.

*grams per capita-day

Figure 2.1 Types of industrial activity in New York metropolitan area (Mueller and Anderson, 1978).

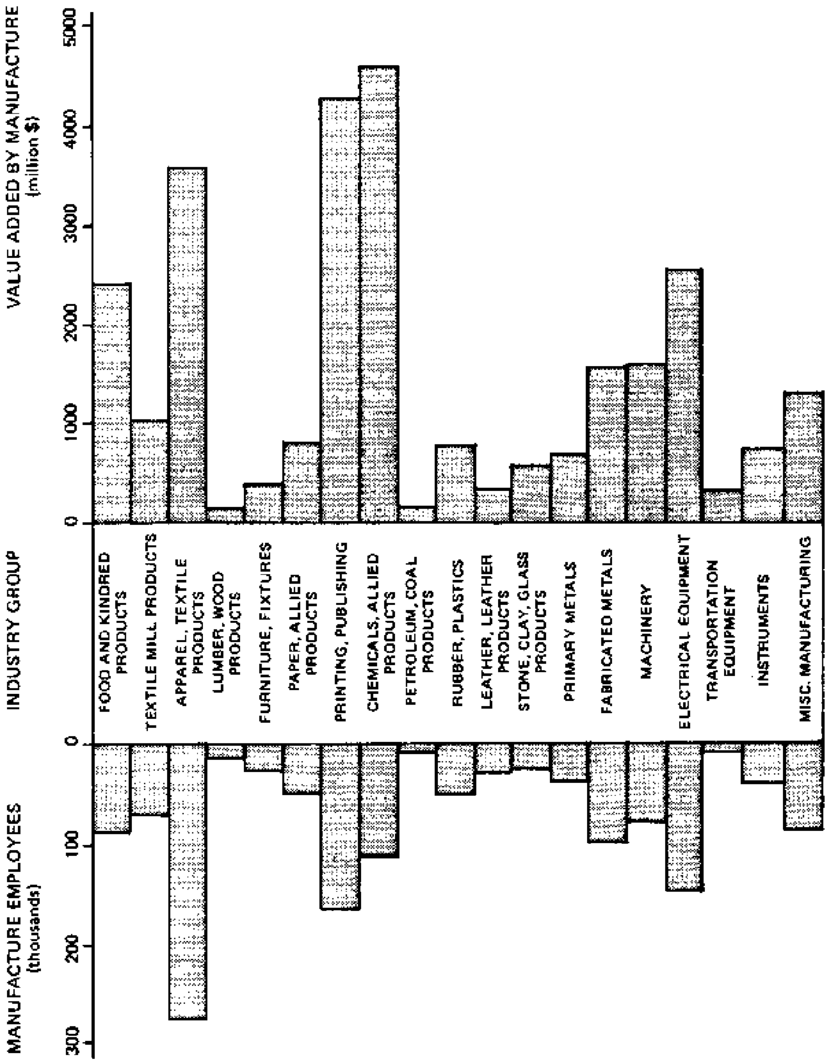

Table 2.4 Coastal Area Raw Wastewater Characteristics

AREA DESCRIPTION

Location	New York City	Northern New Jersey	Southern California: Los Angeles City	Southern California: Los Angeles County
# Plants	11	3-5	1 (Hyperion)	1 (JWPCP)
Year of data base	1972	1972	1971-1974	1975-1977
Total Population	7,000,000	2,800,000	3,000,000	3,000,000
Total flow, m^3/s	49.5	20.4	14.8	15.0
Average per capita flow	0.61 m^3/cap-d	0.62 m^3/cap-d	0.43	0.44

WASTE CHARACTERISTICS (Concentrations in mg/l)

Parameter	New York City	Northern New Jersey	Los Angeles City	Los Angeles County
SS	139	294	251	457
BOD_5	131	364	253	314
Oil & Grease	36	100	--	57
NH_3-N	10.6	27	19.3	--
Org-N	10.4	--	15.6	--
Total-N	21.7	--	35.1	70*
Total-P	4.7	9.4	9.4	14*
As	--	--	0.015	0.035
Cd	0.018	0.035	0.026	0.04
Cr	0.15	0.51	0.57	0.89
Cu	0.23	0.53	0.37	0.64
Fe	2.5	--	1.88	--
Pb	0.26	0.52	0.092	0.37
Hg	--	--	0.0045	0.0012
Ni	--	--	0.25	0.28
Ag	--	--	0.025	0.01
Zn	0.39	1.79	0.58	2.0
T.coli $\frac{\text{MPN}}{\text{100 ml}}$	20×10^6			$>54 \times 10^6$
F.coli $\frac{\text{MPN}}{\text{100 ml}}$	3×10^6			$>32 \times 10^6$

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*Estimated value, based on reported effluent concentrations and removal efficiencies.

Sources: Mueller et al. (1976), Anderson and Mueller (in press) Hydroscience, Inc. (1978c).
Ohara (1978), Miele (1978), Parkhurst et al. (1976), County Sanitation Districts of Los Angeles County (1974), Haug et al. (1977), Dryden (1978).

The ranges of metal concentrations in the raw sewage of 103 municipalities are shown in Figure 2.2. A comparison of these ranges with the data for several industrialized coastal cities (Table 2.4) indicates these cities have wastewaters that have significantly higher raw sewage concentrations than the national median.

The overall percentage of the flow contributed to municipal system by industrial discharges has been estimated as 3 percent for New York City and 34 percent for northern New Jersey (Mueller and Anderson, 1978). However, the fraction of the mass loads of specific compounds, such as the heavy metals, is much greater due to the higher concentrations of the industrial dischargers. Table 2.5 indicates that the industrial contribution of metals to the coastal cities varies from a low of 19 percent for copper in New York City to greater than 99 percent for the same metal in northern New Jersey.

Concentrations of toxic organics in municipal waste streams are not as well defined as for metals. This is primarily because of the large numbers of such compounds, the cost and technology required for analysis, and concern about these compounds is relatively recent. An estimate of some toxic organic substances in wastewater influents is given however in Table 2.6. As would be expected, highly industrialized municipalities are seen to contain toxic organic concentrations about an order of magnitude greater than residential areas.

UNIT PROCESSES FOR TREATMENT OF MUNICIPAL WASTEWATER

From the time wastewater treatment began in this country to the early 1960s, designers used a few, traditional, relatively standard treatment operations. These were combined stepwise, as needed to produce the desired effluent quality. Although treatment processes gradually improved with time, there was litte engineering evaluation of changes in the standard design to improve waste treatment at specific plants. Now the approach to sewage treatment is to engineer processing systems individually for cities and industries. Modern designs are flexibile to account for future changes in effluent quality requirements and plant capacity. Some of the treatment process combinations used in coastal plants that employ ocean disposal are reviewed below. These

Figure 2.2 Range of metals concentrations in raw sewage of 103 municipalities (USEPA, 1978).

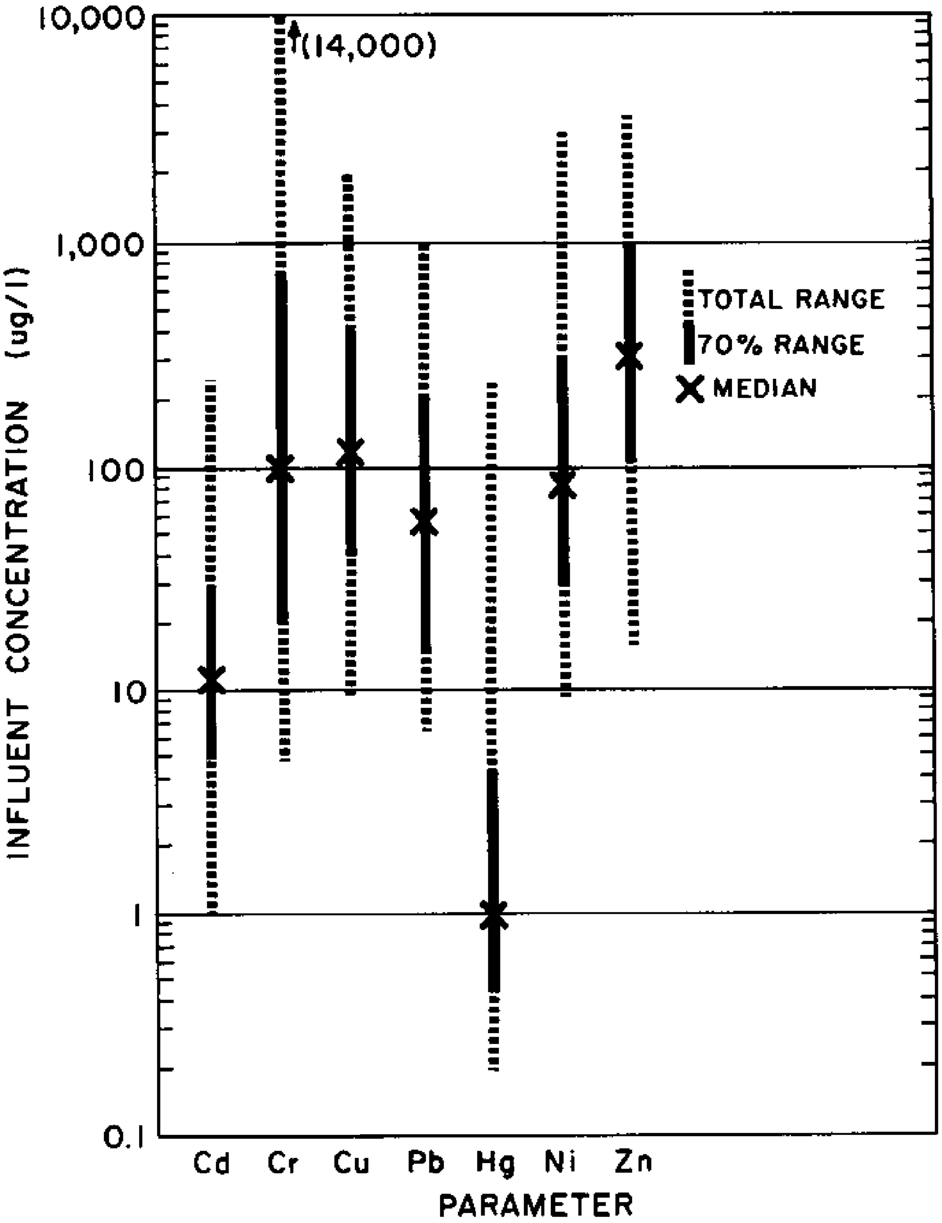

Table 2.5 Industrial Contribution of Heavy Metals to Coastal Municipal Wastewaters

Parameter	% Industrial Contribution		
	Los Angeles[1] JWPCP	Middlesex Co.[2] Northern N.J.	New York City[3]
As	47	-	-
Cd	86	53	39
Cr	88	93	52
Cu	76	>99	19
Pb	75	74	-
Hg	60	-	-
Ni	85	-	-
Ag	73	-	-
Zn	84	65	20
Flow	25	34	3

[1] Eason et al. (1978). Values are Controllable Industrial Percentage, CN = 93% Industrial.

[2] Mueller and Anderson (1978).

[3] Klein, et al. (1974).

Table 2.6 Toxic Organic Concentrations in Wastewater Influents

Parameter	Treatment Plants	Average Values		Range	Ref.
		Concentration (µg/l)	Load (mg/cap-d)	Concentration (µg/l)	
PCB	33 Ontario, Canada plants	0.6	0.42	<0.1-1.8	1
PCB	4 Ontario industrial cities (Toronto, Hamilton, Ottawa, Windsor)	0.88	0.62	0.3-1.8	1
PCB	3 Ontario domestic cities (Waterdown, Newmarket, Grimsby)	<0.20	<0.09	<0.1-0.4	1
PCB	Cedarburg, Wisconsin industrial*	-1.2	-	0.54-3.1	2
PCB	Dayton, Ohio industrial*	-	-	<1.0-2.0	3
PCB	New York City - Northern New Jersey - 9 sampling locations	0.60	-	0.02-0.9	7
PCB	3 New York City, mainly residential plants	0.05	-	0.02-0.07	7
PCB	New York City - Northern New Jersey, 2 plants with high industrial contribution	0.21	-	0.3-0.9	7
Chloroform	Dayton, Ohio industrial*	13	-	3.5-150	3
Chloroform	Muddy Creek, Ohio residential*	1.9	-	0.7-9	3
Trichlor-ethylene	Dayton, Ohio industrial*	78	-	18-360	3
Trichlor-ethylene	Muddy Creek, Ohio residential*	0.2	-	0.2-2.3	3
TICH**	Los Angeles City	3.2	1.4	-	4
	Los Angeles County Sanitation Districts (LACSD)	21.6	-	-	5
Phenol	Los Angeles City	120	51	80-210	4
	LACSD	3,270	-	-	5
	103 POTW - nationwide	16	-	0.1-176	6
Cyanide	Los Angeles City	260	110	190-330	4
	LACSD	430	-	-	5
	103 POTW - nationwide	120	-	10-710	6

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* Grab Samples

** Total Identifiable Chlorinated Hydrocarbons

[1] Shannon et al. (1978).

[2] Dube et al. (1974).

[3] Hannah (1977).

[4] Ohara (1978), Average Yearly Value, 1971-1974.

[5] Parkhurst et al. (1976), LACSD.

[6] USEPA (1978).

[7] Hydroscience (1978d).

processes are termed "physical", "chemical" or "biological" describing the nature but not the degree of treatment.

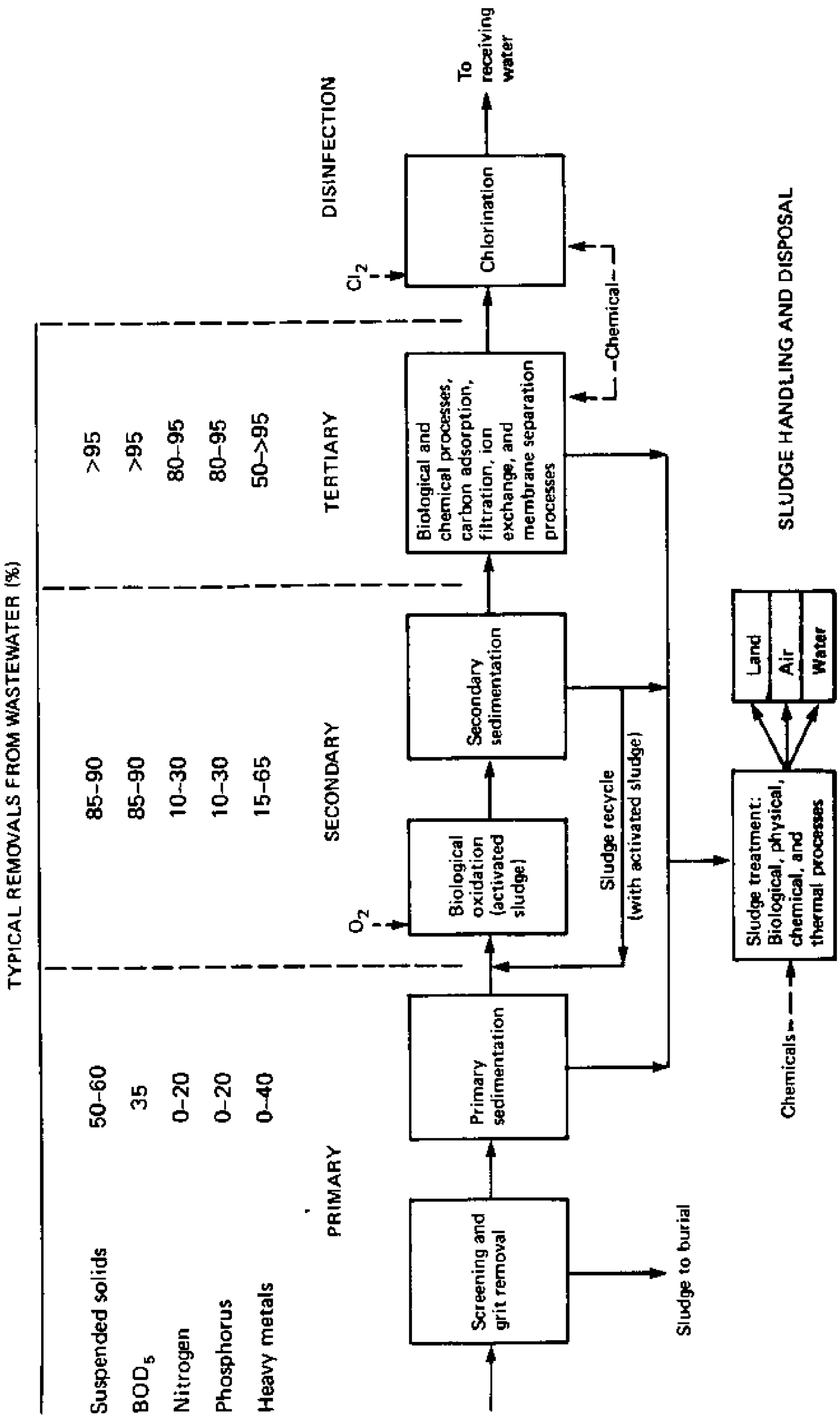
Removal of Conventional Pollutants

Figure 2.3 illustrates the traditional stepwise combination of unit operations in a treatment plant. The terms "primary," "secondary" and "tertiary" refer to the degrees of treatment provided by conventional sewage treatment plants. Primary treatment implies that a plant includes sedimentation with skimming, grit removal and sometimes further treatment of sludge. Suspended solids are allowed to settle out under the effect of gravity in sedimentation tanks; floating material is removed by skimming. A municipal plant using primary treatment can generally remove 35 percent of the BOD_5, by separating out most solids that settle or float. Heavy metals and nutrients associated with the settled solids are removed, but much of these substances may remain in the waste stream as soluble matter. Primary treatment, used alone, affords some protection to the receiving waters by reducing aesthetic impacts, some BOD_5 and sludge deposits.

Secondary treatment implies the presence of biological oxidations following primary treatment. Much of the colloidal and dissolved organic matter remaining after primary treatment of municipal sewage is biodegradable; secondary treatment will generally remove 85 percent or more of this BOD_5. Biological oxidation is usually accomplished by trickling filters, oxidation ponds, some form of activated sludge process or a combination of these. The same biological processes occur naturally in receiving waters, but treatment plants use much higher microbial populations and shorter reaction times. Tertiary treatment implies any process beyond secondary, such as filtration, carbon adsorption or demineralization. It can also refer to nutrient removal. Carbon adsorption, nutrient removal and other tertiary operations designed to remove dissolved material are rarely used with ocean disposal.

Sedimentation is used to separate grit and other incoming solids from wastewater and to separate biological or chemical solids formed in other unit operations. Most wastewater solids are too fine to be removed by screens, but will settle out in a properly designed and operated tank. Primary sedimentation is often preceded by: screening or grinding to remove

Figure 2.3 Wastewater treatment flow diagram and typical removals.



large solids; grit chambers to remove heavy inorganic solids; aeration or chlorination to mitigate odors in the plant.

Chemical addition for precipitation, adsorption or enmeshment of dissolved and colloidal matter on larger particles is generally followed by sedimentation and sometimes filtration to remove the resultant solids. In some cases, the chemical addition may take place near the sedimentation tank influent point rather than in a separate contact tank. Lime, alum, ferric chloride and organic polymers are among the chemicals commonly used.

Biological oxidation processes serving urban areas are generally either activated sludge or trickling filters, with lagoons used in rural areas where land is more abundant. Trickling filters, or biofilters, as they are sometimes called, are beds of rock or plastic media over which wastewater is distributed and allowed to trickle through to a bottom receiving channel. Heterogeneous biological growths attached to the media remove soluble organic matter, typically up to 85 percent of applied BOD_5. Air is often circulated through the biofilter. A sedimentation tank following the biofilter removes biological solids sloughed from the media. The activated sludge process, which uses a biological population suspended in the wastewater to remove dissolved organic matter, has received considerable attention in recent years. This is primarily due to the high organic removal achievable, typically 85 to 95 percent. Activated sludge involves diffusing air through the flow in large tanks, with typical hydraulic detention times from 4 to 8 hours. Bacteria suspended in the flow use the organic matter present for energy and for growth of new cells. Solids, including the active culture, are then separated from the flow in sedimentation tanks for recycling to the aeration tank. Excess cells are wasted to sludge disposal facilities. Activated sludge units generally involve more sophisticated design and operation than biofilters do.

Filtration is employed for removal of suspended or colloidal solids that remain after sedimentation. Approximately 75 percent of the suspended solids and BOD_5 that remain after primary sedimentation, biological oxidation, and secondary sedimentation can be removed by filtration through beds of sand or mixed beds of sand and coal.

The main oxygen demand remaining after secondary treatment is ammonia nitrogen, which can be oxidized to nitrate (nitrification) in the receiving water. Secondary treatment plants can be designed to nitrify, but because of organics this requires greater air quantities and detention times beyond that needed for removal of BOD_5. While nitrate is not an oxygen demanding substance, it can be deleterious to inland waters as a plant nutrient. Nitrate can be converted further to nitrogen gas by biological denitrification, which requires anoxic conditions so that nitrate will take the place of oxygen in the biological oxidation process. A significant portion of phosphorus can also be removed biologically if anaerobic conditions precede aerobic in the treatment plant. Nutrient removal, where necessary, can also be accomplished using physical-chemical operations. For example, phosphorous is typically removed by chemical precipitation, which also enhances removal of heavy metals. Ammonia nitrogen can be removed by air stripping processes in lieu of biological nitrification and denitrification. Carbon adsorption can be used to remove organic matter remaining after secondary treatment and filtration.

Following any treatment, wastewater may be disinfected with chlorine to kill disease-transmitting organisms present in the wastewater. For ocean disposal, this may be needed to protect swimming beaches and shellfish areas or other locations that could be affected by the discharge. For many ocean discharges, with properly designed outfalls, disinfection is not required. Continuous disinfection of wastewaters is still controversial because of the possibilities of toxic effects on biota in the receiving water and formation of chlorinated organics. Other disinfection techniques such as ozonation and ultraviolet radiation are being investigated, but chlorination remains the method of choice in the United States. Dechlorination of the disinfected effluent with sulfur dioxide to reduce chlorine is sometimes necessary. Table 2.7 presents data on coliform bacteria levels in effluents from various processes. While coliform data typically exhibit great variability, these values help define some ranges of removal efficiencies.

Removal of Trace Materials

The removal of trace metals and organics from municipal influents is dependent upon a number of factors, including influent forms and concentrations,

Table 2.7 Coliform Levels in Various Process Effluents Advanced Treatment Plants

	Total Coliform, #/100ml		Fecal Coliform, #/100 ml
Process Effluent	Lake Tahoe[1]	Palo Alto[2]	Palo Alto[2]
Raw	5.0×10^7	1.5×10^7	9.3×10^5
Primary	1.5×10^7	2.3×10^6	9.3×10^5
Secondary	2.5×10^6	$0.33\text{-}2.3 \times 10^6$	$0.78\text{-}4.3 \times 10^5$
High Lime Coag.	-	<2.2	<2.2

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[1] Culp and Culp (1971)

[2] Roberts (1978)

Table 2.8 Concentrations of Chromium Species in Municipal Effluents (SCCWRP, 1976)

	Dissolved Concentration, µg/l			Particulate Concentration,	Total Concentration,	Distribution	
Plant	Cr^{+3}	Cr^{+6}	Total	µg/l	µg/l	% Diss.	% Part.
				Primary Effluent			
Hyperion	48.7	0.30	53.0	87.9	141	38	62
JWPCP	14.0	0.78	15.9	746	762	2.1	98
Orange Co.	15.8	0.11	14.0	48.4	62.4	22	78
San Diego	11.7	0.08	12.7	62.2	74.9	17	83
Oxnard	10.1	0.08	13.6	26.8	40.4	34	66
				Secondary Effluent			
Hyperion, 6/75	55.6	.24	63.3	13.4	76.7	82	17
Hyperion, 11/75	48.2	.19	40.9	4.6	45.5	90	10

wastewater character, and plant design and operation. Studies indicate metal removals are generally related to solids removal except for nickel which is found largely in dissolved form (US Environmental Protection Agency (USEPA), 1978). Many of the trace organics in sewage are also associated with solids and are removed with the sedimentation. However the problem of trace toxics is not solved solely through solids removal.

The removal of metals in different municipal sewage plants is quite variable (USEPA, 1972). This is because metals are found in a number of forms in municipal sewage, including soluble or insoluble, inorganic or organic, reduced or oxidized and free metal, absorbed or complexed. For example, Table 2.8 shows data on chromium in the effluents of five treatment plants. Removal efficiencies of the soluble and particulate metals for one activated secondary sludge treatment plant are shown in Table 2.9. The effect of individual treatment processes on the removal of trace metals is further shown in Table 2.10.

Table 2.9 Concentrations, Forms and Removals of Metals at One Municipal Activated Sludge Plant (USEPA, 1978)

	Total Conc., mg/l		% Particulate		% Removal		
	Influent	Effluent	Influent	Effluent	Total	Soluble	Particulate
Cd	0.25	0.05	76	40	80	50	89
Cr	0.88	0.13	72	39	85	68	92
Cu	1.17	0.19	74	26	84	54	94
Ni	0.37	0.32	32	3.1	14	0	92
Zn	2.8	0.45	84	47	84	53	91

Trace organics can be removed by adsorption to solids or by volatilization. In biological processes they may be completely mineralized, assimilated within microbial cells, metabolized to other compounds, or left untouched. Analysis of trace organic removals is complicated by the great number of compounds in

Table 2.10 Percent Metals Removed by Various Treatment Processes

Parameter	Primary Treatment			Primary With	Chemical	Secondary Treatment		Lime Addition To Sec. Effluent
	Hyperion[1]	JWPCP[2]	EPA[3]	Polymers[4]	Primary[4,5]	LACSD	EPA[3]	WF 21[6]
As	-	35	0	-	-	-	30	40
Cd	30	20	0-8	55	75	90	10	80
Cr	38	25	26	75	80	90	52	65
Cu	35	20	25	65	80	77	70	70
Pb	20	35	24	75	80	90	46	62
Hg	22	-	27	60	75	80	50	48
Ni	8	15	6	30	20	30	9	-
Zn	31	30	30	75	80	80	71	64

[1] Hyperion Treatment Plant, City of Los Angeles 1971-74

[2] Joint Water Pollution Control Plant, County Sanitation Districts of Los Angeles County

[3] Averages for a number of plants

[4] Pilot scale studies at JWPCP

[5] Low lime, alum, or ferric chloride

[6] Water Factory 21, high lime, average of 2 periods

Sources: Ohara (1978), County Sanitation Districts of Los Angeles County (1974), USEPA (1978), McCarty et al. (1978)

sewage, the low absolute values but high variabilities of concentrations encountered, and the analytical difficulties associated with these conditions.

Removal of some halogenated organics for various treatment processes is shown in Table 2.11. Note that, except for some of the chlorination data, these values are non-cumulative and represent data from unit operations run in series. Lime coagulation following secondary treatment has little influence on the removal of trace organics. The ammonia stripping process show good removal in the study indicated, and it was suggested that the efficiencies could be attributed to air stripping or adsorption on the stripping column packing. Carbon adsorption removed smaller but significant portions of the substances. The data on chlorination provides evidence of the formation of chlorinated compounds from the interaction of chlorine and organic precursors. As noted elsewhere, these latter types of reactions are now of environmental concern.

Removal of trace organics in conventional primary and secondary treatment has not been extensively studied. However, Shannon et al. (1978) reported average removals for PCBs of 50 percent in primary plants and 66 percent in secondary plants after studying a number of Canadian plants. Dube et al. (1974) calculated PCB removal in one secondary plant at about 70 percent. Hannah (1977) found 84 percent removal of chloroform in a secondary plant.

SLUDGE TREATMENT AND DISPOSAL

Liquid treatment processes produce enough byproduct sludge so that a major portion of the total plant cost must go toward sludge treatment and ultimate disposal. Grit is primarily inorganic matter removed at the head of the treatment plant. Primary sludge consists of settleable solids from raw sewage; secondary sludge is the excess biological solids produced during biological oxidation. Sludges from advanced wastewater treatment may be biological or chemical, depending on the processes used.

Unit operations commonly employed prior to sludge disposal are thickening, dewatering, thermal conditioning and anaerobic digestion. Thickening, by gravity or air flotation, removes approximately 90 percent of the water from sludge, leaving total solids of 4 to 10 percent. The most common sludge stabilization process for large coastal municipalities

Table 2.11 Trace Organic Behavior Through Various Treatment Processes (Roberts, 1978 and Hannah, 1977)

	Lime Coagulation[2]		Ammonia Stripping		Carbon Adsorption		Chlorination	
	Influent μg/l	% Removal[3]	Influent μg/l	% Removal[3]	Influent μg/l	% Removal[3]	Influent μg/l	% Removal[3]
Chlorobenzene[1]	0.03	(-1300)	0.07-0.43	71-94	-	-	0.026	(-220)
1,2-dichlorobenzene	1.62	1	1.60-4.46	98-99	-	-	0.035	(-94)
1,3-dichlorobenzene	2.52	<18	4.01	98	0.068	70	0.046	(-48)
1,4-dichlorobenzene	2.05	<33	1.49	98	-	-	0.025	(-60)
1,2,4-dichlorobenzene	3.55	<22	3.60	96	0.140	93	0.066	(-110)
Trichlorobenzene	1.88	6	1.77	98	0.055	82	0.035	(-57)
Tetrachloroethylene	5.90	<87	-	-	-	-	-	-
Methylene chloride	29	(-62)	3.4	44	1.6-27.8	56-99	1.9-6.7	(-310)-16
Chloroform	-	-	9.3	(-53)	16.3-51	60-97	0.3-14.2	(-930)-(-75)
Trichloroethylene	-	-	38	97	-	-	7.7	92
Bromodichloromethane	-	-	-	-	7.8-39	87-99	-	-

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[1] And/or o-xylene, as chlorobenzene

[2] High lime following secondary treatment

[3] Negative values indicate increases

is anaerobic digestion, where sludge is held in closed tank reactors for 20 to 30 days under anaerobic conditions. About 50 percent of the volatile solids (organic carbon) in the sludge is biologically converted to methane and carbon dioxide gas; the remainder is a biologically stable, substantially odor-free material. Prior to disposal, the sludge may be dewatered to a cake containing 20-30 percent solids by vacuum filtration, centrifugation, or a similar process. Chemical or thermal conditioning may be required prior to dewatering. Thermal conditioning is also used to further stabilize or dewater sludge prior to its use as a soil conditioner.

For coastal cities, ultimate disposal of the sludge residues may be to the air, land or water. Incineration of sludge produces both gaseous and ash byproducts. Even with the use of air cleaning devices, the poor air quality in some coastal cities makes this incineration unattractive. Ash contains the large fractions of the heavy metals removed in the treatment plant and may require disposal as a hazardous waste. After anaerobic digestion, wet sludge can be spread on crop or grazing land as a soil conditioner. Dewatered sludge can be used as compost or disposed of in a sanitary landfill. Ocean disposal of sludge requires little or no dewatering, but anaerobic digestion is generally practiced for stabilization, reduction of pathogens, and removal of aesthetically objectionable material. However, federal law currently precludes continued ocean disposal of sludge.

Secondary treatment with anaerobic sludge digestion reduces the mass loads to the environment of pathogenic bacteria, oxygen-demanding organic matter, organic carbon, and volatile suspended solids. The process does not, however, modify very much the total discharge of nitrogen, phosphorus, and heavy metals, although it does affect their ultimate fates. The removal rates of these relatively conservative materials from the wastewater effluents merely reflect the quantities discharged in the sludge.

PRETREATMENT AND SOURCE CONTROL EFFECTIVENESS

While industrial effluents discharged directly to water bodies have been subject to regulation for some time, industrial inputs to municipal sewer systems have received attention only relatively recently. Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) authorized EPA to develop and enforce standards for pretreatment of industrial wastes before discharge to municipal systems. These standards will control the discharge of toxic materials and other pollutants that may interfere with, pass through or otherwise demonstrate incompatibility with municipal treatment facilities. Further, the recycling of wastewater and sludge may be facilitated by prior removal of certain contaminants.

Standards, based on available treatment technology, are being developed for 21 industrial categories of greatest environmental concern (Table 2.12). EPA recently redefined these 21 industries into 34 categories. As of January 1981, 13 categories had some regulations promulgated, with those for electroplating partially out in final form. Compliance is required at least three years after the standards are promulgated. For example, pretreatment standards for the electroplating industry, a significant contributor of heavy metals to municipal sewers, are given in Table 2.13. Although some municipalities have standards more stringent than the above, (USEPA, 1978), many heavily industrialized coastal areas do not. For comparison, standards for two large coastal plants in southern California are also shown in Table 2.13.

Industrial waste pretreatment does not eliminate discharge of toxic materials to the environment. For conservative materials such as metals, pretreatment by chemical precipitation at individual industrial sites removes a significant amount of contaminants from the liquid waste discharge, leaving the metals concentrated in an industrial sludge. Ultimate disposal of this waste sludge redistributes the metals to other parts of the environment. A number of cities have experience with the effectiveness of pretreatment programs in reducing industrial contaminant discharges to the municipal wastewater, thus improving the quality of effluent and sludge discharged from the municipal plant. Five years after instituting control measures, the metals concentrations in Chicago's sludge were reduced from 35 to 92 percent (Table 2.14). Effluent metals concentrations were also significantly reduced during this period (Zenz et al., 1975), with cadmium reduced from 0.01 mg/l to near zero and zinc reduced 74 percent from approximately 0.27 mg/l to 0.07 mg/l. Los Angeles County Sanitation Districts (LACSD) has instituted Phase I standards based on good housekeeping procedures for electroplaters. Table 2.15 shows that reductions in raw sewage metals concentrations ranging from 0 to 40 percent resulted from these standards, implemented

Table 2.12 Industrial Categories Subject to Setting of Pretreatment Standards

Automatic and Other Laundries
Coal Mining
Electroplating*
Inorganic Chemicals Manufacturing*
Iron and Steel Manufacturing
Leather Tanning and Finishing*
Machinery and Mechanical Products Manufacturing
Miscellaneous Chemicals Manufacturing
Nonferrous Metals Manufacturing*
Ore Mining
Organic Chemicals Manufacturing
Paint and Ink Formulation Printing
Paving and Roofing Materials
Petroleum Refining*
Plastic and Synthetic Materials Manufacturing
Pulp and Paperboard Mills and Converted Paper Products
Rubber Processing
Soap and Detergent Manufacturing
Steam Electric Power Plants*
Textile Mills*
Timber Products Processing*

*Interim standards promulgated.

Source: Federal Register 40 CFR 403, 26 June 1978

Table 2.13 Pretreatment Standards for Electroplaters

	Allowable Concentration in Industrial Discharge (mg/l)		LACSD[b]	OCSD[c]	
	Maximum for Any Day[a] (EPA)[a]	Average 4-Day Value[a] (EPA)[a]	Phase I	July 1 1978	July 1 1983
Cadmium	1.2	0.70	15	3.0	1.0
Chromium	7.0	4.0	10	2.0	0.5
Copper	4.5	2.7	15	4.0	2.0
Cyanide	1.9	1.0	10	5.0	5.0
Lead	0.6	0.4	40	2.0	2.0
Nickel	4.1	2.6	12	10.0	10.0
Zinc	4.2	2.6	25	10.0	10.0
Total Metals	10.5	6.8	-	-	-

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[a] Federal Register, Volume 45, No. 130, July 3, 1980; Electroplaters (common metals subcategory) discharging over 10,000 gpd.

[b] Los Angeles County Sanitation Districts

[c] Orange County Sanitation Districts, California

Table 2.14 Effect of the Chicago Metropolitan Sanitary District Sewage and Waste Control Ordinance on Metal Content of the Calumet Sewage Treatment Plant Sludge (Zenz et al., 1975).

Metal	Maximum Allowable Concentration in Incoming Sewage by MSDGC Ordinance, 1969 (mg/l)	Concentration in Sludge Source: Lagoons Before 1969 (µg/g dry weight basis)	Concentration in Sludge Source: Anaerobic Digester 1972 (µg/g dry weight basis)	Concentration in Sludge Source: Anaerobic Digester 1974 (µg/g dry weight basis)	Percent Reduction in Sludge, 1969 - 1974
Cd	2.0	190	100	54	72
Cr (Total)	25.0	2100	1100	790	62
Cu	3.0	1500	900	282	81
Fe	50.0	53700	36800	24200	55
Hg	0.0005	3.3	3.0	2.15	35
Ni	10.0	1000	200	77	92
Pb	0.5	1800	1800	486	73
Zn	15.0	5500	3500	2800	49

Table 2.15 Effect of Source Control of Toxic Pollutants for Los Angeles County Sanitation Districts

Constituent	Phase I Industrial Wastewater Effluent Limitation (mg/l)	Concentration in Raw Sewage at JWPCP (mg/l) Prior to Source Control Jan. 75-Sept. 76	 After Source Control Jan. 77-Dec. 78	Percent Reduction
Arsenic	3	-	0.010	-
Cadmium	15	0.033	0.028	15
Chromium (Total)	10	0.71	.37	48
Copper	15	0.42	0.255	39
Cyanide (Total)	10	0.31	0.21	33
Lead	40	0.33	0.19	44
Mercury	2	-	0.0012	-
Nickel	12	0.33	0.255	23
Silver	5	-	0.011	-
Zinc	25	1.45	0.89	36
TICH	None	-	-	-

DDT in JWPCP Effluent

DDT	Before Source Control Dec. 69-April 70*	After Source Control 1971	 1972	 1973	 1974	 1975	 1976	Percent Reduction 1969-1976
Concentration, µg/l	182	42	<12.9	7.5	3.0	2.3	1.9	99
Mass emission rate kg/yr	93,000	21,500	<6000	3720	1440	<1100	940	99

*Before control of major industrial discharge

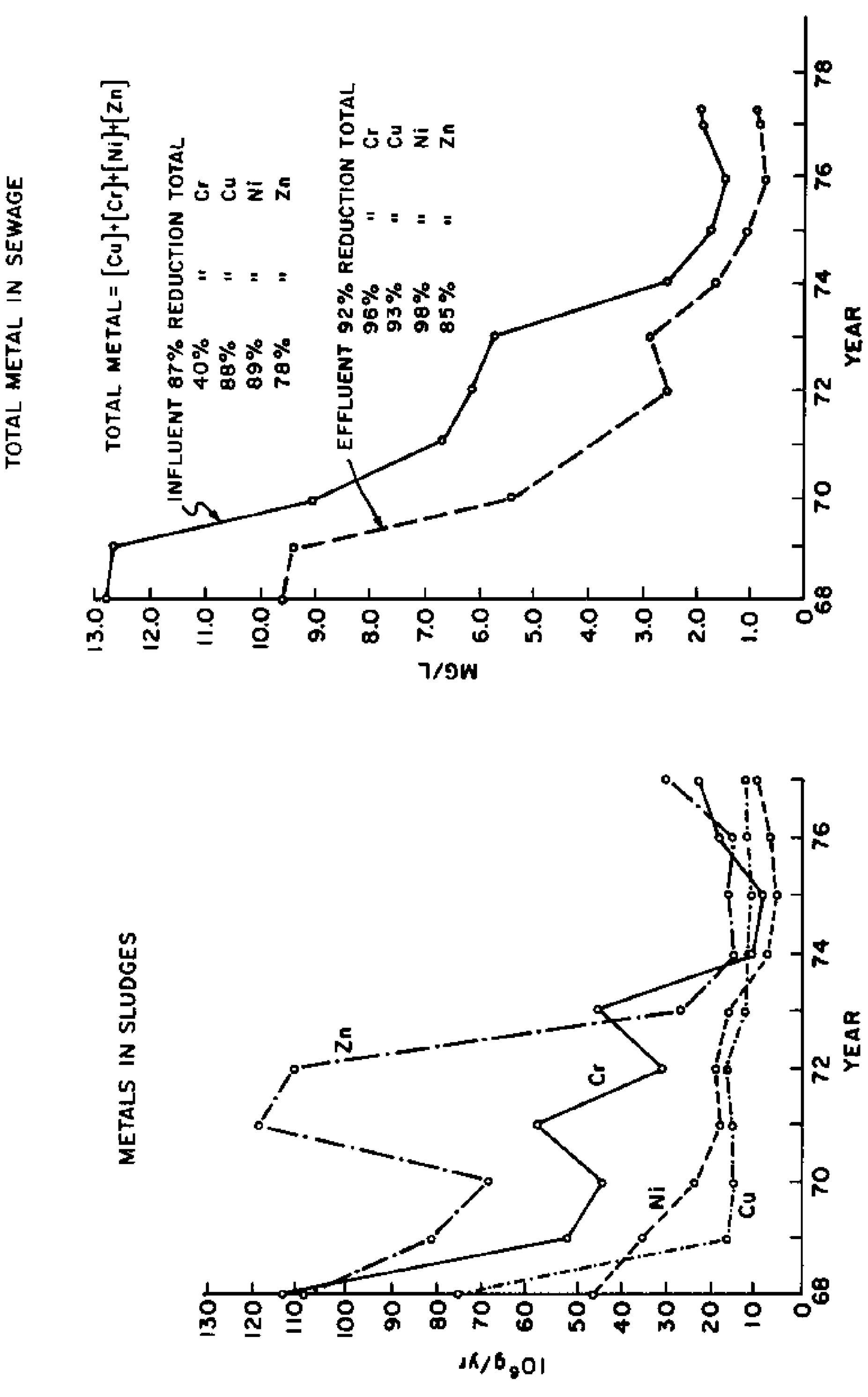
Sources: Eason et al. (1976); SCCWRP Annual Reports (1973-1979); Ackerman, 1979.

with minimum cost to industry. LACSD has also had experience with control of large industrial point sources of DDT. After stopping waste discharge of DDT from one of the largest manufacturers of this product worldwide, effluent concentrations from the treatment plant decreased two orders of magnitude in a six-year period.

In 1969, Grand Rapids, Michigan adopted standards for electroplaters. This area contains one of the largest concentrations of this industry in the country. Figure 2.4 shows the significant reductions that were achieved for several metals through this action alone. The increase in zinc concentration in 1972 is due to air pollution control requirements forcing brass foundries to install scrubbers to remove zinc oxide from stack gases which was subsequently discharged to the sanitary sewer system. Pretreatment of scrubber flows reversed the trend by 1973. Grand Rapids is presently experiencing a difficulty disposing of the chemically precipitated sludges generated during pretreatment of industrial wastewaters. Partial disposal into solid waste sanitary landfills and an abandoned gravel pit led to metals migrating into the groundwater. Both of these disposal operations have been discontinued; now most of the sludge is being hauled out of the state for disposal. Although a local site meets the criteria for licensing as an industrial sludge disposal facility, public reaction has blocked its use. Such institutional problems are becoming the norm.

The future effectiveness of pretreatment and source control will depend on the regulations and the industrial fraction of pollutants handled by specific municipalities. The effect on the heavily industrialized coastal communities will be to significantly improve wastewater and sludge quality. However, where industrial input is less, such as in New York City, a smaller change in quality will result. A study conducted by the Department of Commerce (Washington Notebook, 1978) on New York City indicates that enforcement of the pretreatment program proposed at that time in New York City would cost about $750,000 annually and would close 59 of the 180 electroplating firms in the city. The study concludes that the program costs would be high and benefits minimal due to discharges of metals from other sources to New York Harbor.

Figure 2.4 Effect of source control on Grand Rapids Michigan treatment plant wastewater and sludge metal concentrations (USEPA, 1978).



ALTERNATIVE TREATMENT STRATEGIES

In this section, the cost, treatment performance, energy use and material input requirements for liquid and sludge treatment alternatives are discussed. For this analysis, a 4.4 m^3/s (100 MGD) plant is chosen, typical of the average flow to the New York City plants. Table 2.16 lists assumed wastewater influent characteristics. The chosen suspended solids and nutrient concentrations were intermediate values among the large New York City, northern New Jersey, and southern California wastewater characteristics. However, the metals and toxic organic concentrations were based on influent values after industrial waste pretreatment. The metals concentrations were taken as the maximum values after complete removal of industrial sources for three coastal areas: Los Angeles County, New York City, and Middlesex County, New Jersey. The PCB and chloroform concentrations were taken as typical of residential municipal plants.

Table 2.16 Raw Wastewater Characteristic Utilized for Evaluation of Alternative Treatment Strategies

	Concentration mg/l	Load, kg/day
Flow	4.4 m^3/s	(100 MGD)
SS	230	87,200
BOD_5	210	79,400
Total P	9	3,410
Total N	35	13,200
Organic N	15	5,680
As	.019	7.17
Cd	.014	5.31
Cr	.10	37.9
Cu	.19	71.7
Pb	.09	34.1
Hg	.0005	.189
Ni	.042	15.9
Ag	.0027	1.02
Zn	.32	121
PCB	.0002	.076
Chloroform	.002	.758
Total Coliform	5.0×10^7 MPN/100ml	---

The liquid process trains chosen for analysis are enumerated in Table 2.17. These combinations are aimed toward removal of BOD_5 and suspended solids. Nitrogen and phosphorus removals expected are also listed. No tertiary nutrient removal or organics removal operations are considered because they are rarely proposed or required for ocean discharge (although such treatment is needed for discharge to certain high quality fresh waters). The expected effect of the various treatment schemes on metals removal is summarized in Table 2.18. Toxic metals and organics are difficult to remove when present in the trace concentrations typical of most wastewaters. Relatively more costly treatment schemes are needed to remove additional metals from municipal sewage. Approximately 50 percent of the PCBs are removed by primary treatment. Tertiary treatment by carbon adsorption is needed for total removal.

Regarding coliform levels, it is observed that, although some removals occur through all treatment processes, lime treatment at high pH provides for coliform reductions similar to those obtained by disinfection. Nitrogen removal is due mainly to removal of suspended organic nitrogen via sedimentation processes with some additional removal of nitrogen resulting from the biological use of nitrogen in organism growth. Phosphorus is similarly removed; systems 2 and 3 (Table 2.17) have additional phosphorus removal by chemical precipitation.

The sludge disposal options selected for study are incineration, ocean disposal, land application, and landfill; the unit processes associated with these alternatives are indicated in Table 2.19. Table 2.20 presents estimates of the raw sludge quality from the liquid treatment processes shown in Table 2.17. These data indicate that although BOD_5 and some suspended solids are destroyed, constituents such as the metals are simply partitioned between the effluent and sludge, depending on the efficiency of removal from the liquid phase. Sludge treatment also changes its physical-chemical characteristics. Dewatering removes excess water thereby concentrating and greatly reducing the volume of sludge. Estimated changes produced by incineration and anaerobic digestion are shown in Table 2.21. Air emissions from incineration of sludge show significant volatilization of metals. Furthermore, treatment of stack gases may recycle a portion of these metals back to the liquid treatment process. Anaerobic digestion reduces sludge particle size which should enhance dispersion in ocean disposal.

Table 2.17 Alternative Treatment Strategies and Effluent Quality

System	Unit Process Combination	Suspended Solids (mg/l)	BOD_5 (mg/l)	Total Nitrogen (mg/l)	Total Phosphorus (mg/l)	Total Coliform Bacteria (MPN/100 ml)
R	Raw Sewage (see Table 2.16)	230	210	35	9	$>10^7$
1	Conventional Primary	110	140	30	8	$>10^7$
2	Alum or Ferric Chloride Primary	65	100	27	2	10^7
3	Two Stage Lime Primary	30	40	27	1	10^4
4	Conventional Primary, High-rate Activated Sludge (or Biofilter)	35	40	24	7	10^5
5	Conventional Primary, Activated Sludge	25	20	24	6	10^5
6	Conventional Primary, Activated Sludge, Filtration	5	10	19	5	10^4

Table 2.18 Expected Trace Constituent Removal (Shannon et al., 1978).

Parameter	Raw Sewage	Concentration resulting from stated process, µg/l					
	(see Table 2.16)	1	2	3	4	5	6
Cd	14	9.8	8.1	7.3	8.0	7.7	7.2
Cr	100	74	32	22	28	24	17
Cu	190	120	38	21	38	32	17
Pb	90	68	38	30	33	30	25
Hg	0.5	0.4	0.3	0.3	0.3	0.3	0.3
Ni	42	39	33	18	29	28	27
Ag	2.7	2.5	1.3	1.1	1.2	1.1	0.9
Zn	320	220	90	70	89	90	67
PCB*	0.2	0.1	0.08	0.07	0.07	0.07	0.01

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*Detection limit 0.1 µg/l

Table 2.19 Sludge Treatment Process Options

Process	Name	Stabilization	Dewatering	Incineration	Transport	Disposal
		Unit Processes				
		Conventional sludge, liquid processes 1,2,4,5,6,				
A	Incineration	-	VF	MHI	T	LF
B	Ocean disposal	AD	-	-	B	O
C	Land application	AD	-	-	P	LA
D	Landfill	AD	VF	-	T	LF
		Lime sludge, liquid process 3				
A	Incineration	-------------not applicable--				
B	Ocean disposal	-	-	-	B	O
C	Land application	-	VF*	-	T	LA
D	Landfill	-	VF*	-	T	LF

AD = anaerobic digestion
B = barge
LA = land application
LF = landfill

O = ocean
MHI = multiple hearth incineration
P = pipeline
T = truck
VF = vacuum filter

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*sludge dewatered prior to recalcination or wasting, costs included in liquid process costs.

Table 2.20 Sludge Quality, 4.4 m^3/S (100 MGD) Plant

	Sludge Loads From Liquid Process Number:					
Parameter	1	2	3	4	5	6
Volume, m^3/day	570	2000	600	1300	1400	1400
% Solids	8	4	30	5	5	5
% Volatile Solids	60	46	-	66	67	67
	Loads, 10^6 g/day					
Solids	45	81	180	64	68	68
BOD	26	42	64	35*	38*	38*
Total P	0.4	2.7	3.1	0.7	0.9	1.2
Total N	1.9	3.1	3.2	4.2	4.2	6.1
	Loads, 10^3 g/day					
Cd	1.6	2.2	2.5	2.3	2.4	2.6
Cr	10	26	30	27	29	31
Cu	25	59	64	59	59	64
Pb	8.2	20	23	21	23	24
Hg	0.04	0.09	0.09	0.09	0.09	0.09
Ni	0.95	3.5	9.1	5.0	5.4	5.9
Ag	0.09	0.50	0.64	0.59	0.64	0.68
Zn	38	86	95	86	86	95
PCB	0.04	0.04	0.04	0.04	0.04	0.09

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*For non-chemical portion of sludge calculated from ratio BOD/SS for Wards Island undigested sludge, Mueller et al. (1976).

Table 2.21 Effects of Treatment on Non-Chemical Sludges

A. INCINERATION[1]

Ash produced 30% dry weight of raw sludge.

Parameter	Air Emissions, g/kg dry sludge Uncontrolled	After Scrubber
Particulate	50	1.5
SO_2	0.5	0.4
CO	neg	neg
NO_x (as NO_2)	3	2.5
H_xC_y	0.75	0.5
H Cl	0.75	0.15

Parameter	Average % of Metals in Raw Sludge Emitted to Air - Uncontrolled
Cd	38
Cr	61
Cu	27
Pb	75
Hg	100
Ag	66
Zn	18

B. DIGESTION

55% of volatile solids destroyed during digestion.[2]

	% of Sludge Particles Passing Sieve Number (Size, mm):[3] 30 (0.59)	50 (0.297)	100 (0.149)	200 (0.074)	270 (0.053)
raw	53	51	49	47	46
digested	95	93	91	88	83

---

[1] Metcalf and Eddy, Inc. (1976)

[2] USEPA (1974)

[3] Garber et al. (1975)

Comparisons of effluent and sludge quality for the hypothetical pretreatment case and from actual plants are shown in Tables 2.22 and 2.23. Table 2.22 includes values for primary treatment and Table 2.23 represents secondary treatment. The effect of pretreatment is seen in the lower concentrations of metals in the effluents and sludges derived from a pretreated influent. If pretreatment programs are not effective, values closer to the actual plant data shown would be expected in highly industrialized coastal areas.

It should be kept in mind that for conservative materials, such as heavy metals, industrial pretreatment does not eliminate but apportions. That is, it can be used to change the concentration, character, and location of the contaminant discharge, but not total discharge into the environment. The actual recovery and recycling of material within the manufacturing plant is, however, an important concept because here actual reductions in mass loading can be realized.

COSTS AND ENERGY REQUIREMENTS OF TREATMENT ALTERNATIVES

Capital cost data were taken from two sources (Culp, Wesner, Culp, 1980; Dames and Moore, 1978) and were adjusted to fourth quarter 1980 values using an Engineering News-Record Construction Cost Index (ENR) of 3300. All treatment schemes include raw pumping and preliminary treatment (bar screens, comminutors, grit removal, and flow metering). Processes with lime addition include dewatering and recalcination of lime sludge. Capital expenses are amortized over 20 years at 10 $^1/_4$ percent, a 1980 cost of money to the US Treasury (Federal Register, 1980). The useful life of structures is 30 years, and of mechanical equipment is 15 years. Straight-line depreciation is used. All treatment plant costs are assumed to be 35 percent structures and 65 percent mechanical equipment.

Figure 2.5 presents total annual costs of the various process trains in relation to the percent of suspended solids they will remove. As noted in Table 2.17, BOD_5 removal is closely related to the suspended solids removal. The bases of the costs in Figure 2.5 are described in Table 2.24.

Capital costs for plant and equipment vary up to 20 percent, or more, between different parts of the United States. For example, the location indices

Table 2.22 Primary Effluent and Sludge Quality With and Without Pretreatment

Parameter	Primary Effluent Concentration, mg/l			Primary Sludge Concentration, mg/l		
	Pretreat[1]	MCSA[2]	JWPCP[3]	Pretreat[1]	MCSA[4]	JWPCP[5]
SS	110	74	259	54,000	55,000	33,000
BOD	140	250	226	---	17,300	---
Total P	8.1	12	15	630	430	---
Total N	30	35	77	3,500	1,130	---
	Concentration, μg/l			Concentration, μg/l		
Cd	9.8	18	27	2,900	5,300	3,300
Cr	74	240	720	18,000	14,500	78,000
Cu	120	140	470	46,000	40,000	54,000
Pb	68	240	210	15,000	21,000	39,000
Hg	0.4	---	1.2	93	1,200	160
Ni	39	---	310	1,750	6,400	14,000
Ag	2.5	---	10	150	---	1,500
Zn	220	650	1780	69,000	134,000	190,000
PCB*	0.10	1.70	4.4	69	341[6]	---

---

[1] Expected quality for good pretreatment program in conjunction with treatment #1 (hypothetical 100 MGD plant)

[2] Middlesex County Sewerage Authority, Sayreville, NJ data 1970-72, Mueller et al. (1976), Anderson and Mueller (in press), PCB data 1978 Hydroscience, Inc. (1978d).

[3] 1973 averages, Joint Water Pollution Control Plant, County Sanitation Districts of Los Angeles County (1974), SCCWRP (1974-77).

[4] 1973 undigested sludge, Mueller et al. (1976)

[5] 1974 weekly average digested sludge, LA/OMA Project (1977)

[6] Data from PVSC plant, West (1976)

Table 2.23 Secondary Effluent and Sludge Quality With and Without Pretreatment

Parameter	Secondary Effluent Concentration, mg/l			Combined Primary and Secondary Digested Sludge Concentration, mg/l		
	Pretreat[1]	New York[2]	Hyperion[3,5]	Pretreat[1]	New York[2]	Hyperion[4,5]
SS	25	43	8	36,000	28,700	20,000
BOD	20	36	9	---	8,970	---
Total P	6	3.3	2.8	800	440	520
Total N	24	22	13	3,500	1,880	2,110
	Concentration, µg/l			Concentration, µg/l		
Cd	7.7	10	10	2,000	3,100-6,130	3,100
Cr	24	80	110	24,000	38,000	50,000
Cu	32	150	80	50,000	60,000	46,000
Pb	30	190	60	19,000	52,000	11,000
Hg	0.3	---	1.7	66	---	230
Ni	28	100	150	4,400	9,100	10,000
Ag	1.1	---	10	510	---	2,900
Zn	90	260	180	73,000	85,000	76,000
PCB*	0.07	0.10	.35	78	72	40

---

[1] Expected quality for good pretreatment program in conjunction with treatment #5 (hypothetical 100 MGD plant)

[2] Average of New York City Plants, Mueller et al. (1976), Klein et al. (1974), Hydroscience, Inc. (1978d), West (1976), Stanford (1978).

[3] Hyperion Plant, City of Los Angeles, 1971-74 data, Ohara (1978).

[4] Hyperion Plant, City of Los Angeles, Garber et al. (1975). Secondary treatment applied to only 29 percent of flow, therefore, sludge is predominantly primary.

[5] SCCWP 1975, 1976 for PCB data.

Figure 2.5a Treatment costs as a function of suspended solids removal.

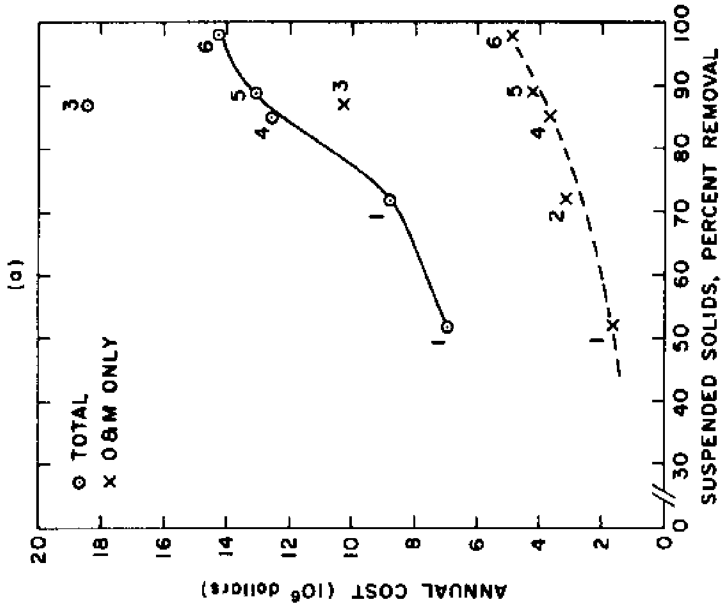

Figure 2.5b Treatment costs as a function of BOD_5 removal.

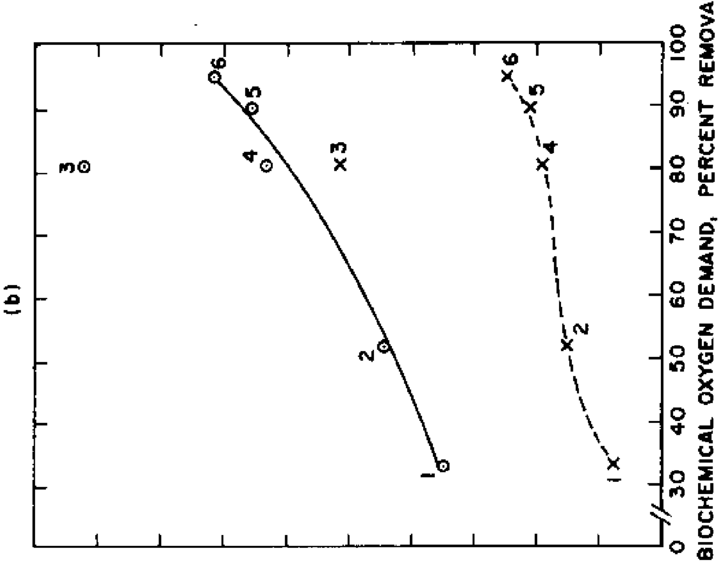

Table 2.24 Estimated 1980 Costs of Sewage Treatment for 100 MGD Plant[a]

Plant Type	Capital Cost of Treatment Facilities (million dollars)		
	Liquid	Sludge	Total
1. Primary	28	13	41
2. Alum primary	35	10	45
3. Lime Primary	39	25	64
4. High-rate secondary	49	20	69
5. Conventional secondary	49	20	69
6. Secondary with filtration	57	20	77

	Annual Costs (million dollars/yr.)				
	Liquid		Sludge		
	Capital	O&M[b]	Capital	O&M[b]	Total
1. Primary	3.5	1.3	1.7	0.5	7.0
2. Alum primary	4.5	2.4	1.3	0.7	8.9
3. Lime Primary	5.0	9.7	3.2	0.6	18.5
4. High-rate secondary	6.3	2.8	2.5	1.0	12.6
5. Conventional secondary	6.3	3.3	2.5	1.0	13.1
6. Secondary with filtration	7.3	4.0	2.5	1.0	14.3

---

[a] Dames & Moore (1978a); Culp, Wesner, Culp (1979); Dames & Moore (1978b)

[b] Operation and Maintenance

published in McGraw Hill's Dodge Guide to Public Works and Heavy Construction Costs for early 1980 for San Francisco, New York and Houston were 1.14, 1.08 and 0.92, respectively. Costs presented above are "national average" estimates, which have a value of 1.00 on that scale.

Wastewater treatment plants also exhibit economies of scale. That is, the cost of constructing two 50 MGD plants is greater than the cost of one 100 MGD plant. Data in a recent analysis of actual construction costs for wastewater plants from 0.02 to 60 MGD indicate that cost is a function of capacity in the form:

$$\text{cost} = (\text{constant}) \times (\text{capacity})^{b},$$

where b is in the range of 0.65 to 0.90, depending on the geographical area and capacity range of interest (Dames and Moore, 1978).

Electrical energy used directly in the treatment plant to operate motors, lights, etc., was derived from the literature (Culp, Wesner, Culp 1977b; Smith 1973; Metcalf and Eddy, Inc. 1976). Representative values are shown in Figure 2.6. Processes, which include aeration for biological treatment (systems 5 and 6 in the figure), are seen to require generally more electrical power due to compressor operation. However, when the energy associated with on site fossil fuel use (South Tahoe Public Utility District 1971) and the off site production of chemicals (Haug et al. 1977; Ohara 1978) is included in the comparison, another situation is uncovered. The major portion of the energy use for the lime process (system 3) is due to the production energy associated with the makeup lime and the on site recalcination of the lime sludge for reuse. The balance between these two functions, purchasing lime and recalcinating, can be adjusted with little change in the net energy use because the unit energy of the operations are approximately equal.

Typical land requirements of 4.4 m^3/s (100 MGD) treatment plants utilizing the various process trains are shown in Figure 2.7 as a function of suspended solids (SS) removal. The area needed increases rapidly with treatment efficiency beyond 80 to 90 percent removal.

Table 2.25 presents costs, energy use, chemical use, and land requirements for chlorine disinfection. To ascertain the economic impact of chlorination these

Figure 2.6 Energy use by liquid treatment process. (Total energy consumption consists of on-site electrical energy use plus fossil fuel and indirect energy for production of chemicals used.)

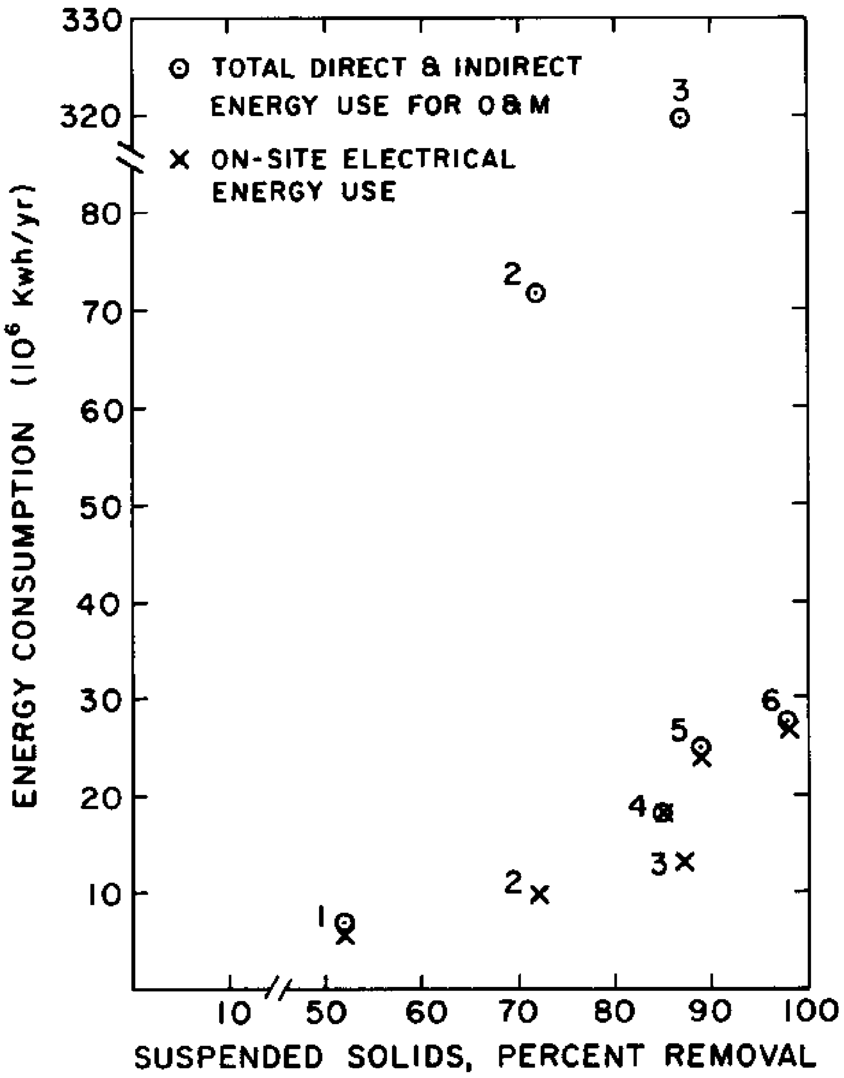

Figure 2.7 Land requirements for liquid treatment process.

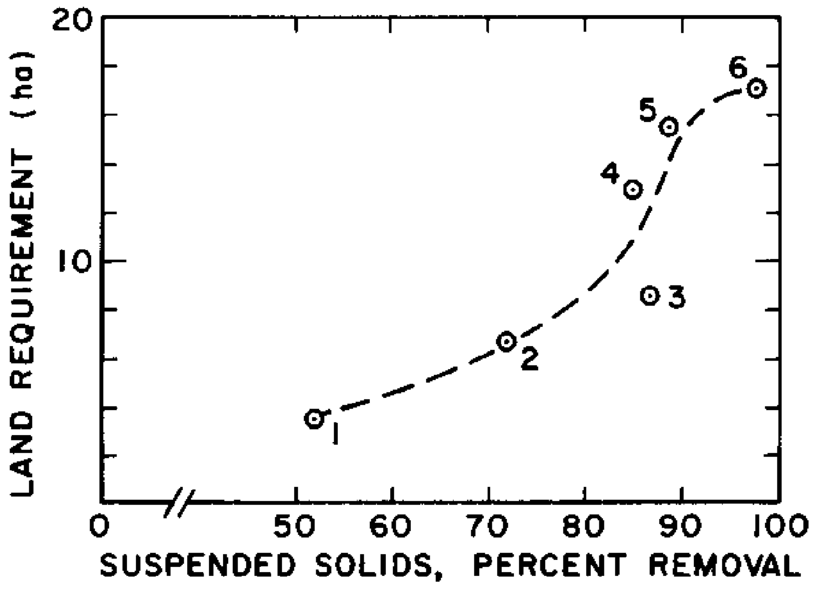

Table 2.25 Treatment Process Modifications for Chlorine Disinfection 4.4 m^3/S (100 MGD) Plant

	Additional Cost $\$10^6$/year			Additional Energy, 10^6 Kwh/year			Quantity Chlorine
Process[1]	Captial	O&M	Total	Electric	Indirect	Total	10^6 g/day
1,2	0.12	1.28	1.40	2.1	9.1	11.2	7.5
4,5	0.12	0.61	0.73	1.0	4.6	5.6	3.8
3,6	0.12	0.33	0.45	0.5	2.3	2.8	1.9

---

[1] Refer to Table 2.17.

==

costs may be compared to Figure 2.5 and Table 2.24 costs. Note that the amount of chlorine needed for disinfection, and hence the cost and energy associated with it, decreases with increasing levels of treatment prior to disinfection. Processes using lime to produce high pH values of 11 and above may require no further disinfection because of the high pH disinfecting properties.

Costs for the selected sludge treatment options in Table 2.19 relative to the various liquid process schemes were developed from the literature (Metcalf and Eddy, Inc. 1976; Culp, Wesner, Culp 1977a; Haug et al., 1977). The costs of incineration are also representative of pyrolysis (Camp, Dresser & McKee, 1975) and composting costs are of the same order as landfill (National Research Council, 1978). Costs for two processes, a lime addition and a biological process, are illustrated in Figure 2.8. Because of the great amount of sludge generated, the lime process is shown to be highly sensitive to transport factors. Costs for land treatment of lime sludge, including 130 km transport, are significantly greater than comparable costs for treatment of biological sludge. A cost and resource use listing for the four options evaluated is shown in Table 2.26. For comparison, unit costs for disposal alternatives recommended by a six-year sludge management study in the Los Angeles/Orange County area are presented in Table 2.27.

Figure 2.8
Total annual sludge treatment costs for two liquid treatment options.

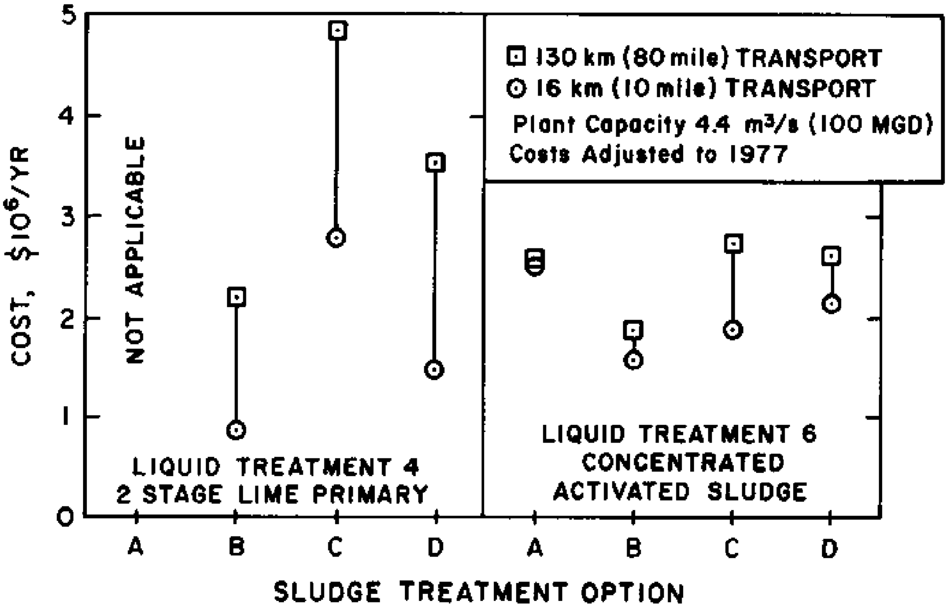

Table 2.26 Characteristics of Sludge Processes for Selected Liquid Processes 4.4 m^3/s (100 MGD) Plant, 16 km Sludge Transport

Liquid Process	Sludge Process	Cost		Energy Use[2]	Chemical Use	Plant Site Land Required, ha
		$\$10^6/yr$	$\$/10^6 g$	10^6 kwh/yr	10^6 g/day	
1	A	2.2	124	51	4.9	0.93
	B	1.4	84	-2.7	5.5	2.6
	C	1.7	106	-2.6	5.5	2.6
	D	1.9	115	5.0	11	3.1
3	B[1]	1.1	16	0	0	0
	C	3.5	52	9.5	0	0
	D	1.9	27	9.5	0	0
5	A	3.2	124	79	10	1.4
	B	2.0	79	-5.1	9.9	3.8
	C	2.4	95	-5.0	9.9	3.8
	D	2.7	108	9.5	22	4.5

---

[1] Assumes waste sludge not dewatered.

[2] Does not include barging, land application, or landfill operation energy.

Table 2.27 Projected Los Angeles Area Sludge Disposal Costs*

Alternative	Net Disposal Cost	
	$/ton (dry solids)	$\$/10^6$ g (dry solids)
Truck dewatered sludge to landfill	59	65
Dewatering and composting	62	68
Energy recovery from sludge	67	74

Source: LA/OMA Project (1980) Draft Facilities Plan/Program, Whittier, CA

*For full secondary treatment.

SUMMARY AND CONCLUSIONS

This chapter evaluates the municipal wastewater characteristics of large coastal treatment plants for both the east and west coasts of the United States. The raw wastewater concentrations show significant variability among the municipalities due mainly to variations in industrial contributions. The ability of industrial waste pretreatment or source control to significantly reduce toxic constituents in coastal municipal wastewaters is evaluated. Based on this evaluation, the future municipal wastewater characteristics for a large coastal community are selected providing a basis for quantitative evaluation of municipal wastewater treatment processes.

Six wastewater treatment processes are analyzed for their efficiency in removing fourteen constituents from the wastewater prior to discharge. Four techniques are evaluated for ultimate disposal of the sludges generated in each of the processes. Yearly costs and energy utilization along with the required land area are estimated for each process. Finally the processes are compared on the basis of marginal costs for suspended solids removal.

The following conclusions have been reached in this chapter:

1. If effective industrial pretreatment is practiced in the future, reduction of 20 to over 90 percent of the metals discharged to coastal municipal systems will result, the magnitude for specific locations being dependent on the degree of industrial development and specific metal. This will provide significant improvement in the quality of the sludge and effluent discharged from municipal systems. However, the large scale disposal, in an environmentally acceptable and economical manner, of industrial pretreatment sludges generated from numerous sources remains to be demonstrated.

2. Biological treatment is significantly more cost effective and less energy intensive than two-stage lime chemical treatment for removal of suspended solids and BOD_5. If energy costs for both producing chemicals and operating the plant rise relative to other costs, this difference could widen. Single-stage chemical primary, as with alum, is cost effective for an intermediate level of suspended solids removal,

between conventional primary and conventional secondary. Operating costs are highly sensitive to chemical and energy costs, however.

3. In evaluating removals attainable by various treatment processes, wide ranges of removal efficiency are obtained for primary and secondary treatment processes. This is a function of waste characteristics as well as plant design and operation.

4. Increasing removals of contaminants from municipal wastewater increases the cost of treatment processes. Secondary treatment by activated sludge costs approximately 1.7 times as much as primary while increasing suspended solids removal over 30 percent (e.g., from 52 to 89 percent in the example given). With present technology, reduction of soluable wastewater constituents to very low levels by advanced treatment, or in some cases by secondary treatment, is impractical when ocean disposal of effluents is practiced.

5. Compared to conventional primary and secondary treatment, primary treatment with chemical addition (see alternatives 2 and 3) is an efficient means for removing suspended solids. However, secondary treatment, either high rate or conventional, provides significantly greater BOD_5 removal at a small increase in costs. For influent wastewaters with higher suspended solids concentrations, the chemical primary alternatives will show greater cost advantages due to the greater anticipated removal of suspended solids. Conversely, for wastewaters with higher soluble BOD_5 or where BOD_5 is of primary interest, the secondary treatment alternatives could be more cost effective.

6. Ocean disposal of sludge is the cheapest ultimate disposal technique. For conventional secondary treatment, the sludge treatment and disposal costs for ocean disposal (16 km transport) are 45 percent of the liquid treatment costs while for land disposal at the same distance they are 50 to 60 percent of liquid costs. For incineration or land disposal at sludge transport distances of 130 km, sludge treatment and disposal costs rise to about 75 percent of liquid treatment costs.

7. When considering the removals of heavy metals and non-biodegradable toxic organics in the treatment processes, materials removed from the liquid phase are discharged from the plant in the sludge. Although anaerobic digestion reduces the sludge particle size, no decrease in these conservative compounds occurs in a treatment plant unless incineration is used to destroy the organics and/or volatilize the metals into the atmosphere. Thus, if ocean disposal of sludge continues in the future, the degree of liquid treatment will have no effect on quantity of toxics disposed of in the ocean (although the chemical forms and disposal in the ocean will vary).

ACKNOWLEDGMENTS

Roger Bales, a graduate student at the California Institute of Technology, updated cost estimates after the original study was completed in 1978.

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3

The Coastal Ocean: The Regional Background

M. Grant Gross

INTRODUCTION

The coastal ocean, the relatively shallow ocean near the shore, receives municipal wastewater discharges from pipelines and barges (Gross, 1976). Conditions and processes occurring in the ocean constitute the background and set limits for waste disposal operations as well as regulatory or planning options related to these disposal operations.

This chapter summarizes general knowledge of coastal processes and their variability as a factor in controlling the physical, chemical, geological, and biological processes that affect waste disposal in coastal waters. Three major technical issues are apparent:

- Variability in coastal ocean characteristics and processes. Is a single waste-disposal strategy appropriate for the wide variety of ocean conditions and processes?
- Predictability. How well do we understand the time and space scales of the major processes concentrating or disposing of wastes?
- Fates of dissolved and particulate substances. Is it possible to predict what will happen to dissolved or particulate wastes? Can appropriate safeguards be planned into disposal operations to guard against undesirable effects?

OCEANIC REGIMES

The ocean can be divided into two major domains: the coastal and the open ocean. The coastal ocean, which receives most wastewater discharges, includes estuaries and adjacent wetlands, lagoons, and the waters over the continental shelves. These are the waters most used for human activities: recreation, transportation, fishing.

The open ocean lies generally seaward of the continental shelf and is not significantly affected by the continents nor the ocean bottom. No clear-cut boundary separates the two oceans, but for our purposes, waters deeper than 1000 m (3000 ft) are considered part of the open ocean and have few wastes discharged into them. Hence, this chapter deals primarily with the coastal ocean.

The coastal ocean is markedly affected by river discharges, the topography of the continental shelf, and the climate of adjacent coastal lands. These waters exhibit a high degree of variability and are commmonly divided into regions based on shoreline features, current regimes, variations in temperature and salinity, and river discharges. Each of these parameters is reasonably well known for each coastal region, Tables 3.1 and 3.2 show the significant variations among them.

Beyond the continental shelves, movements of surface waters are relatively unaffected by the ocean boundaries or the ocean bottom. There are no lateral restrictions and the ocean is about 4 to 7 km (2.5 to 4 mi) deep. Over most of the open ocean, warm surface waters are separated from colder, deeper waters by the pycnocline, a layer of water exhibiting a marked change in density with depth which inhibits surface and deeper ocean waters from mixing. After forming in polar regions, primarily the Antarctic, deeper waters move sluggishly through the major ocean basins; they take about 600 to 1,000 years to return to the surface and do not affect the fate or movement of materials discharged in surface waters. For most problems associated with wastewater discharges, we can ignore movements of the deep ocean and concentrate on the shorter term processes affecting nearshore surface waters.

THE COASTAL OCEAN

The coastal ocean lies near the shore, where fresh waters discharged by rivers and local winds strongly influence nearshore movement and mixing. The coastal ocean varies in width, has ill defined outer boundaries, and is quite narrow along coasts where the

Table 3.1 Major Features of U.S. Coastal-Oceanic Regions (FWPCA, 1970)

Coastal Region	Shoreline	Continental Shelf	Boundary Current
Gulf of Maine	Rocky, embayed by drowned river valleys; fjords	Rocky, irregular, 250-400 km wide	Labrador
Middle Atlantic	Smooth coast, embayed by drowned river valleys and lagoons	Smoothly sloping, 90-150 km wide	Labrador
South Atlantic	Smooth, low-lying, marshy; many lagoons	Smoothly sloping 50-100 km wide	Gulf Stream
Caribbean	Irregular; mangrove swamps, coral reefs	Eastside 5-15 km wide; Westside 300 km wide	Gulf Stream
Gulf of Mexico	Smooth, low-lying; barrier islands, marshes, lagoons	Smoothly sloping, 100-240 km wide	Seasonally variable Loop Current
Pacific Southwest	Mountainous, few embayments	Irregular, rugged, average 15 km wide	California
Pacific Northwest	Mountainous, few embayments, some fjords	Irregular (Oregon) to smoothly sloping (Washington), 15-60 km wide	California
Southeast Alaska	Mountainous, many embayments and fjords	Rocky and irregular in places, 50-250 km wide	Alaska

Table 3.2 Variations of Oceanographic Parameters in U.S. Coastal-Oceanic Regions (FWPCA, 1970)

	Temperature	Salinity		River Discharge	
Coastal Region	average (range) (^{o}C)	average (range) ($^{o}/oo$)	Tide+	Water (km^3/yr)	Sediment (10^6tons/yr)
Gulf of Maine	8(18-0)	30.3(31-29)	SD	64	?
Middle Atlantic	12(23-2)	31.5(31.8-31.3)	SD	95	15.3
South Atlantic	24(30-10)	35.5(36.0-32.5)	SD	137	58.1
Caribbean	27(30-22)	35.7(36.3-34.9)	SD	10	?
Gulf of Mexico	23(30-12)	32.3(37.0-30.3)	D	712	360
Pacific Southwest	15(20-13)	33.6(33.8-33.3)	M	21	24
Pacific Northwest	10(13-7)	30.8(32.5-28.5)	M	113	127
Southeast Alaska	5[13-(-1)]	31.9(32.1-31.2)	M	?	?

+SD - semidiurnal tide
M - mixed tide
D - diurnal tide

edge of the continental shelf, typically about 140 m deep, lies close to shore; the Pacific coast of North America has these characteristics. Conversely, on a wide continental shelf, such as the Atlantic and Arctic coasts of North America, the coastal ocean extends hundreds of kilometers from the shore.

Coastal ocean circulation is bounded seaward by open-ocean boundary currents. A conspicuous example is the Gulf Stream which separates the circulation of the US Middle Atlantic coast from the open ocean and the Sargasso Sea offshore. Coastal currents can set in the opposite direction to the boundary current offshore.

Although the coastal ocean makes up only 12.5 percent of the ocean surface, these waters are extensively used for transportation, recreational and commercial fishing, boating and waste disposal. Despite these often conflicting uses, coastal waters are still the most biologically productive part of the ocean; more than 90 percent of the world's marine food resources, primarily finfish, are harvested there. These same coastal waters are most often affected by pollution from numerous waste disposal operations (Gross, 1972, 1976).

Coastal water movements driven by tides, river discharges, waves, and winds, vary markedly in space and time. These conditions make it difficult to predict the behavior of wastes released nearshore, especially on broad continental shelves where storm effects are especially important (Beardsley, et al. 1976.)

Tidal currents are normally the strongest currents near the shore. They generally parallel the coast and either oscillate or rotate, depending on local geography. In most coastal areas, tidal currents are predictable and relatively well known near shore; they can, however, be substantially altered by strong winds.

Coastal currents, which generally parallel the coastline, are usually strongest when freshwater discharge is large and winds are strong. For example, along the west coast of the United States, surface waters are blown shoreward and held there by seasonal prevailing winds, depressing the pycnocline. A sloping sea surface results, creating currents which parallel the coast. The Davidson current, moving northward along the Oregon-Washington coast during winter when river discharge is large and the prevailing winds are landward, illustrates the phenomenon.

When winds diminish, or river discharge is low, coastal currents, like the Davidson, weaken or disappear. Such conditions are common in late summer, when coastal currents are often weak, forming large, sluggish eddies, rather than well-defined currents. With the onset of winter storms, surface waters are mixed and coastal currents are reestablished in a day or two.

Surface coastal currents are dominated by the patterns of the prevailing winds and offshore currents. Subsurface currents move in relationship with the tides, except possibly when strong winds blow for more than a few hours and stability is low. During times of weak winds or weak tidal currents, residual currents apparently related to the offshore circulation system may dominate water movements at all depths on the shelf.

In general, surface currents have a greater velocity than those below 15 to 20 m. Differences between surface and subsurface currents are most pronounced during summer, when stability is highest and stratification is most pronounced.

Waves are another factor that influence nearshore currents. Where surface waves approach the shore obliquely, a longshore current usually develops. Such longshore currents flow generally parallel to the shoreline. Longshore current direction depends upon the angle at which waves approach the shore. For example, along a north-south coastline with the ocean to the east, waves approaching the shoreline from the northeast produce a longshore current that flows southward. Longshore currents are highly variable because they depend on local waves and can reverse direction and change speed within a few hours, when the wave regime changes.

Outside the surf zone, where waves break on offshore bars before striking the beach, local winds and salinity gradients, caused by runoff from the land, combine to dominate non-tidal currents in nearshore areas. Furthermore, waves breaking on a shoreline generate currents near the beach that can move in the opposite direction from those currents that are seaward of the surf zone, depending upon the angle at which the waves strike the beach.

Upwelling, a phenomenon whereby cooler and often nutrient-laden subsurface waters are brought to the surface, can be quite important in the transport and dispersion of wastes. The condition occurs when winds transport warmer surface waters offshore. This is particularly true when the wind blows at such an angle to the shoreline that an observer with his back to the wind has the shore on his left. In the Northern Hemisphere, the resulting density distribution produces a current flowing along the coastline with the shore to the left of the current (looking down current). Upwelling can bring a submerged waste field to the surface, and can also cause waste constituents to move shoreward when upwelling ceases.

Exchanges of coastal waters with the open ocean are inhibited by the coastal current regimes discussed. We know little about the processes which renew or mix nearshore waters with open ocean waters. Where there is sufficient runoff of freshwater from the land to produce measurable salinity gradients in the coastal ocean, and where the rates of fresh water inflow can be determined, the mean residence time (or replacement time) for nearshore waters can be estimated. Such estimates have been made for the coastal ocean waters bordering the United States between Cape Hatteras and Cape Cod. Considering the salinity of the waters in this segment of the coastal ocean and the annual volume rate of flow from all rivers discharging from the adjacent coast, about one year's river flow would be needed to provide the fresh water observed in the system. Typical resident times range from a few months for a large estuary (about 100 days for Chesapeake Bay) to several years for large coastal-ocean sectors such as the Middle Atlantic Bight (Ketchum and Keen, 1955).

Suspended sediment concentrations are usually high in coastal waters, providing ample particle surface area for chemical reactions and for attachment of bacteria and viruses. Particles play major roles in transporting and removing many pollutants in estuarine and coastal ocean systems. They are especially important in transferring pollutants and microorganisms to filter-feeding commercial organisms such as clams and oysters. The general behavior of particles in estuarine and coastal waters is known (Meade, 1969, 1972), but little is known about the chemical reactions between particles and dissolved substances, and still less is known about the roles of bacteria and other organisms in such processes.

ESTUARIES AND ESTUARINE CIRCULATION

An estuary is a semi-enclosed coastal body of water that has a free connection with the ocean (Pritchard, 1952). Within an estuary, seawater is measurably diluted with fresh water from river discharges. Four types of estuaries are recognized: drowned river valleys (e.g., Hudson River, Chesapeake Bay), bar-built estuaries (e.g., Pamlico Sound), fjord-like estuaries (e.g., Strait of Georgia, Puget Sound) and tectonically formed estuaries (e.g., San Francisco Bay). Some of the characteristics of these and other estuaries are indicated in Table 3.3. Drowned river valleys, which are the most familiar, occur along the Atlantic Coast of the United States. Because they are generally confined to areas with relatively wide coastal plains, these waterways have also been called coastal-plain estuaries.

The long-term circulation pattern (averaged over many tidal cycles) for estuarine waters is well known and reasonably predictable (Pritchard, 1955). In a typical estuary, the water salinity increases with depth (often very slightly) and proximity to the sea. The least saline waters occur near river mouths, the saltiest near the ocean. There is usually a surface layer in which vertical salinity changes little, an intermediate layer in which salinity increases rapidly with depth, and a deep layer in which the rate of salinity increase with depth is small. Vertical mixing takes place between surface and bottom waters.

Tidal currents usually dominate short-term (a few hours) water movements in estuaries. Superimposed on the tidal currents, which are usually oscillatory, is a weaker net pattern, called the estuarine circulation. Here there is a net seaward flow of near-surface waters and net flow from the mouth toward the head of the estuary in subsurface waters when currents are averaged over many tidal cycles. There is also a net flow from deeper to the surface layers. The volume of water flowing toward the head of the estuary, per unit time, decreases from the mouth to the head of the estuary, since water is simultaneously being moved upwards from the deeper to the surface layers. Consequently, the amount of seaward flow of surface waters increases from the head toward the mouth of the estuary.

Estuarine circulation prevails in coastal ocean areas where the input of the fresh water from river runoff and rainfall exceeds the loss by evaporation from the ocean surface. Thus, over most US

Table 3.3 Characteristics of Some North American Estuarine Systems (Gross, 1982)

	Estuary area	Estuary volume	Mean water depth*	Annual fresh-water discharge	Land area drained	Major Rivers
	(km^2)	(km^3)	(m)	(km^2/yr)	($10^3 km^2$)	
Chesapeake Bay System (Maryland-Virginia)	11,000	67	6.1	65	110	Susquahanna
Potomac River	1,280	7.3	5.7	12	36	Potomac
James River	650	2.3	3.5	10	26	James
Raritan Bay (New York-New Jersey)	230	1.1	4.5	7.8	3.4	Raritan
New York Harbor	159	1.2	7.5	19.4	34.7	Hudson
Long Island Sound (New York-Connecticut)	3,180	62	19.4	21	40.7	Connecticut
Pamlico-Albemarle Sound (North Carolina)	6,630	23.9	3.6	7.8	51	Neuse
Strait of Juan deFuca (Washington-British Columbia)	4,370	490	112	nd+	nd+	
Puget Sound (Washington)	2,640	185	70	36.5	37.6	Skagit
Strait of Georgia (British Columbia)	6,900	1,025	156	145	270	Fraser
San Francisco Bay (California)	1,190	6.2	5	40	161	Sacramento San Juan
Laguna Madre (Texas)	158	1.1	0.9	-0.85**	nd+	

+nd = no data
*Mean depth = volume/area
**Evaporation exceeds river runoff plus rainfall.

continental shelf areas, surface waters generally have a net motion seaward, while near-bottom waters move generally toward the shore. Both surface and subsurface waters move along the coast.

Where tidal currents compared to river discharge are relatively large, estuarine waters tend to be less stratified. Conversely, increased river flow and deeper channels, which are often dredged, cause increased stratification. In a shallow estuary with low river flow, but large tidal range and tidal currents, the waters may be mixed almost completely from top to bottom.

Most river water is discharged on the ebb tide and enters the ocean as a series of pulses of cloud-like parcels of low-salinity water. When surface waters are turbid with suspended sediment, these "clouds" are easily recognizable from aircraft and satellites. They tend to mix, forming a complex of irregular fronts. As the cloud-like masses move away from the river mouth, waves and tidal currents cause mixing over the continental shelf. Boundaries are obscured and eventually a large lens or plume of low-salinity water forms. Such a plume can be traced for many tens or hundreds of kilometers off the mouths of major rivers.

Particles discharged to estuaries tend to be retained in the estuary or deposited in adjacent wetlands. Particles settling out of the seaward-moving surface layer will be entrained in the landward moving subsurface waters. These particles will be deposited in the estuary or transported to the most turbid zone where high concentrations of suspended sediment are maintained by the estuarine circulation and by tidal current scouring of deposits (Schubel, 1972).

FACTORS CONTROLLING PRODUCTIVITY IN THE OCEAN

Seawater is a nearly constant solution of salts dissolved in variable amounts of water. Salinity of seawater is most variable near the air-sea interface at boundaries of ocean currents and in coastal ocean areas.

The concentrations of substances, such as the chloride and sulfate ions and other major constituents, are changed only by physical processes, such as mixing, dilution, evaporation, freezing, and are known as "conservative" constituents. Many minor elements in seawater are non-conservative because they exhibit pronounced changes in relative abundance or because of biological processes and chemical reactions. Non-conservative constituents are mostly involved in interactions with particles or organisms. They are usually removed from the water and incorporated in sediment deposits as they near the ocean.

Organic particles are also important constituents suspended in seawater; they commonly exceed the amount of inorganic matter in open ocean surface waters. Below the photic zone (the lighted surface layer where photosynthesis occurs) this organic matter usually consists of siliceous shells of diatoms, and skeletal and fecal pellet fragments of zooplankton; wood fibers and pollen grains are also common nearshore. Where large amounts of sewage plant effluents and sewage solids are discharged into coastal rivers or ocean waters, cellulose fibers also occur (Conomos, 1968; Manheim, et al., 1970).

Particles in the ocean are typically coated by microbes, or related organisms, or by organic matter, and may be particularly significant for marine bacteria because they: 1. provide a substrate; 2. concentrate dissolved substances, holding them on the substrate so that they may be attacked by bacteria; and 3. retard diffusion of bacterial enzymes away from the bacterium (Harvey, 1955). Interactions between particles and dissolved substances are little known and commonly ignored in predicting the fates of waste discharges in the ocean over periods of a few hours to a few days.

Most life in the ocean depends ultimately on food produced by the photosynthesis of phytoplankton living in the sunlit surface layers of the ocean. Factors that limit phytoplankton production thus have a pronounced effect on marine ecosystems. Phytoplankton growth is primarily limited by three factors: availability of light, nutrients, and trace organic materials in the water.

During winter, insufficient sunlight limits phytoplankton growth over much of the ocean, especially in mid- and high-latitude waters. When insolation increases in early spring, phytoplankton begin to reproduce rapidly. Under favorable conditions they may become so abundant that dense accumulations of cells near the surface shut off light from those below. If this happens, light again becomes a limiting factor and growth of plants is then restricted to the uppermost surface waters. In coastal and estuarine waters, limited light is due to turbidity from suspended sediment and abundant phytoplankton growth.

Nutrient scarcity, especially nitrates or phosphates, in near-surface waters usually limits plant growth over much of the open ocean. This is particularly true near the centers of ocean basins and in deep, tropical waters for two reasons:

1. Some dying plants and animals sink below the pycnocline before their tissues decompose releasing nitrogen and phosphorus compounds into the water. The sinking process removes nutrients from surface water. The rate of nutrient return from deep to surface waters in most areas is very slow, requiring hundreds to thousands of years.

2. In the tropics seasonal differences are slight and light levels are uniform throughout the year, phytoplankton continuously use available nutrients and concentrations never have the opportunity to build up.

In coastal waters, nutrients recycle fairly quickly. During winter, when phytoplankton growth is light limited, dissolved nutrient concentrations are high and mixed through the water column by storms. Thus when light increases in early spring, phytoplankton increase markedly, causing a bloom. The first spring bloom greatly reduces the nutrient concentrations in the surface waters. Nutrient concentrations then apparently limit phytoplankton growth until fall when winter storms again stir the water column, bringing deeper nutrients to the surface and permitting a short period of increased productivity before light again becomes the limiting factor.

In most coastal and estuarine waters, nitrogen compounds are usually limiting (Ryther and Dunstan, 1971). Thus, releases of nitrogen compounds by wastewater or sludge discharges (Duedall et al, 1975) may locally increase phytoplankton production (Segar and Berberian, 1976) and may have a deleterious effect on regional water quality.

Farther out on the continental shelf, in deeper waters, the spring bloom does not occur until a pycnocline develops. Then, as organic matter decomposes it sinks far below the photic zone. Nutrients released are not recycled to near-surface waters until winter storms mix surface and subsurface waters and a new annual cycle begins. Thus, one pronounced bloom is the rule rather than the two that occur closer to shore.

Besides dissolved phosphorus and nitrogen compounds, many other substances are essential to marine plants, and some are typically present in quantities that limit the growth of a particular species of organism. Lack of silicon, for example, can limit growth of diatoms, a common mid-latitude phytoplankter.

A third factor limiting phytoplankton growth may be the presence, or absence, of organic materials in trace amounts. Substances such as vitamins, antibiotics, toxins, hormones, and trace nutrients are frequently secreted into the water by bacteria, plants, or animals. One or more of these substances may be necessary or detrimental to the growth rate of other plant or animal species.

ROLE OF SEDIMENTS AND OTHER PARTICULATE MATERIAL

Particles in the ocean carry a variety of constituents from wastewaters, including metals and synthetic organic compounds as well as bacteria and viruses. Thus it is necessary to know the fate of particles to understand the behavior of wastewater constituents in the ocean.

Particle concentrations in open ocean surface waters typically range from 0.1 to 1 mg/l and from about 1 to 30 mg/l in surface water within a few tens of kilometers of the coast (Conomos, 1968; Manheim, et al., 1970). Particle concentrations in near-bottom waters are generally much higher and quite variable owing to resuspension of previously deposited sediment (Conomos, 1968; Schubel, 1972). Particle concentration of a few tens of mg/l are typically observed in estuarine waters.

In coastal waters, organic matter typically constitutes 20 to 40 percent of the particles, commonly increasing to more than 50 percent offshore. In open ocean waters organic matter commonly makes up more than 80 percent of the suspended particles (Manheim et al., 1970). Relatively little is known about particle composition; therefore we have limited capability to predict which waterborne constituents will become associated with particles.

Particles in seawater come from riverborne detritus, waste discharges, atmospheric fallout, growth of organisms, chemical reactions, and resuspension of particles from sediment deposits on the bottom. Riverborne detritus is an obvious, although not always the most important, source of particles. Much of the river's sediment load remains near the river mouth.

Estuaries, deltas, and wetlands form effective traps that prevent particles from reaching the continental shelf (Meade, 1969, 1972). Rivers carrying little sediment have not filled their estuaries since the ocean reached its present level, about 3,000 years ago. Coastal ocean areas near such estuarine rivers receive little sediment. Where rivers have filled their estuaries, riverborne sediments can more readily reach the ocean. If present in large amounts, the sediment load may exceed the ocean's capacity to transport it away from the river mouth, and a large accumulation is formed, usually called a delta. When the sediment load is not large enough to form a delta, sediment particles recently brought by the river commonly move along the continental shelf approximately parallel to the coast (Gross, 1966).

The estuarine-like circulation that prevails along most coasts (where river discharge exceeds evaporation) inhibits particle movement across continental shelves, in a way similar to that observed in estuaries. Subsurface currents are generally directed landward. Thus materials removed from surface layers and caught up by near-bottom currents move landward and into estuaries. Considering the rate of sediment supply to the ocean and the apparent rate of accumulation in deep ocean basins, it seems likely that virtually all of the particles from rivers or wastewater discharges are deposited on continental shelves, or in coastal wetlands, never reaching the deep ocean bottom (Meade, 1972).

Atmospheric fallout is yet another source of particles. Natural major sources of airborne dust include deserts, high mountains devoid of vegetation, and volcanic eruptions. Relatively small particles, commonly 2 to 10 microns in diameter, carried by winds, are eventually deposited over large parts of the open ocean where they can be recognized by mineral composition and characteristic grain surface features. Although atmospheric particle transport is most conspicuous in the open ocean where there are few other sources of particles (Rex and Goldberg, 1958), it is an important pathway to coastal waters for some contaminants (see Chapter 2).

Since the industrial revolution, industrial and agricultural activities have contributed particles to the atmosphere, many of them carried long distances (Delaney et al., 1967). Fly ash from burning coal, lead aerosols from internal combustion engines, aerosols of industrial minerals, and carbon particles from incomplete combustion are examples. These grains commonly have unusual properties as well as chemical and mineral compositions not found in naturally occurring particles.

Tidal currents, waves, and surges resuspend sediments, causing large particle concentrations in near-bottom estuarine waters (Schubel, 1972), coastal waters (Conomos, 1968), and deep ocean waters (Ewing and Thorndike, 1965). In shallow continental shelf areas, this is an important source of suspended particles.

Particulate wastes are commonly discharged to the ocean by surface runoff, other wastewater sources, municipal wastewater treatment plants, and by stormwater sewage systems. Most of these particles settle out near the points of discharge, often in estuaries. Particulate wastes are also discharged directly into the coastal ocean. The largest amount of such wastes comes from the disposal of dredged materials, removed from navigation channels and slips (Boyd, et al., 1972). Much smaller amounts of wastes are discharged by barges in the New York Bight and by pipeline off southern California (see Chapter 2).

Processes controlling movements of wastewater particles are poorly known. Most sediment movement on the continental shelf apparently occurs during storms (Swift et al., 1976; Sternberg et al., 1979). Presumably waste solids would behave in much the same way as ordinary fine-grained, low-density bottom sediments. The less dense constituents of wastes are likely to be more readily put into motion by wave action of currents and to move farther than the denser grains.

Most waste disposal programs in the United States assume that particulate wastes remain in the discharge area. As long as no identifiable wastes wash up on beaches or interfere with recreation or commercial fishing, there is likely to be little immediate complaint. Although waste solids dumped in the coastal ocean remain out of sight for a time, there is still some level of probability (not yet determined) that some waste-derived particles will be moved into areas where they could cause problems, such as washing up on a beach. And there are clearly documented effects of the accumulation of waste solids in many areas (Gross, 1976).

Disposal of sewage sludges in relatively shallow, well-mixed (strong tidal) waters of the United Kingdom has been considered acceptable (see Appendix E). Even though the particulate wastes are widely dispersed, significant effects have not been detectable. Particles and particle-associated substances are probably most important in long-term problems because sedimentary processes tend to be slow. In dealing with persistent toxins, particles and sediment deposits are likely to be extremely important. Originally, low concentrations of dangerous substances may be concentrated by particles and then retained relatively unchanged, buried in sediment deposits over long periods. Also, filter-feeding organisms may concentrate materials associated with particles (Bryan, 1976).

COASTAL REGIONS

The coastal ocean regions and estuaries of the United States exhibit marked differences. Thus it is appropriate to consider typical examples of these regions. Four different regions are discussed as examples of variability and are compared to other urbanized estuaries and coastal regions in Table 3.4:

1. Wide, mid-latitude continental shelf with western boundary current - New York Bight;
2. Narrow, mid-latitude continental shelf with eastern boundary current - Southern California Bight;
3. Coastal plain (shallow), mid-latitude estuaries - Chesapeake Bay;
4. Fjord-like (deep mid-latitude estuary - Puget Sound

Three of these regions (New York Bight, Southern California Bight, and Puget Sound), as well as some of the British regions, are more thoroughly discussed in

Table 3.4 Urban Estuaries and Coastal Regions

	Long Island Sound	New York Harbor	Delaware Bay	Chesapeake Bay	San Francisco Bay	Puget Sound	Lake Erie
Estuary							
Surface area ($10^3 km^2$)	3.2	0.39	2.00	11.4	1.2	2.6	25.9
Volume ($10^9 m^3$)	62	3.3	22.2	76	6.2	185	33.0
Flushing Time (days)	100	25	nd	440	~100	1850	920
River Discharge (m^3/sec)	668	618	550	1950	580	1160	5900
Sewage discharge (m^3/sec)	10	110		57	14	nd	66
Industrial discharge (m^3/sec)	8	~100		70	16	nd	420
Power plant discharge (m^3/sec)	170	545	230	280	78	nd	145
Storm sewer overflow (m^3/sec)	nd	80	nd	nd	nd	nd	nd
River drainage basin							
Population (millions)	5(1960)*	11(1960)	7(1960)	10(1970)	3(1960)	2(1960)	13(1970)
Drainage area ($10^3 km^2$)	40.7	34.7	32.7	164	161	37.6	102
Discharge (m^3/sec)	670	620	630	1950	580	1160	na

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* Year of census
na Not applicable
nd No data

the case studies presented in the appendices. Gross (1978) reviewed the effects of waste disposal operations on estuaries and coastal ocean areas.

Broad Continental Shelf - New York Bight

The New York Bight (see Figure C.2 in Appendix C), between Long Island, New York, and Cape May, New Jersey has had a long maritime and urban history. This region, typical of the coastal ocean from Cape Cod, Massachusetts, to Cape Hatteras, North Carolina, includes the harbors for the New York metropolitan area. The Gulf Stream system moves well offshore. Currents and environmental conditions in the New York Bight are fairly well known (Ketchum et al., 1951; Gross, 1976).

In these regions, as in most mid-latitude coastal waters, temperatures, salinity, and currents change markedly with the seasons. Surface-water salinities tend to be highest (29 to $32.8^{o}/_{oo}$) in late winter (February or early March) when frozen rivers reduce river discharge. At this time, surface-water temperatures are at their lowest, ranging from -1^{o} to $+1^{o}$C. Ice forms in partially isolated shallow waters. Because of strong cooling and intensive mixing caused by winter storms, coastal waters are nearly homogeneous; there is almost none of the stratification or vertical stability that is typical of summer and autumn conditions. Put another way, in winter the cold is "felt" all the way to the bottom of the coastal ocean.

Fresh water discharged by rivers is quickly mixed with seawater. Surface water moves obliquely away from the coast. Coastal currents transport it southeastward, while there is a net flow seaward as part of a basic estuarine-like circulation.

River discharge peaks during spring between late March and the end of May, about 50 percent of the annual total river discharge flows into the ocean. At this time, surface-water salinity off New York Harbor drops to $26^{o}/_{oo}$, and the surface water salinity throughout the region falls to $32^{o}/_{oo}$ or less. A combination of lowered salinity and warming forms a low-density surface layer so that the water column is stratified. A shallow plume of Hudson River effluent floats generally southward, parallel to the New Jersey coast but a few kilometers offshore. It is usually separated from the coast by a belt of more saline water. Upwelling can occur along the shore under favorable wind conditions.

These stratified conditions persist into summer; surface water becoming slightly less saline and surface-water temperatures rising due to insolation. The layer of low-salinity water is usually about 10 to 20m thick, although it may locally contact the bottom, apparently as a result of wind-induced sinking (also known as downwelling) of coastal waters. As river flow diminishes during the summer and wind speed decreases, the plume of water coming from New York Harbor becomes less obvious and forms a series of ill-defined patches of water which move slowly over the continental shelf. Currents are sluggish at this time, in the absence of large river discharge and strong winds.

During winter, stratification of the coastal water is broken down as surface waters are chilled, and low salinity surface waters are mixed by storm winds and seas. Eventually, isohalines and isotherms become nearly vertical and trend parallel to the coast; the water becomes warmer and more saline as you go farther from shore. Through the winter, cooling is most intensive nearest the coast, where the water is most shallow. There is some flow of warmer ocean water along the bottom.

Although about $2^1/_2$ years of river discharge would be needed to replace all the ocean water in the 2,000 km^2 of coastal ocean nearest New York Harbor, it requires generally only about 6 to 10 days for a tracer solution (a dye, for example) introduced into the river mouth to move through this part of the ocean. This results from the flow of water involved in the coastal currents. In general, variations in river flow have little demonstrable effect on the average rate of movement through the area; total water flow through this stretch of coastal ocean is anywhere from 50 to more than 200 times the incoming river flow. Wind-driven currents carry water from the region of Nantucket shoals southward along the Long Island-New Jersey coast.

Within a few kilometers of New York Harbor, the flow near the bottom is generally landward. Elsewhere, the near-bottom flow tends to parallel the coast, moving slightly landward. On the edge of the continental shelf, net flow seems to be slightly seaward. Subsurface currents appear to be little affected by variability in winds or river runoff.

Perhaps the overlying water acts as some sort of filter to average out these effects. It may also be that our data are too crude to show short-term variation in subsurface flows.

Depletion of dissolved oxygen (DO) in near bottom waters near the waste disposal sites was observed in July 1976, leading eventually to anoxia and hydrogen sulfide (up to 1.8 mg/l) in near-bottom waters. By late September, low oxygen water (less than 2 ppm DO) extended over about half the New York Bight, down current from New York Harbor and the waste disposal sites. Associated with the low oxygen conditions were widespread die-off of benthic organisms and some fish kills (Swanson and Sindermann, 1979). Dissolved oxygen depletion may occur commonly in late summer in the Bight but the 1976 occurrence was the first documented case of anoxia in open coastal waters. Among the possible causes of the unusual severity of the anoxic conditions in 1976 were (Swanson and Sindermann, 1979):

- Unusually warm winter, spring, and summer, causing early stratification;
- Floods in May 1976 discharging unusually large amounts of carbon-rich materials and nutrients from the river;
- Unusual persistence of winds from the southwest reversing coastal currents and greatly increasing residence times of waters in the New York Bight and causing some upwelling;
- Concentration of organic debris by estuarine circulation on continental shelf.

Currents on the Mid-Atlantic continental shelf are strongly influenced by the presence of ring currents (also called warm core rings). These features are formed by cutoff meanders of the Gulf Stream which enclose warm Sargasso Sea waters. Each ring, typically 100 km across, is bounded by strong currents which extend to depths of about 1,000 m and inhibit mixing between waters in the ring and the colder slope waters outside through wich the rings move at speeds of 10 to 20 km/day. These rings persist for several months between formation and resorption by the Gulf Stream near Cape Hatteras.

Such rings, cause intrusions of slope waters onto the continental shelf and cause substantial movements of waters across the shelf. Ring currents may also play an important, but little known, role in transferring wastes and organisms through slope waters and into coastal waters.

Narrow Continental Shelf - Southern California Bight

The Southern California coastal region is an example of an urbanized coastal zone with a rugged narrow continental shelf. It is one of the largest coastal urban complexes in the United States. Its population of about 11 million is concentrated along 575 km (360 mi) in the Los Angeles, Long Beach, and San Diego urban areas.

The Southern California Bight (See Figure A.1 in Appendix A) is the open embayment of the Southern California coast, between Pt. Conception, California and Cabo Colnett, Baja California in northern Mexico. It is bounded on the west by the broad, slowly moving California current, an area of about 100,000 km^2 (39,000 mi^2) overlying a narrow continental shelf and a complex of nearly closed basins and troughs (Southern California Coastal Water Research Program (SCCWRP), 1973).

Unlike the New York Bight, the southern California region is semi-arid and stream beds are dry much of the year. Industrial and domestic wastes are discharged into the Southern California Bight and most of the water reaching the sea flows through the sewers. Most of the wastes are discharged through pipelines into relatively deep water (60-100 m) within 2 to 11 km of the shore (SCCWRP, 1973).

The offshore current is part of the overall circulation system of the Pacific Ocean. In the deeper waters, minor perturbations in the overall circulation patterns result from winds and tidal forces.

Tidal currents along the coast of California tend to have greatest velocity more or less parallel to the shore. The current velocity vector at a given point tends to describe an ellipse approximately every 12$^1/_2$ to 25 hours (hr), depending upong the relative strength of the main tidal components. Tidal currents are also strongly influenced by the bottom topography.

In addition to these types of currents, local water movements include upwelling, currents in submarine canyons, currents in the surf zone, and internal waves. Upwelling is more pronounced and submarine canyons more important on the southern California coast than on the broader Mid-Atlantic continental shelf.

Upwelling occurs seasonally in the Southern California Bight. In spring, northwesterly winds blow more or less parallel to the coast and are strongest off Baja and southern California. These winds drive surface waters offshore and cause upwelling of subsurface waters, primarily during April, May, and June.

Upwelling may also be induced by tidal currents in an area having an irregular sea floor. Local upwelling has been observed in Santa Monica Bay and on the San Pedro shelf in every month of the year.

In southern California there are continuous interchanges between waters of the surf and offshore zones because of the narrow continental shelf. Offshore water is transported into the surf zone by breaking waves, carrying with it floatable substances: grease, oil and other materials. Longshore currents with velocities in excess of 250 centimeters per second (cm/sec) and rip currents with velocities in excess of 150 cm/sec have been measured. The littoral zone is easily penetrated by offshore surface waters; and materials that have reached the surface offshore have a high probability of penetrating to the shoreline area. There, they may be spread widely, escaping to the waters outside the breaker zone only through rip currents, or they may be deposited on the beach along the uprush where the water sinks into the beach material.

The numerous submarine canyons on the southern California coast represent a potential "short-cut" between the nearshore waters and the deeper waters offshore. Upwelling is often associated with submarine canyons, which provide a means of more rapid dispersal of waters, constituents, and marine organisms. However, there has been little study of currents in these canyons.

Turbidity associated with wastewater plumes, tends to form submerged layers because California coastal waters are stratified throughout the year. As most particles are not much denser than seawater, the layers have already reached approximate hydrostatic equilibrium (from dilution of the effluent). It is unlikely that the density of the particles influences the motion of these layers in any substantial way. Density currents caused by wastewater particles are probably restricted to density flows of settled particles on sloping bottoms. Turbidity currents caused by pipeline discharges of wastewaters can move down the nearshore submarine canyons into deeper basins offshore.

The implications of internal waves to the conditions and processes of waste transport and dispersion in the Southern California Bight have not yet been evaluated.

Coastal Plain Estuary - Chesapeake Bay

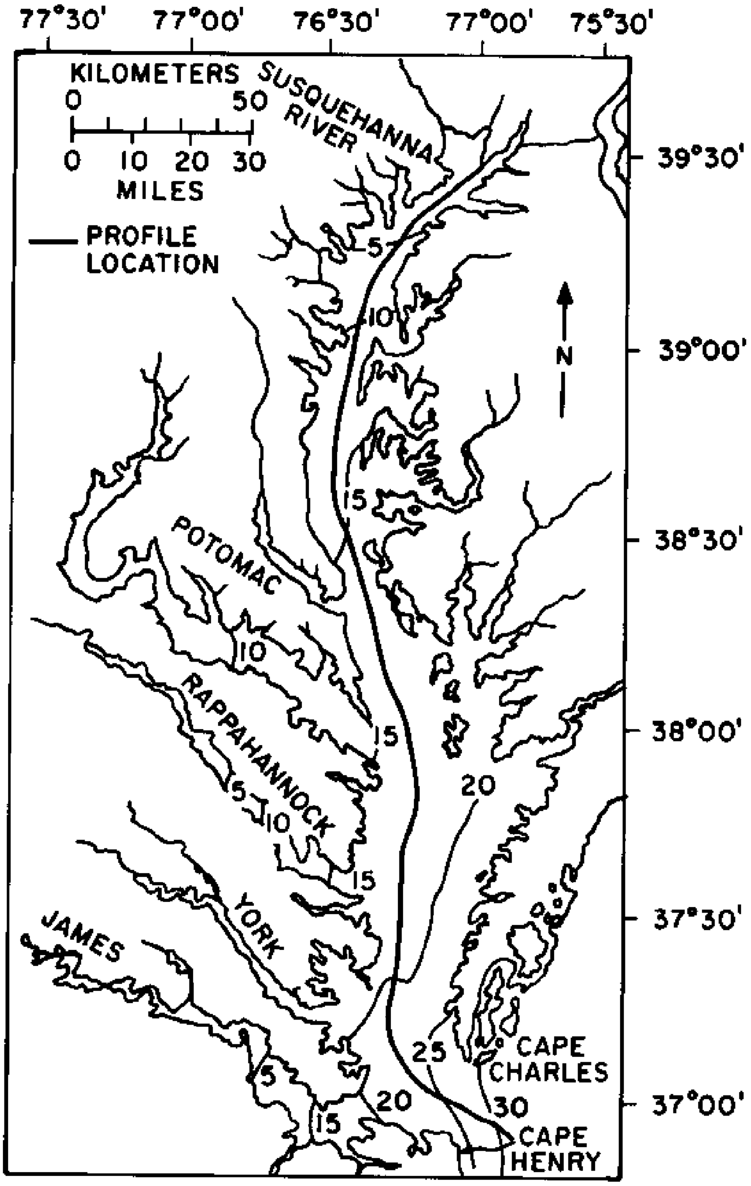
Chesapeake Bay is a coastal-plain estuarine system, formed from the drowned valleys of the Susquehanna River and its many tributaries, including the Potomac, the James, the York, and the Rappahannock (See Figure 3.1).

The total volume of fresh water discharged each year by rivers flowing into Chesapeake Bay approximately equals the total volume of the estuary. The Susquehanna River supplies 49 percent of the annual freshwater discharge, the Potomac River contributes 18 percent, and the James River about 15 percent. Nearly all the fresh water is discharged into the Bay along its western margin, from rivers draining the Appalachian Mountains. Little fresh water comes from the small rivers and low lying areas along the eastern shore of the Bay.

Tidal currents in Chesapeake Bay, which are mainly the reversing type, are generally well understood. Depending upon location in the Bay, maximum current speed may be as low as 25 cm/sec or as high as 50 cm/sec. As in all estuarine systems, net flow at the surface is seaward, resulting in ebb currents that begin sooner and persist longer at the surface. Inflow at the bottom is reflected in the early initiation of the flood tides and their greater persistence.

Salinities are lowest during spring at times of high river flow. In summer and fall, low river discharge results in maximum salinities. Because of the large discharge of fresh water along the western shore and the deflecting influence of the Coriolis effect, surface water salinity is generally greater on

Figure 3.1 Chesapeake Bay and its tributary estuaries. Countours show surface salinity in water (Pritchard, 1952).



the eastern side of Chesapeake Bay than along the western side. Estuarine currents contribute to this effect by moving surface water parallel to the eastern shore.

Salinity variation with depth is typical of estuarine systems (see Figure 3.2). In January, surface-water salinity in the middle of the Bay may be as low as $14^{o}/_{oo}$, while bottom-water salinities are about 18 percent. In the same area during September, the salinity of the surface layer is higher ($16^{o}/_{oo}$) because of the reduced river flow. Likewise, the salinity of the bottom water is also higher ($22^{o}/_{oo}$), due in part to changes in ocean conditions at the mouth of the estuary. There is also a reduction in the fresh water, which is mixed downward from surface layers owing to the effects of the tidal currents.

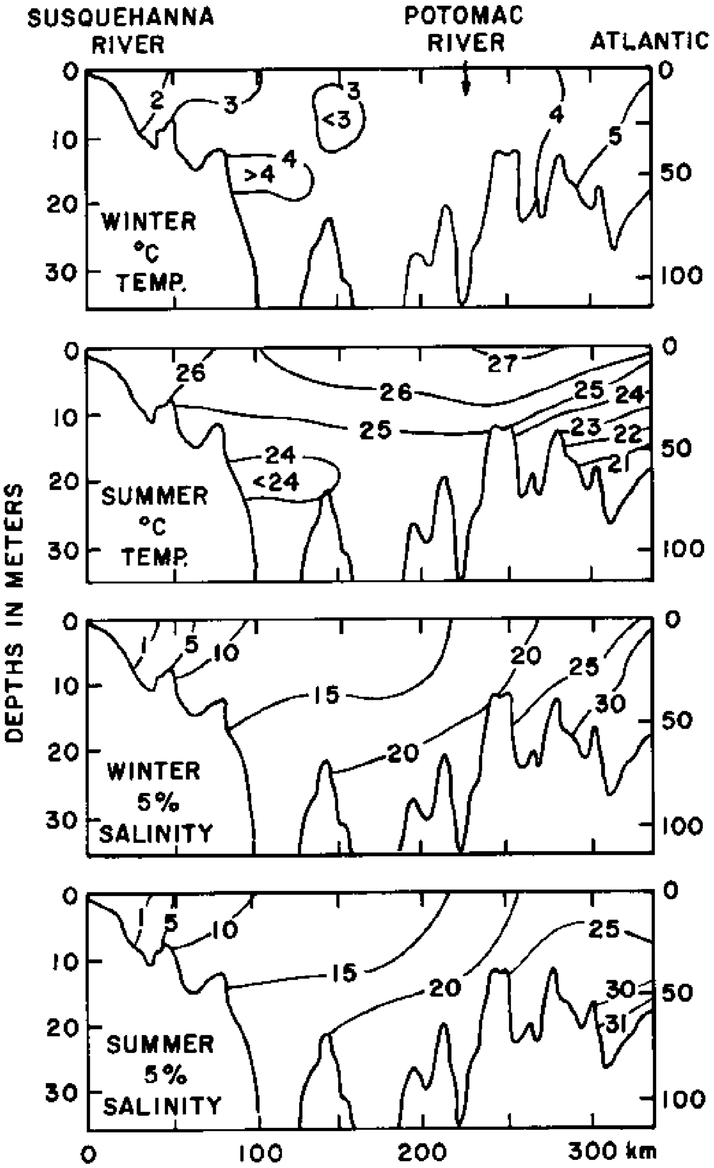
Temperature in Chesapeake Bay does not show as clear cut a distribution as does salinity. The Bay is relatively shallow, so that the surface-water temperatures are controlled primarily by local weather conditions, particularly in summer, and by the local discharge of waste heat from along the shores.

During the winter, water temperature generally decreases toward the head of the Bay, as a result of the inflow of warmer oceanic water near the mouth. The cooling of low salinity waters at the head of the Bay frequently causes ice formation during January and February. Ice forms first in the shallow, protected bays and inlets along the shore, and then gradually extends out toward open water. In especially cold winters, ice covers large areas stretching from shore to shore in the northern Bay and the more protected tributaries.

Strong winds have a pronounced effect on the Bay. In addition to the waves they generate, storm winds can also change sea level locally, sometimes causing flooding of low-lying coastal areas. Winds modify currents in Chesapeake Bay for periods of several days, even reversing circulation patterns. Currents set up by river discharge and tides are the dominant influence over the long term.

Wastewaters are discharged in two different types of estuarine conditions. Baltimore, Maryland, Richmond, Virginia, and Washington, D.C. discharge wastewaters into low-salinity waters far from the ocean entrance. Waste constituents from these discharges are likely to be retained within the

Figure 3.2 Distribution of temperature and salinity with depth in Chesapeake Bay in winter and summer. (Data from Chesapeake Bay Institute, Johns Hopkins University).



estuary, relatively close, within a few tens of kilometers, to the discharge point. Wastes from the Hampton Roads, Virginia (Norfolk) are discharged into relatively high salinity waters near the ocean entrance. These wastes are likely to be primarily deposited in local tributary estuaries; some fraction may be widely dispersed in the estuary by the movements of subsurface waters.

Fjord-Like Estuary - Puget Sound

Puget Sound is a deep fjord-like estuary quite unlike the Chesapeake Bay. It is part of a large, inland waterway that includes the Strait of Georgia to the north. The Strait of Juan de Fuca connects this system with the coastal north Pacific Ocean (see Figure 3.3.).

The Puget Sound basin was carved by glaciers from an older river-cut valley system. The glaciers cut a very irregular basin which has not yet been smoothed out by sediment deposits or by erosion. Within the Puget Sound are elongated basins as deep as 280 m, (920 ft) separated by ridges of sills that come to within 45 to 60 m (150-200 ft) of the surface (see Figure 3.4).

Tides control the currents in Puget Sound. About 5 percent of the total volume of the Sound is exchanged on each tide, twice daily; much of the water taken out on an ebb tide returns on the following flood tide. Still, there is substantial exchange of water between Puget Sound, the Strait of Juan de Fuca, and the adjacent northeast Pacific Ocean.

Tidal currents provide much of the energy that mixes the waters in Puget Sound. Tidal currents are quite strong, especially over the sills: 2.4 m/sec (4.7 knots) at Admiralty Inlet, 2.6 m/sec (5.1 knots) at Tacoma Narrows. These, combined with irregular topography, cause extensive mixing of surface and deeper waters at the sills. Away from the sills, tidal currents are much weaker, usually less than 50 cm/sec (1 knot).

Because of the large river discharge and heavy rainfall, Puget Sound surface waters have relatively low salinities. Subsurface waters entering the Strait of Juan de Fuca typically have salinities of $33.8^{o}/_{oo}$. Passing through the Strait they are mixed with waters diluted by river discharge until they reach the Sound, where salinities are between 29 and $31^{o}/_{oo}$.

Figure 3.3 Puget Sound and its adjacent water bodies. Location of profiles is indicated.

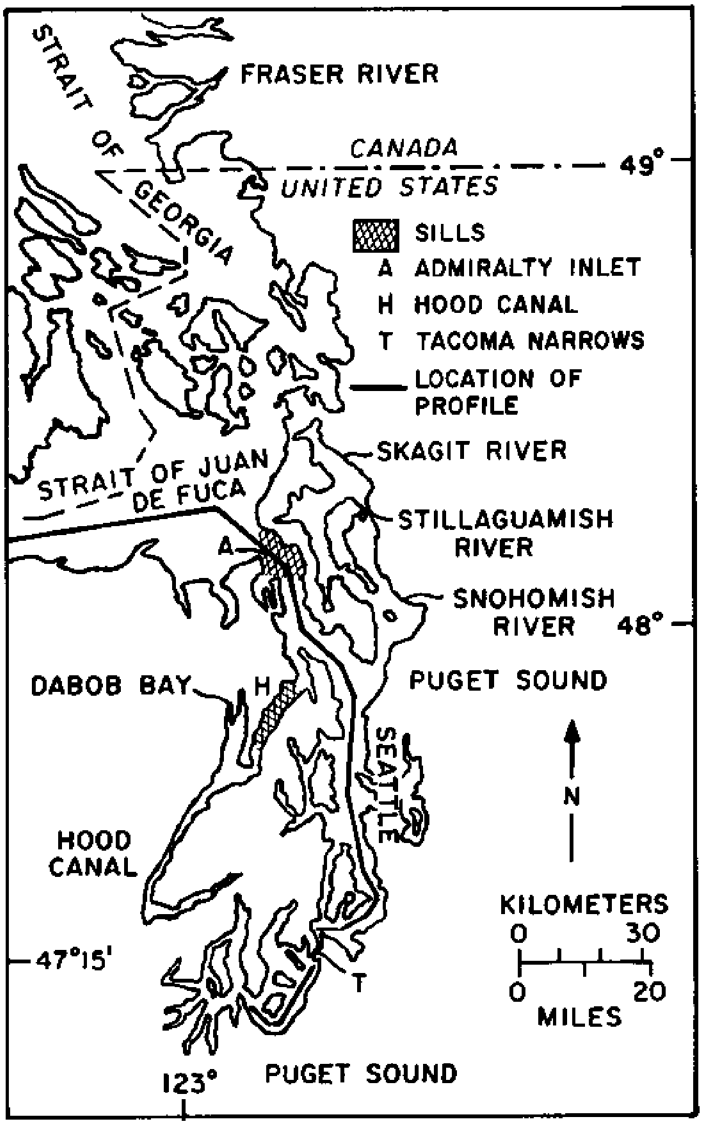
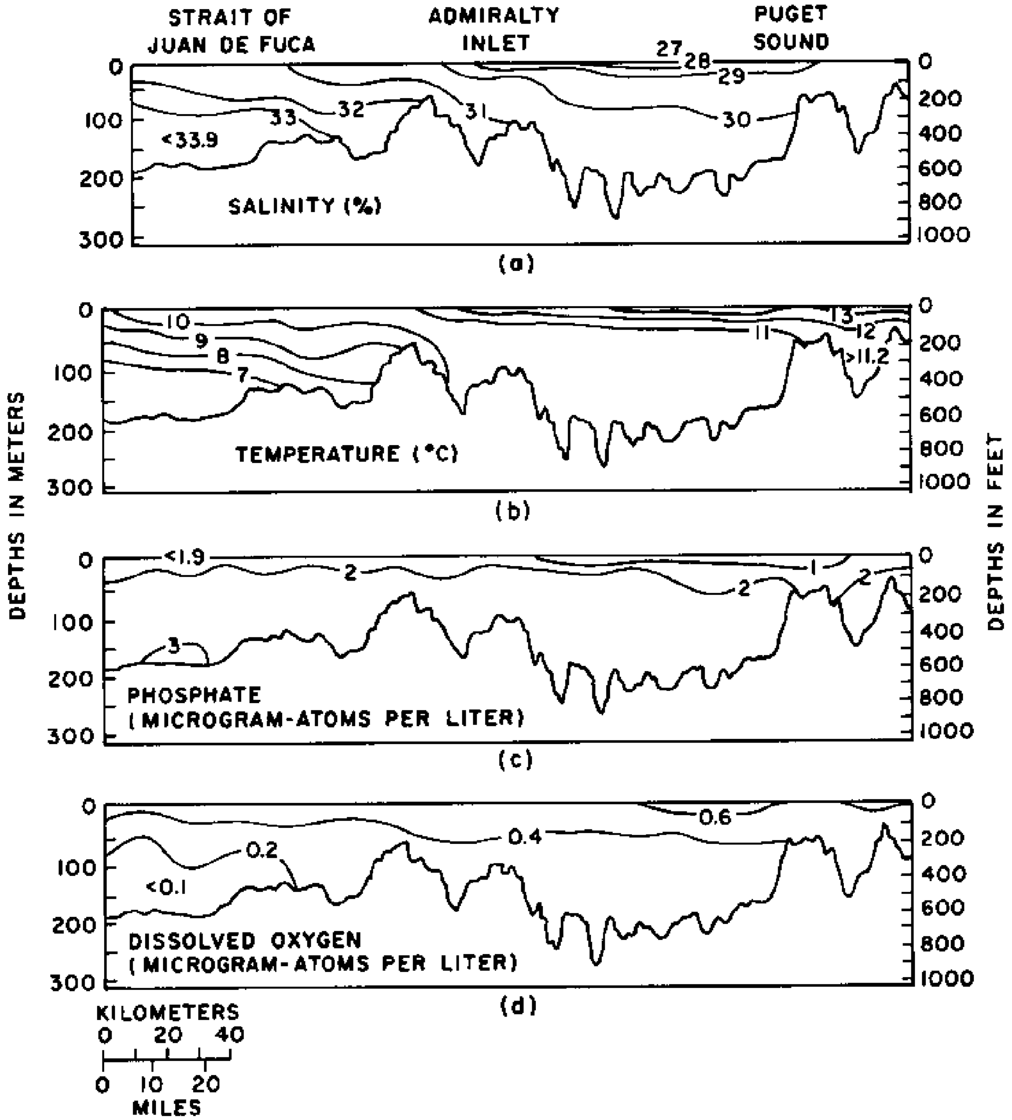


Figure 3.4 Variation with depth of salinity (a), temperature (b), phosphate concentration (c), and dissolved-oxygen concentration (d), during summer (University of Washington, 1954).



The surface area of Puget Sound is relatively small compared to its volume. Thus only a limited amount of surface water can be warmed by the sun. Mixing keeps surface waters well supplied with nutrients necessary for phytoplankton growth. Rarely if ever is phytoplankton growth limited by nutrient depletion in Puget Sound, although in winter it is often inhibited by insufficient light because of the cloudy, rainy climate.

Mixing processes also supply abundant dissolved oxygen to subsurface waters throughout most Puget Sound basins. Some isolated basins, such as Hood Canal, or silled basins, such as Dabob Bay, exhibit seasonal depletion of dissolved oxygen in subsurface waters, especially during late summer. It seems that the productivity of the surface layers is high in these inlets, and the rate of resupply of dissolved oxygen is not rapid enough to make up the loss from decomposed organic matter that sinks out of the surface layers.

In contrast to shallower estuaries, Puget Sound is little affected by wind. Mixing near river mouths is strongly affected by local winds, but circulation patterns and water levels are influenced only by the largest storms. In part, this is a consequence of the protected location of the Sound; it is bordered on three sides by mountains that greatly reduce wind velocities. Wastewaters discharged in Puget Sound are likely to be widely dispersed through the estuary by the strong tidal currents.

SUMMARY

1. There are pronounced differences among and within coastal ocean regions of the United States which can markedly alter the behavior of wastewaters discharged to the ocean and possibly the fate of wastewater constituents.

2. Relatively few major types of coastal circulation systems can be differentiated for purposes of control and regulation. Example:

    - Broad continental shelf

    - Narrow continental shelf

- Coastal plain estuaries
- Fjord-like estuaries

3. Ability to predict movements of dissolved conservative wastes in coastal waters is best developed for average or long-term (months to years) conditions. Ability to predict shorter term (days to weeks) movements of waters is less developed for short-term events, such as storm passing across the shelf or the passage of warm-core rings along the edge of the Mid-Atlantic shelf.

4. Limited ability exists to predict movements of particles or particle-associated constituents from waste discharges.

5. Little or no capability exists to predict many types of events or coastal ocean processes, such as anoxia in near-bottom waters on a broad continental shelf.

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4

Delivery Systems and Initial Dilution

Robert C.Y. Koh

INTRODUCTION

The discharge of municipal waste into the ocean has been practiced for many decades by coastal communities. There are basically two methods of transporting the waste from the treatment works to the discharge point: 1. via an outfall pipeline for effluent or sludge, and 2. for sludge, by means of barges or vessels.

In the continental United States, there are two major groups of ocean discharges of municipal waste. (Chapter 1 summarizes the total extent of municipal discharges for the nation.) On the Atlantic coast, there is a major assemblage of ocean discharges from both outfalls and barges into the area known as the New York Bight. On the Pacific coast, there is another major cluster of ocean discharges from outfalls into the Southern California Bight. While there are other discharges along most shorelines, these two clusters not only are the largest, but also the most studied. Extensive and detailed measurements from these two areas will undoubtedly shed much light as to the effects of ocean discharges of municipal wastes. Table 4.1 summarizes the characteristics of selected major outfalls along the Pacific coast and Hawaii. The discharges into the New York Bight are more diffuse and have been documented in Gross (1976) and Mueller and Anderson (1978). The appendices at the end of this book contain more detailed descriptions of these and a few other areas.

Also included in Table 4.1 are costs and dates construction contracts were awarded. Construction costs of marine outfalls not only vary from one region to another, but also depend on size of pipeline, construction method, wave protection features, and special structures required, such as Y-structures to diffuse the flow into two legs.

Table 4.1 Summary of Characteristics of Major Pacific Ocean Outfalls (USA). (Notes on following page)

	White Point No. 3[1]	Hyperion[2]	San Diego	White Point No. 4[3]	West Point[4]	Orange County[5]	Sand Island[6]
Year Operation began	1956	1960	1963	1965	1965	1971	1975
Pipe diameter (inside)-(inches)	90	144	108	120	96	120	84
Length of Main Outfall (excl. diff.)-(ft)	7,900	27,525	11,500	7,440	3,050	21,400	9,120
Length of Diffuser L_d (ft)	2,400	7,920	2,688	4,440	600	6,000	3,384
Depth of Discharge (nominal)	200-210	195	200-210	165-190	210-240	175-195	220-235
Design average Flow Q (ft^3/sec)	232	651	363	341	194	450	164
Port diameters[a] (inches)	6.5-7.5	6.75-8.13	8.0-9.0[b]	2.0-3.6	4.5-5.75	2.96-4.13	3.00-3.53
Port spacing (average)[c]-(ft)	24	48	48	6	3	12	12
Velocity of Disch. (nominal) for ave. flow-(fps)	8	13	15	9	6	13	10
Q/L 2 d (ft/sec)	0.097	0.082	0.135	0.077	0.323	0.075	0.048
Area Factor (Total Port Area/Pipe Area)	0.63	0.44	0.39	0.51	0.60	0.45	0.44
Date Contract Awarded	10/54	5/57	9/61	5/64	7/64	10/15/68	10/73
Construction Cost (Million $)	2.18	20.21	7.78	4.46	1.23	8.95	13.57

[a] Exclusive of end ports, which are usually somewhat larger.

[b] Blocked by orifice plates with openings of 6.5-7 inches for early years' low flow.

[c] Length of diffuser divided by number of ports; real spacings on each side of the pipe are twice the values indicated.

[1] Sanitation Districts of Los Angeles County Whites Point No. 3
[2] City of Los Angeles at Hyperion
[3] Sanitation Districts of Los Angeles County White Point No. 4
[4] Metrop. Seattle (West Point)
[5] Sanitation Districts of Orange County, CA.
[6] Honolulu (Sand Island)

Along the southern California coast, the offshore bathymetry is relatively steep (slopes are of order 1 on 100) so that a water depth of 60 m is attained at a distance of about 6 km from shore. Outfall pipes often reach beyond that distance and discharge into water depths in excess of 60 m. Figure 4.1 shows the plan and profile of the Sand Island outfall system for the city and county of Honolulu, Hawaii. Equipped with long diffusers, these outfall structures result in wastewater plumes which attain initial dilutions on the order of 10^2 to 10^3. In contrast, the shelf slopes offshore of New York-New Jersey are much flatter, on the order of 1 in 500. To reach an equivalent depth would therefore require a distance five times as long.

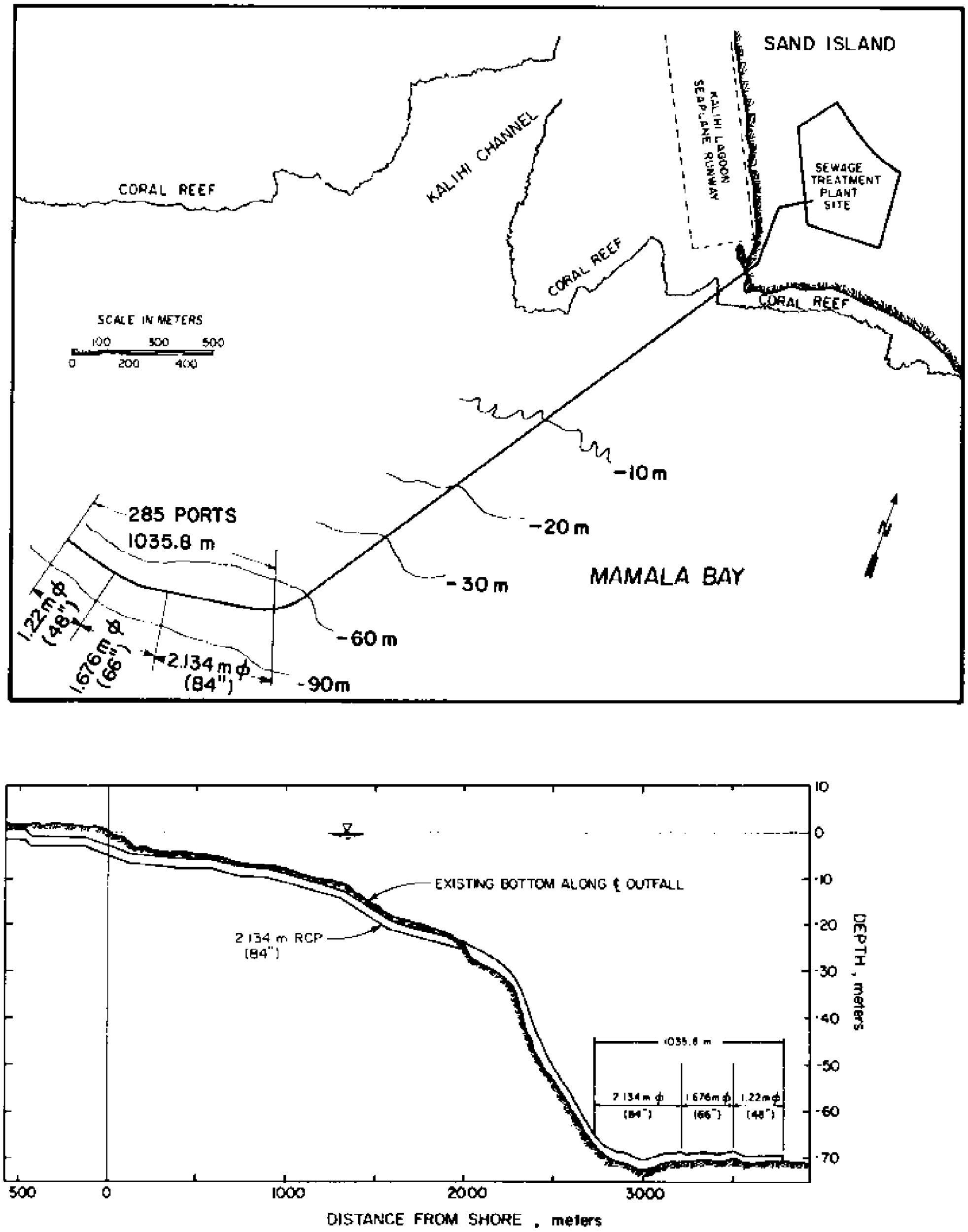
Traditionally, New York has used barges to dispose of solid wastes, including sewage sludge, in the ocean. These disposal operations take place in designated dumping sites. After 1934, when the ocean dumping of refuse, garbage, and floatable waste was stopped, the types of waste discharged from barges have included sewage sludge, dredge spoil, cellar dirt, and industrial waste, with dredge spoil accounting for the largest fraction.

The purpose of this chapter is primarily to describe the physical mixing processes which occur when waste is discharged into the ocean via either outfall or barge. In chapter sections, the general physical mechanisms are discussed; the concept of initial dilution is described; results of research conducted in the past two decades which permit estimation of initial dilutions as a result of ocean waste disposal are presented; marine environmental conditions influencing mixing processes are discussed; and the chapter is summarized.

MIXING PROCESSES

Sewage effluent is primarily fresh water. When discharged from an outfall into the ocean, it rises due to its buoyancy. During the buoyant rise, it mixes with the ambient ocean water. The density of the mixture thus gradually increases as the diluted effluent contains progressively more seawater. If the ocean water is density stratified, as is often the case in summer due to presence of a thermocline, the diluted effluent may stop rising before it reaches the surface. This occurs if the effluent is mixed

Figure 4.1 Plan and profile of Sand Island Outfall (R.M. Towill Corp., 1972)



sufficiently with the heavier water below the thermocline such that the mixture density is greater than that of the water above the thermocline.

Sewage sludge is also primarily fresh water. Digested sludge, which contains several percent solids, is normally lighter than seawater so that, if discharged into the ocean, it tends to rise towards the surface. For discharge from an outfall, the sludge from the city of Los Angeles is prediluted with two parts effluent to reduce the risk of deposition in the pipeline. For discharge from barges, the sludge can be thickened to reduce its bulk. This also tends to render it heavier than seawater.

The initial behavior of sludge discharged from a barge depends on both the method of discharge and on the sludge characteristics. When heavier-than-seawater sludge is pumped from a barge, the resulting plume would sink much like the buoyant plume would rise from an outfall. If a bottom opening hopper barge is used, the sludge, if thickened to the point of cohesion, may fall in a unit without much dilution with the receiving water, like a lightweight rock. During this time, pieces may ablate from the mass. A more typical occurrence is when it falls as a loose cloud of solid particles in water. In this case, its physical behavior is similar to that of the rise of a thermal in the atmosphere. Mixing with the ambient water occurs while the sludge cloud still retains its identity. From the physical point of view, the solid particles in the sludge need not be considered except for their contribution to the density of the descending sludge cloud, because the settling velocity of individual particles is several orders of magnitude less than the advective velocity of the cloud. If the ocean water is density stratified, the descending sludge cloud may not reach the bottom but spread out horizontally in a layer of neutral density. The solids in the sludge would gradually settle out.

The initial phase of motion is thus strongly influenced by the difference in density between the waste cloud (or plume) and the ambient water. It is interesting to point out that this phase of motion occurs in a matter of minutes rather than hours. The extent of mixing accomplished during this phase is generally accepted as initial dilution. Since it is the only phase under the control of the design engineer, it has received the most attention both in research studies and regulatory posture.

Ocean current is another variable which affects the behavior of the discharge plume. The plume tends to bend over in the direction of the current and the effectiveness of mixing is generally greater when there is a current. However, it is usual in typical coastal waters to have periods of very low or effectively zero current. Since initial mixing occurs in minutes, design calculations of initial dilution are often based on zero current.

Figure 4.2 illustrates the behavior of the wastewater plumes under these various ambient conditions and discharge methods.

Following the buoyant transport, the diluted waste material would be in one of three vertical locations: 1. in a layer of neutral buoyancy, 2. on the bottom, where the diluted waste material is heavier than the local seawater, or 3. at the surface, where the diluted waste is lighter than the surface seawater. The next phase of motion of the waste cloud is horizontal spreading. The driving force in this case is either the residual density difference between the diluted waste and the local seawater or the difference in vertical density gradient within and outside the waste field. This spreading is resisted by fluid inertia, pressure gradients, interfacial shearing which may include some mixing, and possibly wind, if on the surface, or bottom friction, if on the bottom.

Both the buoyant ascent or descent and the horizontal spreading occur over relatively short periods of time, from minutes to an hour. Subsequent to those, the diluted waste field is dynamically passive and further mixing and transport are dominated by ocean currents and turbulence. This part of the mixing process is treated in Chapter 5.

INITIAL DILUTION

The term dilution, as has been used in the literature on waste disposal, denotes the reciprocal of the volume concentration of discharged waste in the receiving water (Rawn and Palmer, 1930). Thus, if c is volume concentration, and S is dilution, then

$$S = \frac{1}{c} = \frac{\text{total volume of a sample}}{\text{volume of discharged waste in the sample}}$$

and S = 1 for an undiluted sample

Figure 4.2a Schematic of wastewater plume behavior for various ocean conditions and discharge methods.

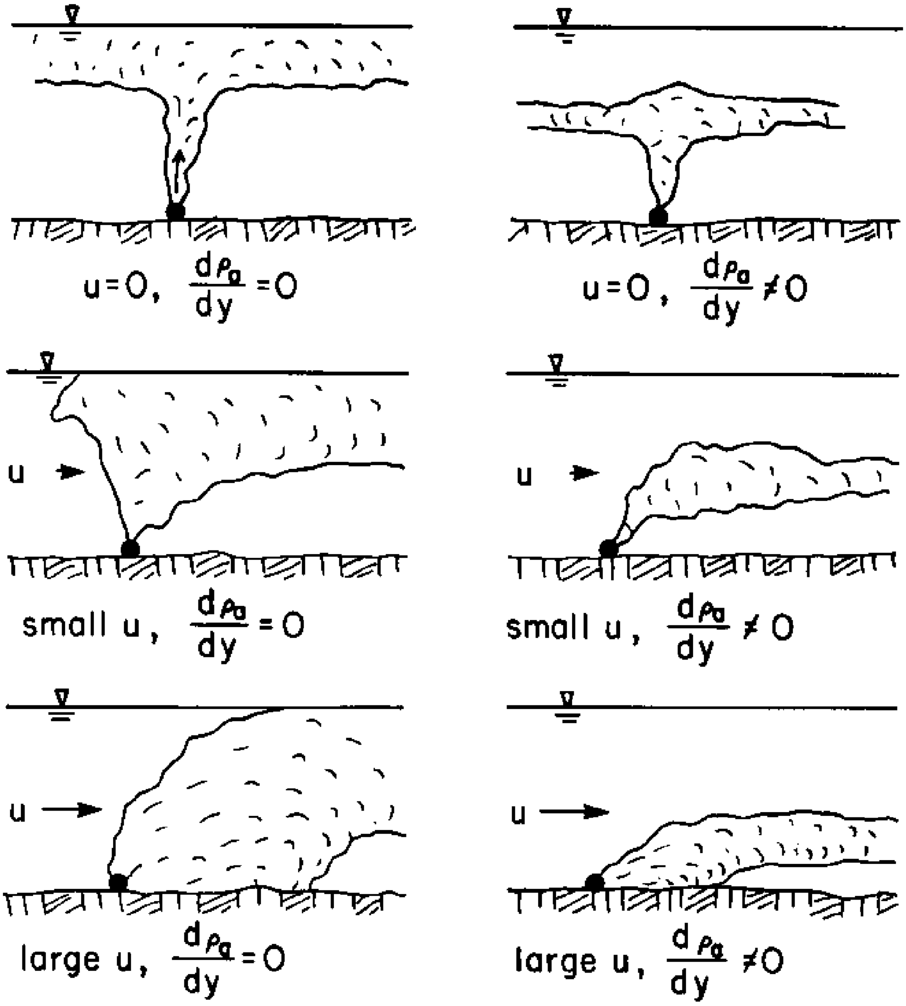
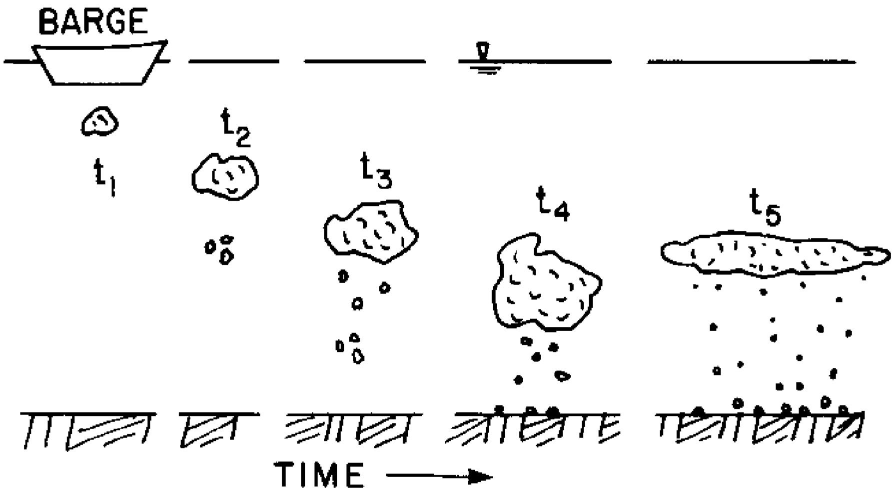
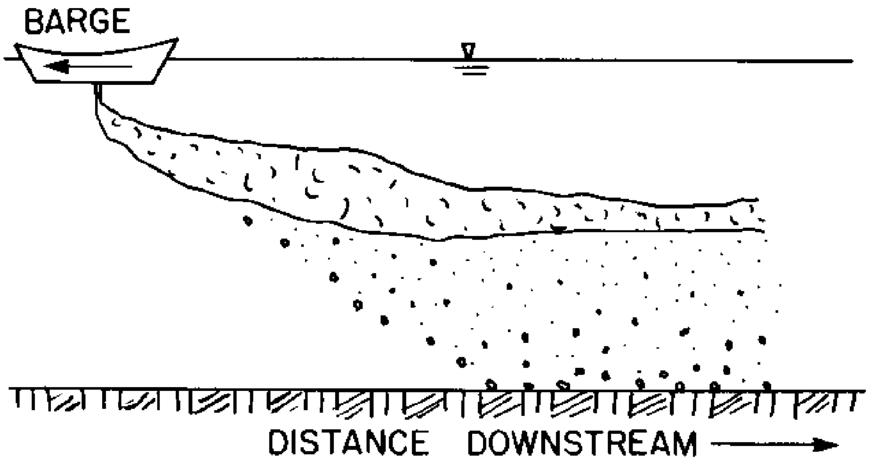


Figure 4.2b Schematic of waste behavior for discharge from barge.



Various stages after heavier-than-seawater sludge is discharged instantaneously from a bottom opening hopper barge.



To the extent that it is possible to take as small a sample as desired, one can define dilution at a point. In general, dilution is a function of space and time and can take on any value larger than or equal to unity. It should be noted that a dilution of 10, as used herein, implies the mixture of 9 parts of water with 1 part wastewater, not 10 parts to 1 part, as sometimes used by others. The primary reason for using dilution rather than concentration is probably a matter of convenience.

Initial dilution for wastewater discharged through an outfall denotes the dilution resulting from mixing which occurs during the buoyant-rise phase of the plume, dominated by the buoyancy and momentum fluxes at the point of discharge. For discharge of heavier-than-seawater sludge from a barge, it is also possible to designate as initial dilution the mixing which results from the sinking of the waste cloud either to the bottom or to its level of neutral buoyancy. The mixing which results after the plume rise or fall is sometimes referred to as subsequent dilution, or further dilution. The term "initial dilution" is not precisely defined, since not only is it difficult to mark the point where initial dilution ends and subsequent dilution begins, but also sometimes it is not even possible to designate a phase of motion as strongly influenced by the discharge momentum and buoyancy. For example, if a slightly lighter-than-seawater sludge is discharged at the surface from a barge, no sinking plume may be manifested since the waste would simply spread out on the surface.

Dilution, as defined by the reciprocal of the volume concentration, is a function of both position and time. Within a steady rising plume, the dilution at a fixed location varies with time. It is possible to define a time-averaged dilution $\bar{S}$ by

$$\bar{S} = \frac{1}{\bar{c}}$$

where $\bar{c}$ is the time-averaged volume concentration. $\bar{S}$ is then a function only of position, and hence varies across the plume cross-section. It has generally been found that a minimum in $\bar{S}$ occurs at the center of the plume cross-section. This value of $\bar{S}$ is commonly referred to as centerline dilution, which, of course, still varies with distance along the plume. In addition to centerline dilution, there is another often utilized notion for a measure of mixing, viz. that of average dilution. It should be noted again that dilution values should not be averaged. Rather the averaging should be performed on the concentration values and the reciprocal taken on the result. The term average dilution, as commonly used in waste disposal, refers to an averaging process based on the flux of the waste material. For this reason, it is sometimes more explicitly referenced as flux-weighted-average dilution. Thus, if c and u are the time-averaged concentration and axial velocity in the plume, then the flux-weighted average dilution S_a is defined as

$$S_a = \frac{\int_A u\,dA}{\int_A cu\,dA}$$

where A is a plane normal to the plume axis.

The above definitions of centerline and average dilutions apply to a plume such as is formed above an outfall. These definitions are the commonly accepted ones found in the literature on waste disposal. For discharge from a vessel such as a barge where the waste load may be released in a short time period rather than continuously, the concepts of centerline dilution and average dilution become less well defined. Dilution can still be defined as the reciprocal of the volume concentration. However, ensemble averaging is required in place of time averaging to arrive at readily interpretable dilution values. This case is handled in the next section where physical phenomena are examined.

In this section, the concepts of dilution for buoyant jets have been defined, including the commonly used terms, initial dilution, centerline dilution, and average dilution. This is done primarily because regulatory documents make specific reference to these terms and because they are sometimes misinterpreted.

ESTIMATION OF INITIAL DILUTIONS

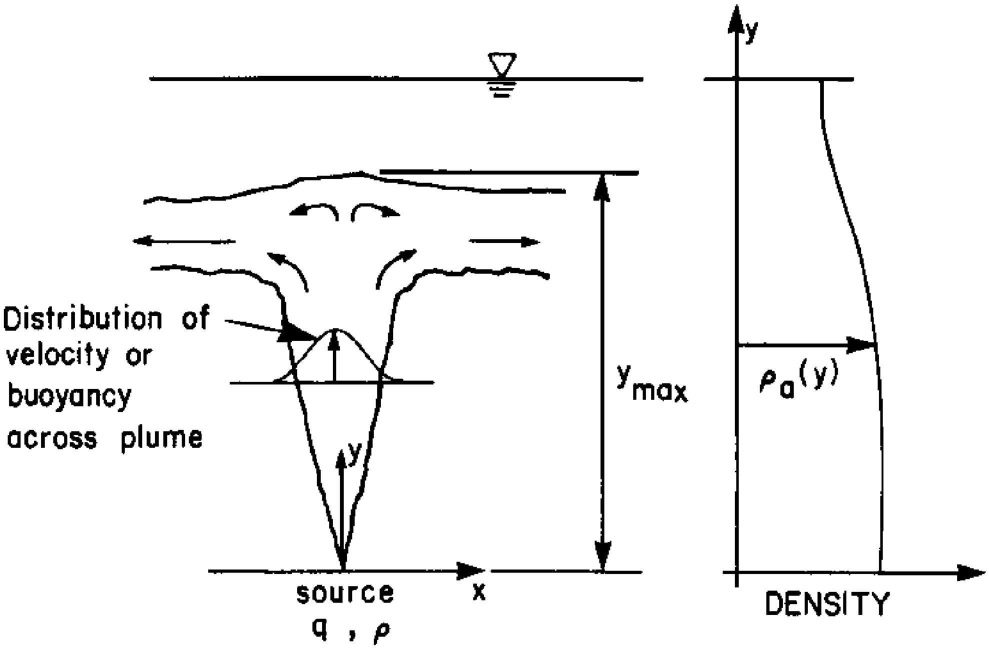
Initial dilution results from that part of mixing which occurs due to the momentum and buoyancy of the discharge and represents the only part under the control of the designer of the discharge method. In this section, the results of research directed at development of methods to estimate initial dilution will be discussed.

Historically, the calculation of primary interest to sanitary engineers involved with ocean sewage outfalls has been the area of ocean pollution as indicated by bacteriological surveys. Prediction of such areas was based largely on a factor which gives the number of "acres-per-second-foot-of-sewage." ("Second-foot" is an old engineering unit synonymous with cubic-feet-per-second.) This factor was used generally as a constant independent of the particular design. The first attempt to investigate the mixing characteristics which result from the discharge of sewage effluent into seawater was probably by Rawn and Palmer (1930) who performed small scale experiments in the sea. Dyed fresh water was discharged through submerged nozzles and dilutions measured by color comparisons. However, it was not until 1956 that the analysis of mixing from buoyant jets and buoyant elements was put on a sound theoretical basis by Morton, et al. (1956). In that classic paper, they presented analyses for both continuous and instantaneous point sources of mass, momentum, and buoyancy fluxes. The former is related to the discharge of buoyant effluent from outfalls, while the latter is related to the discharge of heavier-than-seawater sludge from hopper barges. Subsequently, there have been a large number of investigations on the subject of buoyant jets and plumes (fewer on instantaneous sources of buoyant elements). The methods as well as results may differ in form but not in substance. Summaries of this type of research on buoyant jets and plumes are found in Brooks (1973), Koh and Brooks (1975), and Fischer et al. (1979).

Continuous Source

Consider a steady, continuous line source of mass, momentum, and buoyancy fluxes along the z-axis of a rectangular coordinate system, as shown in Figure 4.3. The case for a point source can be analyzed similarly (see Morton et al., 1956). The line source is chosen here because many large outfalls are equipped with long multiple-port diffusers which can be approximated by line sources.

Figure 4.3 Definition sketch of line plume in a stratified environment.



Assume that:

1. the ambient fluid is motionless (except for the motion induced by the plume);
2. the ambient fluid is infinite in extent and stably stratified in density;
3. all density changes are small (so that density changes need only be considered when associated with gravity) and are linearly related to the agent causing the stratification;
4. flow in the plume is fully turbulent; and
5. pressure distribution is hydrostatic.

The integral form of the conservation equations can be written as follows:

Conservation of mass flux

$$\frac{d}{dy}\left\{ \int_{-\infty}^{\infty} \rho^* u^* dx \right\} = E\rho_a \tag{4.1}$$

where ρ^*, u^* are the density and axial velocity, E is the rate of volume entrainment and ρ_a is the density of the ambient water being entrained.

Conservation of momentum flux

$$\frac{d}{dy}\left\{ \int_{-\infty}^{\infty} \rho^* {u^*}^2 dx \right\} = g \int_{-\infty}^{\infty} (\rho_a - \rho^*) dx \tag{4.2}$$

were g is gravitational acceleration.

Conservation of buoyancy flux

$$\frac{d}{dy}\left\{ g \int_{-\infty}^{\infty} (\rho_1 - \rho^*)\ u^* dx \right\} = Eg\ (\rho_1 - \rho_a) \tag{4.3}$$

where $\rho_1 = \rho_a(0)$.

The equation 4.3 has made use of assumption 3. The same assumption also permits the replacement of ρ^* by ρ_1 (a typical constant value) in the left hand side of equations 4.1 and 4.2.

Rather than dealing with ρ^*, it will be convenient to introduce the variable Δ^* defined by

$$\Delta^* = g \frac{\rho_a - \rho^*}{\rho_1} \tag{4.4}$$

Equations 4.1 through 4.3 can now be written

$$\frac{d}{dy}\left\{ \int_{-\infty}^{\infty} u^* dx \right\} = E \tag{4.5}$$

$$\frac{d}{dy}\left\{ \int_{-\infty}^{\infty} u^{*2} dx \right\} = \int_{-\infty}^{\infty} \Delta^* dx \tag{4.6}$$

$$\frac{d}{dy}\left\{ \int_{-\infty}^{\infty} \Delta^* u^* dx \right\} = \frac{g}{\rho_1} \frac{d\rho_a}{dy} \int_{\infty}^{\infty} u^* dx \tag{4.7}$$

The quantities u^*, and Δ^* are functions of x, y and time. They may each be decomposed into the time averaged part ($\bar{u}$ and $\bar{\Delta}$) and the fluctuating part (u' and Δ'). Thus

$$u^* = \bar{u} + u' \tag{4.8}$$

$$\Delta^* = \bar{\Delta} + \Delta' \tag{4.9}$$

Substituting into equations 4.5 to 4.7 and taking time averages of the resulting equations gives

$$\frac{d}{dy}\left\{ \int_{-\infty}^{\infty} \bar{u} dx \right\} = E \tag{4.10}$$

$$\frac{d}{dy}\left\{ \int_{-\infty}^{\infty} (\bar{u}^2 + \overline{u'^2}) dx \right\} = \int_{-\infty}^{\infty} \bar{\Delta} dx \tag{4.11}$$

$$\frac{d}{dy}\left\{\int_{-\infty}^{\infty}(\bar{\Delta}\,\bar{u} + \overline{\Delta' u'})dx\right\} = \frac{g}{\rho_1}\frac{d\rho_a}{dy}\int_{-\infty}^{\infty}\bar{u}dx \qquad (4.12)$$

where the overbar denotes time averages. For closure, it is now necessary to specify $\int_{-\infty}^{\infty}\overline{u'^2}dx$, $\int_{-\infty}^{\infty}\overline{\Delta' u'}dx$, and E. The customary closure assumptions are to neglect $\int_{-\infty}^{\infty}\overline{u'^2}dx$ and $\int_{-\infty}^{\infty}\overline{\Delta' u'}dx$, and to assume that E is proportional to $\bar{u}(x=0)$ with a proportionality constant to be determined by experiments. For the line plume, E is found to be 0.28 $\bar{u}(x=0)$ based on experiments by Rouse et al. (1952).

Before proceeding further, it is well to examine in detail the above closure assumptions. The basis for the neglect of the terms $\int_{-\infty}^{\infty}\overline{u'^2}dx$ and $\int_{-\infty}^{\infty}\overline{u'\Delta'}dx$ has been primarily one of ignorance since they were difficult to measure. Measurements carried out in the laboratory have typically employed the use of some type of probe. Probes for the measurement of fluid velocity include total head tube, propeller meter, hot wire or hot film probes and more recently laser doppler velocimetry. It must now be emphasized that use of these probes for measurement may require careful interpretation. For example, suppose a Pitot tube in combination with a pressure transducer is used to measure velocity. Thus, the basic measurement is not of velocity but of dynamic pressure which is proportional to the square of the velocity. The measured "average velocity" may not be $\bar{u}$ as in equation 4.8 but rather related to the root-mean-square of u*, the exact relationship being dependent on the detailed nature of u* as well as the response of the instrument. Detailed measurements by Kotsovinos (1975) using laser doppler velocimetry combined with a fast response thermistor for the two-dimensional buoyant plume indicate that the quantities $\int_{-\infty}^{\infty}\overline{u'^2}dx$ and $\int_{-\infty}^{\infty}\overline{u'\Delta'}dx$ may not be negligible at all. Similar measurements by George, et al. (1977) for the axisymmetric buoyant plume also show that turbulent transport should not be ignored.

From the above discussions, it is seen that there may be a certain amount of confusion in the interpretation of experimental results. On the other hand, the use of the traditional closure assumptions (neglect of the turbulent transport terms) have yielded predictions which compare favorably with experiments. In this chapter, the traditional closure assumptions will be adopted; however, the reader is cautioned that further research on the turbulent transport terms may necessitate some adjustments in the future.

Return now to equations 4.10, 4.11 and 4.12, and neglect the turbulent transport. From experiments by Rouse et al. (1952), and confirmed by others, e.g., Kotsovinos (1975), it was found that the crossplumes profiles of $\bar{u}$ and $\bar{\Delta}$ are similar and well approximated by Gaussians of the form

$$\bar{u} = ue^{-x^2/b^2} \tag{4.13}$$

$$\bar{\Delta} = \Delta e^{-x^2/b^2\lambda^2} \tag{4.14}$$

where b, a characteristic width of the velocity profile, is a function of y. The corresponding width of the density profile is λb. For line plumes a reasonable approximation is $\lambda = 1$, which is used in the analysis below for simplicity. Here u and Δ are the values of $\bar{u}$ and $\bar{\Delta}$ at x=0 (i.e., centerline values). Substituting equations 4.13 and 4.14 into the conservation equations, performing the integrations, yields the result

$$\frac{d(ub)}{dy} = \frac{2\alpha u}{\sqrt{\pi}} \tag{4.15}$$

$$\frac{d}{dy}(u^2b) = \sqrt{2}\ b\Delta \tag{4.16}$$

$$\frac{d}{dy}(ub\Delta) = -\sqrt{2}\ ubG \quad \left(G = \frac{-g}{\rho_1}\frac{d\rho_a}{dy}\right) \tag{4.17}$$

where the closure relation E = $2\alpha u$ has been used. (α is known as the entrainment coefficient and the factor 2 represents the two sides of the plume.) This is a set of three equations for three unknown functions u, b, and Δ and is in the form of an initial value problem with initial conditions specified at y=0 which characterizes the source. For a given G(y) (the density gradient in the ambient fluid) and initial conditions u_o, b_o, Δ_o at y=0, the system can be readily solved numerically. The case for a point source can be investigated using the same technique and also results in an initial value problem. Computer programs have been published which utilize this type of analysis (known as the integral approach) to give dilutions along the rising buoyant jet discharging at an arbitrary angle into a motionless stably stratified fluid (e.g., round jets: Baumgartner et al., 1971; Ditmars, 1969; slot jets: Sotil, 1971; a row of equally spaced round jets which later merge to a slot jet: Koh and Fan, 1970.)

The entrainment coefficient α as used in this type of formulation was assumed by early investigations (e.g., Fan, 1967) to be a constant. Later research such as by Fox (1970) and List and Imberger (1973) have taken the view that α should depend on the local buoyant jet characteristics. In this chapter, α will be assumed constant and equal to the value appropriate for the two-dimensional plume because discharges from outfalls are nearly plumelike.

For a pure line plume (source of buoyancy flux only) in a uniform environment ($\rho_a=\rho_1$=constant), the solution is particularly simple:

$$u = \text{constant} = (g' q_o/\alpha)^{1/3} \tag{4.18}$$

$$b = \frac{2}{\sqrt{\pi}} \alpha y \tag{4.19}$$

$$\Delta = \frac{g' q_o}{\sqrt{2}\, u \alpha y} \tag{4.20}$$

where $g' = g\left(\frac{\rho_1 - \rho_o}{\rho_1}\right)$ and q_o is the discharge per unit length. The centerline dilution is found from the conservation equation for the flux of a tracer quantity

$$\sqrt{\pi/2}\, cub = c_o q_o \tag{4.21}$$

i.e.,

$$S = \frac{c_o}{c} = \sqrt{2}\,\alpha^{2/3} g'^{1/3} y / q_o^{2/3} \qquad (4.22)$$

For α = 0.14 (see Brooks, 1973)

$$S = 0.38\,\frac{(g'q_o)^{1/3} y}{q_o} \qquad (4.23)$$

For a linearly stratified environment (G=constant) and assuming α = 0.14, the pure plume solution gives

$$S_t = 0.31\,\frac{(g'q_o)^{1/3} y_{max}}{q_o} \quad \text{(terminal centerline dilution)} \qquad (4.24)$$

where

$$y_{max} = 2.84 (g'q_o)^{1/3} G^{-1/2} \quad \text{(maximum height of rise)} \qquad (4.25)$$

For horizontal slot discharge with values for initial parameters chosen to correspond to typical sewage outfalls, the corresponding formulae are (Brooks, 1973)

$$S_t = 0.36\,\frac{(g'q_o)^{1/3} y_{max}}{q_o} \qquad (4.26)$$

$$y_{max} = 2.5 (g'q_o)^{1/3} G^{-1/2} \qquad (4.27)$$

For point source, the results are:

$$\left[\begin{array}{c}\text{uniform}\\ \text{environment}\\ (G = 0)\end{array}\right] \quad S = 0.09\,\frac{(g'Q_o)^{1/3}}{Q_o}\, y^{5/3} \qquad (4.28)$$

$$\left[\begin{array}{c}\text{linear}\\ \text{stratification}\\ G=\text{constant}\end{array}\right] : \quad S_t = 0.07\,\frac{(g'Q_o)^{1/3}}{Q_o}\, y_{max}^{5/3} \qquad (4.29)$$

$$y_{max} = 4 (Q_o g')^{1/4} G^{-3/8} \qquad (4.30)$$

corresponding to equations 4.23, 4.24, and 4.25, respectively.

All the above are for centerline dilutions. The average dilution is related to the centerline dilutions according to the integral approach by

$$S_a = \sqrt{2}\,S \quad \text{for two-dimensional or slot buoyant jets} \qquad (4.31)$$

$$S_a = 1.74\ S \quad \text{for axisymmetric buoyant jets} \qquad (4.32)$$

(corresponds to = 1.16 in Eq. 4.14)

The reader is again cautioned that all the above results are based on the integral approach where turbulent transport represented by terms of the form $\overline{u'c'}$ are ignored. While these have been used quite successfully in the design of many outfall diffusers, more recent research (Kotsovinos, 1975) has indicated that the turbulent transport may not be negligible. Fischer et al. (1979) should be consulted for a more detailed discussion.

Among the results detailed above, the ones of most engineering usefulness are those for the two-dimensional plume (i.e., equations 4.23 to 4.27). This is because a multiport diffuser is an engineering approximation to a two-dimensional or line source. The design variables of primary importance in determining the initial dilution are the overall length of the diffuser and the depth of discharge. The details of port spacing and number of ports are secondary provided that they are sufficiently numerous and close together to approximate a line source. A frequent misconception is to assume the dilution would be optimized by choosing the port spacing sufficiently large that the plumes from neighboring ports do not interfere. However, such a diffuser can almost always be improved by having more smaller ports closer together for the same overall diffuser length.

When sewage effluent is discharged continuously from an outfall, it rises and becomes progressively more diluted. Upon reaching either the ocean surface or a submerged level if there is sufficient density stratification in the ocean, it will spread out horizontally. A layer of diluted effluent is then formed above the outfall. It is clear that dilution of the effluent with uncontaminated ocean water effectively ceases above the bottom of this layer. The results of the integral analyses presented herein relate the dilution to height of travel assuming continual availability of uncontaminated ocean water. Application of these results to evaluation of outfall performance must include a determination of the location of the bottom of the sewage field. This, in turn, requires the solution of the problem of horizontal spreading of a layer either buoyant at the surface or more homogeneous and submerged in a density stratified ocean. Thus, to obtain the expected initial dilution from a given design, the results of integral analyses should be coupled with the solution of the parallel problem of horizontal spreading. This latter phenomenon has received less investigation. It is similar in nature to that of oil spreading on water, the spread of river discharge upon entering the ocean, or the vertical collapse and horizontal spreading of a mixed region in a stratified fluid.

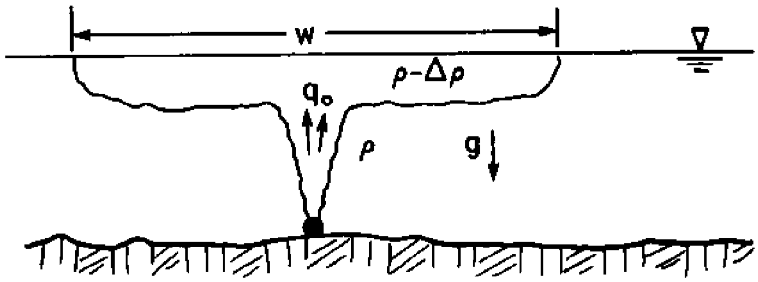


Figure 4.4 Definition sketch of surface spreading of buoyant fluid.

The spread of buoyant fluid on the surface of an otherwise stagnant fluid has been examined by Sharp (1969), Koh and Fan (1970), Koh (1976), Chen and List (1976), and Chen (1980). For a two-dimensional continuous source started at t=0, the width of the spreading field w grows with time as (see Figure 4.4)

$$w = K\ (g'q_o)^{1/3}t$$

for the time in the range of interest for application to outfalls. K was found from experiments to be about 1.2. This result can be combined with equation 4.23 to yield the initial dilution to be expected at the bottom of the spreading sewage field. This is found to be (Koh and Brooks, 1975)

$$S_b = 0.27 \frac{(g'q_o)^{1/3}d}{q_o} \quad \text{centerline dilution} \qquad (4.33)$$

$$S_{ab} = 0.38 \frac{(g'q_o)^{1/3}d}{q_o} \quad \text{average dilution} \qquad (4.34)$$

where d is the total depth of water. It is coincidental that the centerline dilution without considering the effect of blocking by the sewage field is the same as the average dilution including the effect of blocking.

The initial dilution obtained from typical large outfalls equipped with multiport diffusers can be readily estimated based on equation 4.33 or 4.34. Referring to Table 4.1 it can be seen that q_o is of order 0.1 cfs/ft or 0.01 m^2/s. Also $g' = 9.81 \times 0.025$ m/sec^2 where the difference in density between seawater and effluent has been assumed to be 0.025 gm/cc. For d=60 m,

$$S_b \cong 220$$

$$S_{ab} \cong 310$$

These values assume the ambient stratification is not sufficient to prevent the rising plume from reaching the water surface. In the event stratification stops the vertical rise of the plume after, say 30 m, the initial dilutions obtained would be effectively half the above values (approximately calculated from Eqs. 4.33, 4.34, with $d \cong y_{max}$).

For older outfalls which use a single open-ended pipeline, the initial dilutions are usually quite a bit less. As an example, consider a hypothetical outfall discharging 2 m^3/s from a pipe at the bottom depth of 15 m. Equation 4.28 then gives $S \cong 3$.* This is estimated based on the plume rising to the surface and without taking into account the effect of blocking. While these estimates are not necessarily of great accuracy, the marked difference between the

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* For this case the initial momentum and mass flux would undoubtedly be important. For horizontal buoyant jets see Brooks (1980) or Fischer, et al. (1979).

initial dilutions obtainable from multiport diffusers in relatively deep water compared with single point discharges should be obvious. Whereas the former are typically several hundred, the latter are often less than ten.

For ready reference, Figures 4.5 to 4.7 are included here. These are graphical representations of equations 4.34, 4.27, and the combination when 4.27 is substituted into 4.34, respectively (density difference between effluent and seawater assumed to be 0.025 gram per cubic centimeter (gm/cc)). From these, the order of magnitude of dilutions obtainable from multiple port diffusers can be readily gauged. The accuracy of the analysis and the graphs is probably only ± 20 percent because of the assumptions involved.

The analyses presented in this section pertain to the discharge of wastewater effluent into the ocean from long multiple-port diffusers located in relatively deep water. In particular, it assumes that the flow rate and water depth are such that the diluting water can approach the discharge structure relatively unimpeded. This is the case for all major ocean discharges of sewage effluent. However, if the flow rate per unit length of diffuser is large and the ocean relatively shallow, such as in cooling water discharge from power plants, the above can no longer be applied because the entire water column around the discharge structure may be actively involved in the plume. Analysis of the latter type of mixing is not treated herein. The reader is referred to Jirka and Harleman (1973) and Jirka et al. (1975) for detailed discussions.

Instantaneous Source

Some waste discharge operations, such as disposal of heavier-than-seawater sludge from a hopper barge, are more appropriately simulated as instantaneous sources rather than continuous ones. The discharged sludge can be approximated by a sinking cloud containing both fluid and solids. For small solids, their effect on the physical behavior is primarily the contribution to an increase in the bulk density. As the cloud descends due to its submerged weight (negative buoyancy), it mixes with the ambient seawater. The basic physical phenomenon during this convective descent phase is similar to the rise of thermals in

Figure 4.5 Initial average dilution for an outfall diffuser based on line plume approximation. Graph of Eq. 4.34 (density difference assumed = 0.025 gm/cc).

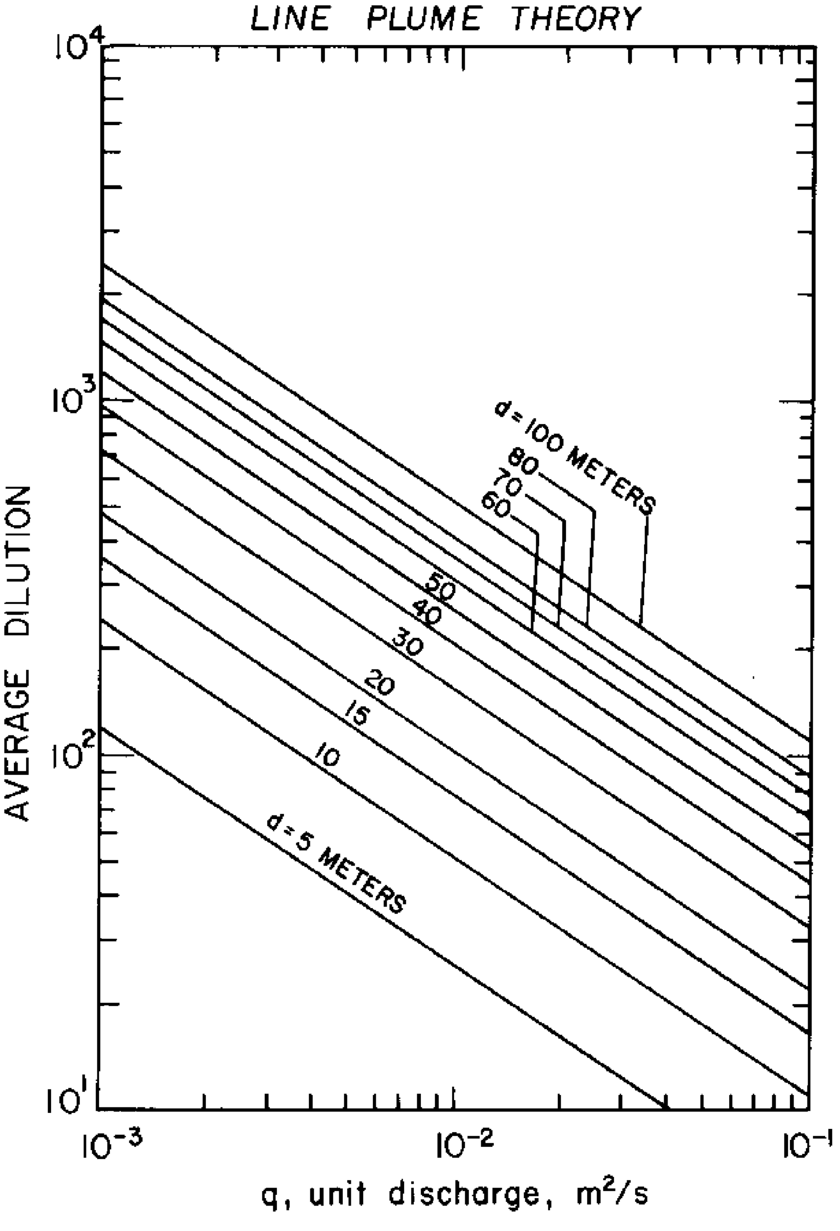


Figure 4.6 Maximum height of rise of wastewater plume from outfall diffuser in linearly stratified ocean based on line plume approximation. Graph of Eq. 4.27 (density difference assumed = 0.025 gm/cc).

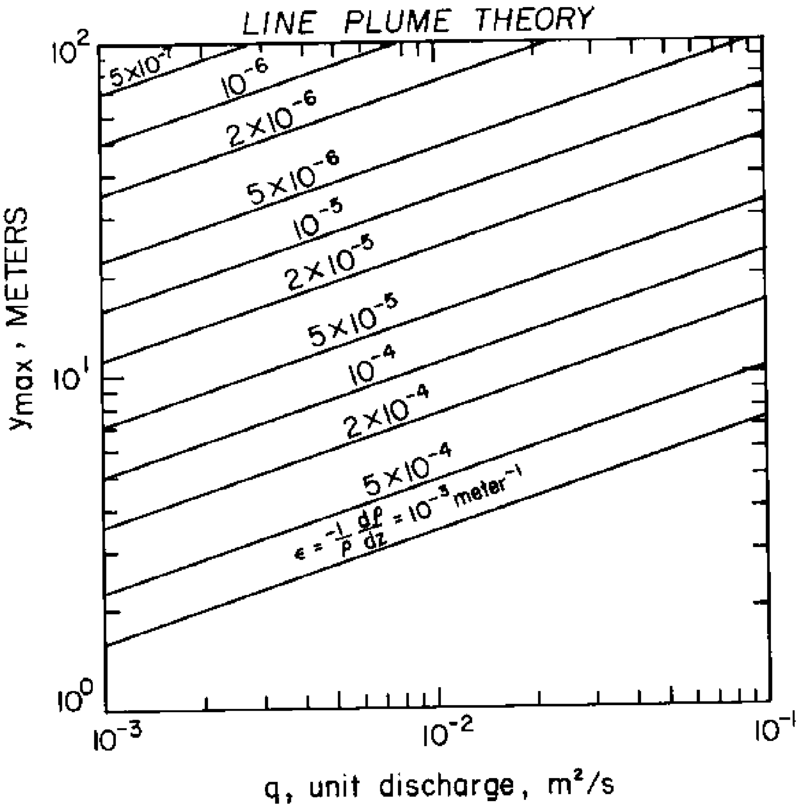
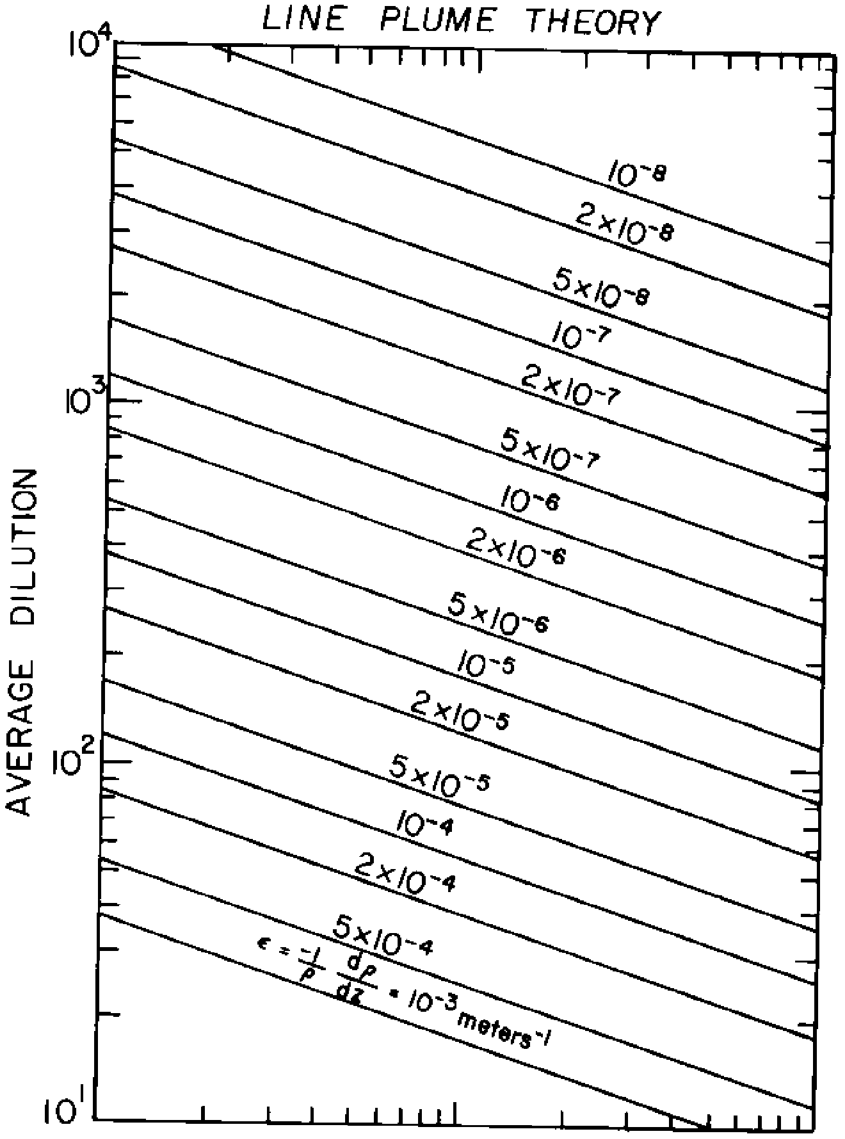


Figure 4.7 Initial average dilution at maximum height of rise for outfall diffuser in linearly stratified ocean. Graph of combined Eq. 4.34 and 4.27 (density difference assumed = 0.025 gm/cc).



the atmosphere. The flow field in and around a thermal (Scorer, 1957) can be summarized as in Figure 4.8. (For a sinking sludge cloud, the direction of travel should be reversed.) The subject is summarized in Turner (1973).

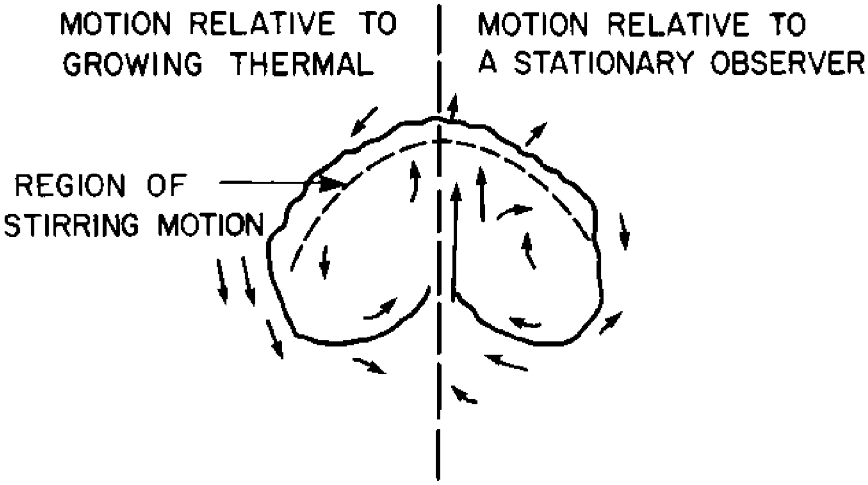


Figure 4.8 Flow field around thermal.

Based on the entrainment concept and similarity assumption, Koh and Fan (1968) developed a calculation procedure for the Navy to estimate the distribution of radioactive debris following deep underwater nuclear explosions. Their model was used by Clark et al. (1971) in assessing the impact of barged waste disposal. The model was later extended by Koh and Chang (1973) to apply specifically for barged disposal. Several disposal methods were considered and the model includes separate calculations for the fluid portion as well as several size fractions of the solid components.

In the following, the simple case of the downward motion of an isolated sludge mass will be examined in a density stratified ocean. It will be assumed that the shape of the cloud as well as the velocity and concentration distributions within the cloud are similar as the cloud descends. Let b, v, c, and ρ denote the half width, average velocity, average concentration, and average density in the cloud. Assume the shape of the cloud can be approximated by a hemisphere. The equations of motion considering the cloud as an entity can be written approximately as

$$\frac{d}{dt}\left(\frac{2\pi}{3}b^3\rho\right) = \rho_a E \tag{4.35}$$

$$\frac{d}{dt}\left[C_M \frac{2\pi}{3} b^3 \rho u\right] = \frac{2\pi}{3} b^3 g\,(\rho - \rho_a) - F_D \tag{4.36}$$

$$\frac{d}{dt}\left[(\rho - \rho_1)\frac{2\pi}{3} b^3\right] = (\rho_a - \rho_1)\,E \tag{4.37}$$

where E is rate of volume entrainment into the cloud, F_D is a drag force on the cloud, and C_M is the apparent mass coefficient. ρ_a is the density of the ambient water, ρ_1 is a reference density and t is time. Due to the fact that the cloud is an isolated mass moving in the ambient water, hydrostatic pressure distribution (assumed in the continuous source case) may not be realized. The drag term F_D is introduced to account for the overall effect of the nonhydrostatic pressure distribution around the cloud. The value of C_M for a solid sphere is 3/2. One therefore expects $1 \leq C_M \leq 1.5$. For F_D, a standard drag term of the form

$$F_D = \frac{1}{2} C_D \rho u^2 \pi b^2 \tag{4.38}$$

might be adopted. For the entrainment rate E, in analogy with the continuous source, one might write

$$E = 2\pi b^2 \alpha u \tag{4.39}$$

where α is an entrainment coefficient, normally assumed constant. In addition to the above equation, an equation is also needed which expresses the kinematic relation

$$\frac{dz}{dt} = u \tag{4.40}$$

where z is the vertical coordinate, positive downward.

The conservation of buoyancy equation can be written using the conservation of mass equation as

$$\frac{d}{dt}\left[(\rho - \rho_a + \rho_a - \rho_1)\ \frac{2\pi b^3}{3}\right] = (\rho_a - \rho_1)E = \left(\frac{\rho_a - \rho_1}{\rho_a}\right)\ \frac{d}{dt}\left[\frac{2\pi}{3}\ b^3\rho\right] \tag{4.41}$$

Invoking the Boussinesq assumption,

$$\frac{d}{dt}\left[(\rho-\rho_a)\ \frac{2\pi b^3}{3}\right] + \frac{2\pi b^3}{3}\ \frac{d\rho_a}{dz}\ u = 0 \tag{4.42}$$

For simplicity, assume $C_D = 0$ and $C_M = 1$ and let

$$\Delta = g\ \frac{\rho-\rho_a}{\rho_1} \tag{4.43}$$

then

$$\frac{d}{dz}\ \left(\frac{2\pi}{3}\ b^3\right) = 2\rho b^2\alpha \tag{4.44}$$

$$u\frac{d}{dz}\ \left(\frac{2\pi b^3}{3} u\right) = \frac{2\pi b^3}{3}\ gc \tag{4.45}$$

$$u\frac{d}{dz}\ \left(\frac{2\pi}{3}\ b^3\Delta\right) = -u\ \frac{2\pi\ b^3}{3}\ g\left(\frac{d\rho_a}{dz}\right) \tag{4.46}$$

which reduces to

$$\frac{db}{dz} = \alpha \tag{4.47}$$

$$\frac{d}{dz}\ (b^3u) = \frac{g\Delta b^3}{u} \tag{4.48}$$

$$\frac{d}{dz}\ (b^3\Delta) = -b^3G \tag{4.49}$$

where $G = \frac{g}{\rho_1}\ \frac{d\rho_a}{dz}$ which is positive since z is positive downward.

Under the assumption that α is a constant, the mass conservation equation can be integrated at once to yield

$$b = \alpha z + b_o \qquad (4.50)$$

where b_o is the value of b at $z = 0$. Hence the cloud increases in radius linearly in distance. The concentration of any conservative tracer which is absent in the ambient water, therefore, must be

$$c = \frac{c_o b_o^3}{(b_o + \alpha z)^3} \qquad (4.51)$$

The dilution S then, can be written

$$S = \frac{c_o}{c} = \frac{(b_o + \alpha z)^3}{b_o^3} \qquad (4.52)$$

For large distances compared with b_o ($z/b_o >> 1$),

$$S = (\frac{\alpha z}{b_o})^3 \qquad (4.53)$$

which increases very rapidly with distance travelled.

Note that these results (equations 4.50 to 4.52) are independent of the ambient density stratification, being dependent only on the assumption of similarity and entrainment relation. Laboratory experiments (e.g., Scorer, 1957; Richards, 1961) showed that the linear growth of the cloud is observed. However, the growth rate appears to be variable among seemingly identical runs. In other words, α , the entrainment coefficient is a constant for each individual experiment but varies between experiments. Turner (1960), in investigating the dynamics of buoyant vortex rings, found by assuming similarity that

$$\alpha = \frac{B}{2\pi g \ c_1 K^2} \qquad (4.54)$$

where B and K are buoyancy and vorticity in the vortex ring. c_1 was found to be about 0.16. When waste material is dumped from a barge, vorticity can be generated from the initial momentum and buoyancy.

However, as the cloud descends in a stratified ocean, the vorticity decreases and approaches zero so that the relation cannot hold.

Experimental data on the entrainment coefficient for the buoyant element shows a relatively large degree of scatter varying generally between 1/7 and 1/3. The effect of this more than two-fold range in α on the dilution is quite significant. For our purpose in this chapter, the average value $\alpha = 0.25$ as found by Scorer (1957) will be adopted for definiteness.

Return now to equations 4.47 to 4.49 and consider the case G = constant. Let the initial conditions be $u = u_o$, $b = b_o$, $\Delta = \Delta_o$ at $z = 0$. Then the solution is given by

$$b = b_o + \alpha z \tag{4.55}$$

$$\Delta = \frac{\Delta_o b_o^3}{b^3} \left\{ 1 - \frac{H}{4\alpha} \left(\frac{b^4}{b_o^4} - 1\right) \right\} \tag{4.56}$$

$$u = \frac{u_o b_o^3}{b^3} \left\{ 1 + \frac{2}{4\alpha F^2} \left[\left(1 + \frac{H}{4\alpha}\right) \left(\frac{b^4}{b_o^4} - 1\right) - \frac{H}{8\alpha} \left(\frac{b^8}{b_o^8} - 1\right) \right] \right\}^{1/2} \tag{4.57}$$

where

$$H = \frac{G b_o}{\Delta_o} \quad \text{and} \quad F = \frac{u_o}{\sqrt{\Delta_o b_o}} \tag{4.58}$$

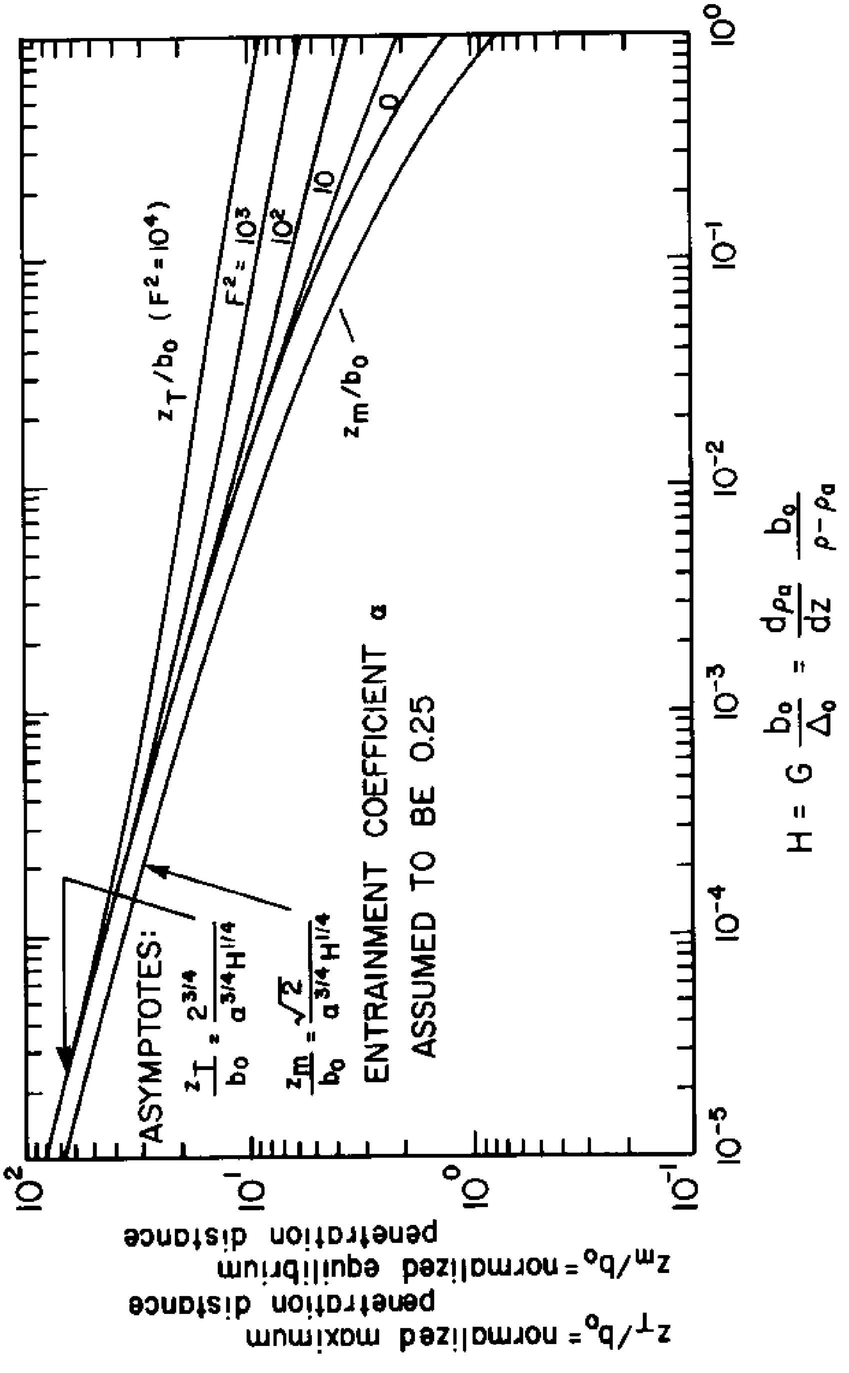
Two interesting features of the solution can be deduced from this. Two distances of fall may be defined: the first will be denoted by z_m which is the depth at which $\Delta=0$; the second will be denoted by z_T which is the depth at which $u=0$. The final depth at which the waste cloud resides will be in between these two depths. These depths can be obtained from the solution to be

$$z_m = \frac{b_o}{\alpha} \left[\left(1 + \frac{4\alpha}{H}\right)^{1/4} - 1) \right] \tag{4.59}$$

$$z_T = \frac{b_o}{\alpha} \left\{ \left[1 + \frac{4\alpha}{H} \left(1 + \sqrt{1 + HF^2}\right) \right]^{1/4} - 1 \right\} \tag{4.60}$$

Equations 4.59 and 4.60 are shown plotted in Figure 4.9.

Figure 4.9 Normalized penetration distances for instantaneous barge dump based on buoyant thermal analysis (Eqs. 4.59 and 4.60).



Recall that dilution is given by

$$\frac{c_o}{c} = \left(\frac{b_o + \alpha z}{b_o}\right)^3 = \left(1 + \alpha \frac{z}{b_o}\right)^3 \qquad (4.61)$$

Thus if we use z_T as the value of z to estimate dilution,

$$S = \frac{c_o}{c} = \left\{1 + \frac{4\alpha}{H}\left(1 + \sqrt{1 + HF^2}\right)\right\}^{3/4} \qquad (4.62)$$

This is shown plotted in Figure 4.10.

As an example consider the case when a load of sludge with bulk density 1.03 gm/cc is discharged downward from a hopper barge in an ocean depth of 15 m. Let the ocean water density be 1.024 and the ambient density gradient be 10^{-5} m^{-1}. Assume no appreciable initial momentum and let the radius of the cloud be 5 m. Then $H = 10^{-5}/.006 \times 5 = 3.3 \times 10^{-4}$. From Figure 4.9, the cloud would reach the bottom. At that point, the dilution would be approximately

$$\left(1 + \frac{1}{4} \cdot \frac{15}{5}\right)^3 = 5$$

For a smaller load, say, with radius 1 m, $H = 10^{-5}/.006 = 1.67 \times 10^{-3}$ and $z_T/b_o \cong 20$, so that it would still reach the bottom. In this case, the dilution would be approximately

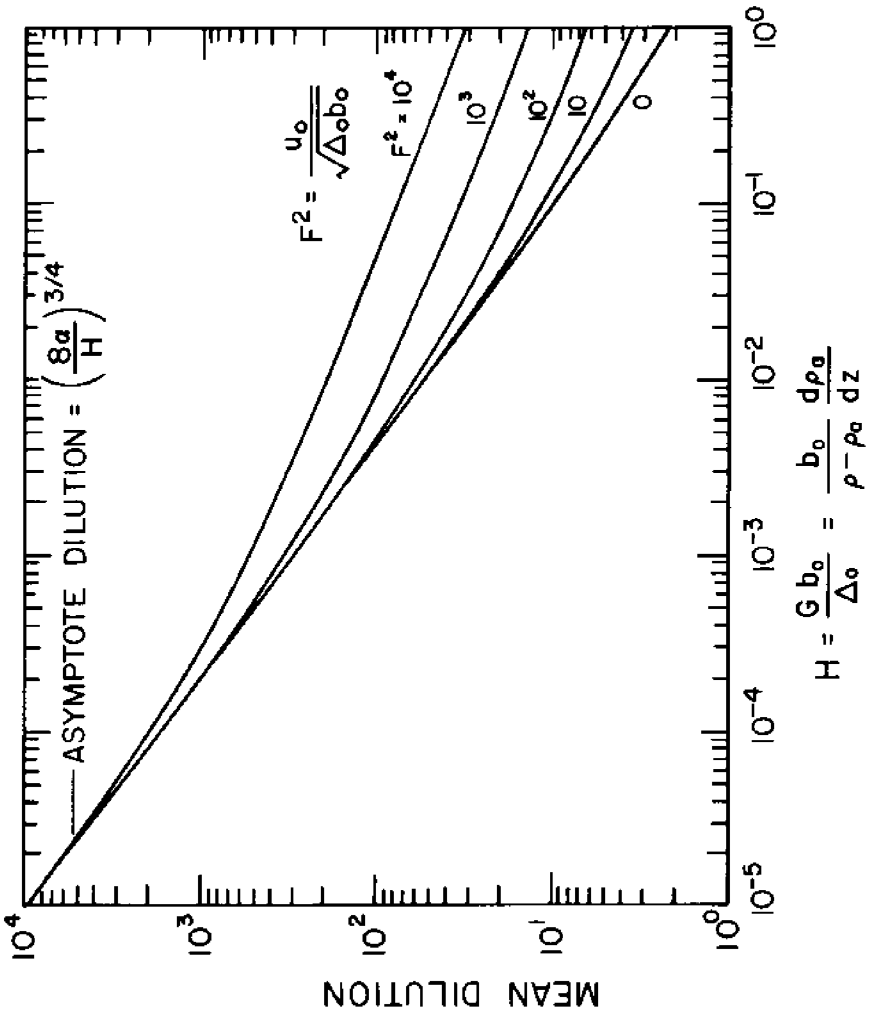
$$\left(1 + \frac{1}{4} \cdot \frac{15}{1}\right)^3 \cong 100$$

It is thus seen that the initial dilution obtainable from instantaneous discharges of heavier-than-seawater sludge from hopper barges depends very much on the size of the dump.

OCEAN ENVIRONMENTAL CONDITIONS

The physical fate of the discharged waste material (both initial dilution and subsequent mixing and transport) depends not only on the characteristics of the material itself, the mode of discharge, but also the ocean environmental conditions. This chapter has concentrated thus far on the first two aspects. In this section, we shall discuss those ocean environmental conditions which most influence the initial phase of the mixing process.

Figure 4.10 Dilutions at maximum penetration depth z_T (Eq. 4.62) for instantaneous dump.



Density Stratification

One of the most important ocean environmental conditions which influences the initial mixing processes is the density stratification. (Figures 4.11 and 4.12 show the density profiles chosen for the design of the Sand Island outfall and the resulting dilutions respectively.) The ocean is often stratified in density due either to temperature or salinity variations. Due to the large dilutions obtainable from a multiport diffuser within a short distance of travel of the discharged waste material, the presence of an ambient density stratification frequently results in the waste field terminating its vertical motion before reaching the surface. In the development of the analyses presented in previous sections of this chapter, the ambient density profile has been incorporated as part of the formulation. While solutions were shown only for simple forms of this variable (e.g., linear profile), there is no inherent limitation in the formulation.

It is noted that the important quantity is not so much the density itself but the density gradient. In fact throughout this chapter, it has been assumed that density changes are small and density variation need be considered only if it occurs as a difference. Because of this, determinations of density must be made accurately so that when differences are taken, sufficient precision is retained. Measurements of ocean density profiles are made indirectly by measuring instead the temperature and salinity and then using an empirical relation to determine density. Hydrographic tables (such as US Navy Hydrographic Office Pub. 615, 1952) are available for this purpose. A more concise table for typical ocean salinities can be found in Appendix A of Fischer et al. (1979).

The density profile in the ocean varies with both location and time. The temporal variations consist of both seasonal and diurnal components. This implies that evaluations of dilution should be made for a variety of density stratifications. For each evaluation, it may be assumed that the ambient density is constant with time. This is because the time scale of vertical motion of the waste material is relatively short (being on the order of minutes) compared with that for material changes in the density stratification. Representative density profiles may be constructed by averaging several measured profiles

Figure 4.11 Density profiles chosen for design calculations for Sand Island Outfall, Honolulu, Hawaii (R.M. Towill Corp., 1972).

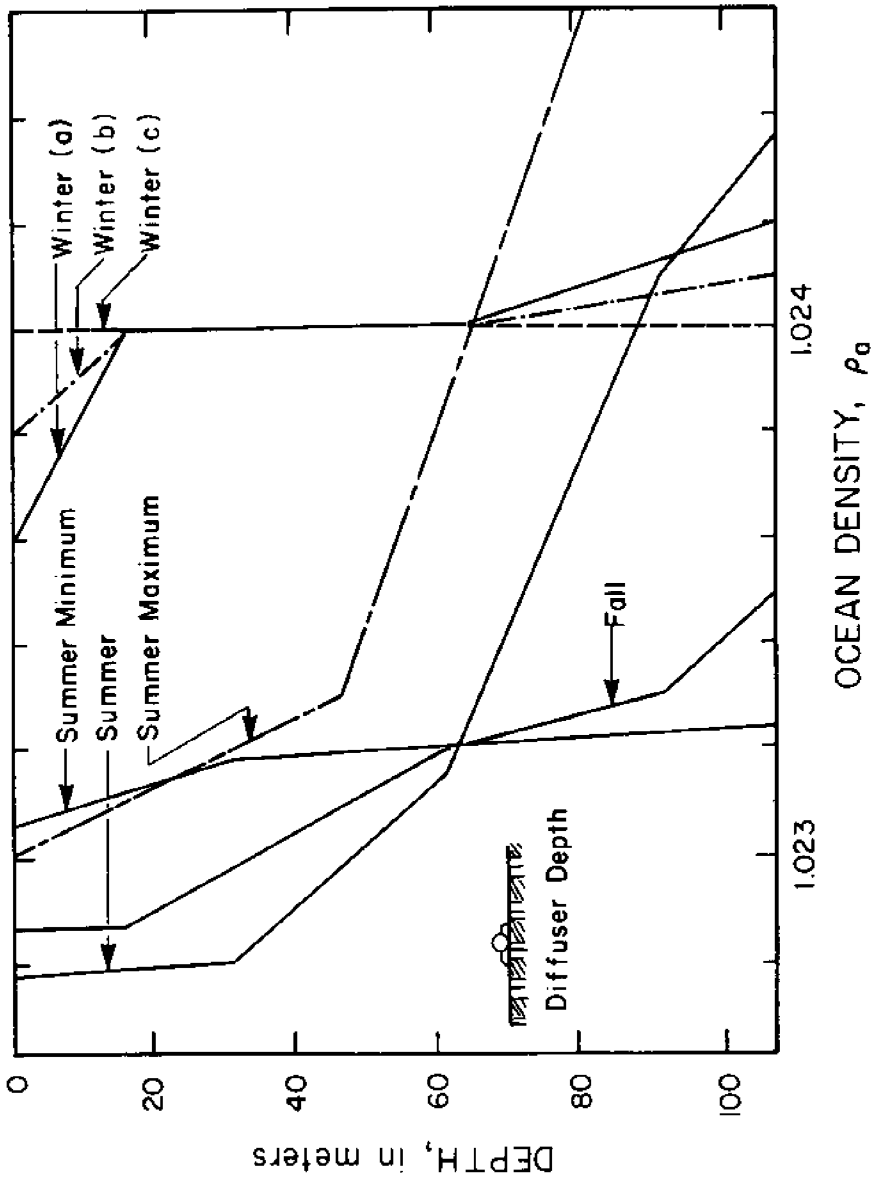
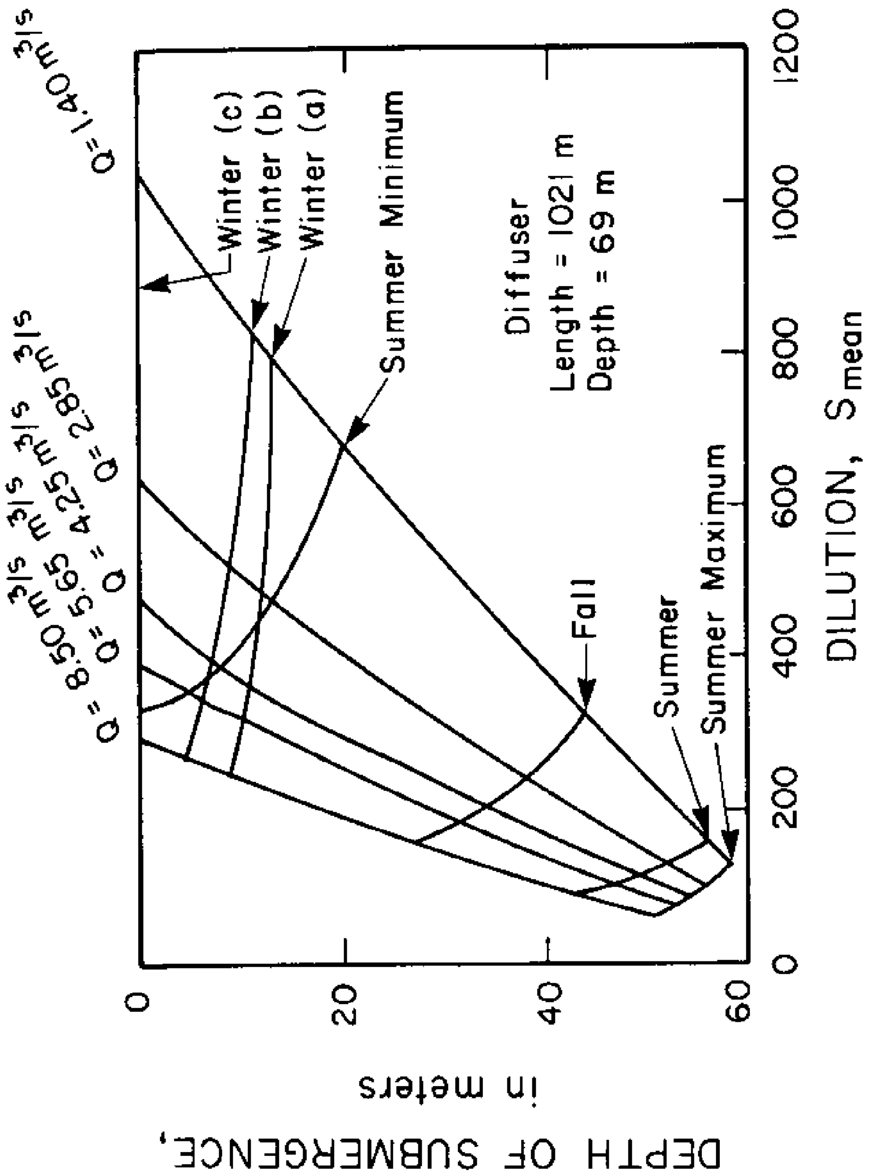


Figure 4.12 Dilutions and submergence of wastewater field for Sand Island Outfall, Honolulu, Hawaii (R.M. Towill Corp., 1972).



for each period of a year. Design of outfalls often involves evaluation of initial dilution under these conditions.

Ocean Currents

Ocean currents are another environmental variable which influence the mixing processes. A current will tend to bend the plume trajectory from an outfall and thus increase its travel length and promote larger dilutions for the same vertical travel. This results in general in both larger dilutions and lower height of rise. For barge disposal of sludge, the current of interest is the relative velocity between the barge and the ocean water.

Measurements of currents in the ocean are made by means of either current meters or drogues. The former gives an Eulerian time-series of current velocity at fixed locations (lasting typically on the order of a month for each record). The latter can give a Lagrangian view of the water movement (however, the duration of the measurements are limited by the ability to follow the drogues, typically less than one day). Both types of data are useful for evaluation of waste disposal consequences. Figure 4.13 illustrates some current meter data taken off southern California. It is possible to simulate the movement of a hypothetical drogue from current meter data if it is assumed that the spatial correlation is perfect. This is done by integrating the current meter data. The result is known as a progressive vector diagram as illustrated in Figure 4.14. For continuous discharge, it is also useful to construct the streakline from the current time series by reversing the data string and integrating. The streakline simulates the plume centerline observed at the final time of the current sequence again assuming perfect spatial correlation. This is shown in Figure 4.15. This type of display permits a clearer visualization of the water movement than the simple plot shown in Figure 4.13.

The behavior of a single round buoyant jet in a cross current has been investigated using the integral approach by Abraham (1970), Hirst (1971), among others. Near the source, the behavior is dominated by the buoyant jet. As the jet bends over, it gradually takes on the characteristics of a line thermal. Wright (1977) studied the same problem in the laboratory for the case when the ambient is both flowing and density stratified. Roberts (1977)

Figure 4.13 Measured (solid) and low-pass filtered (dashed) currents near Orange County Outfall.

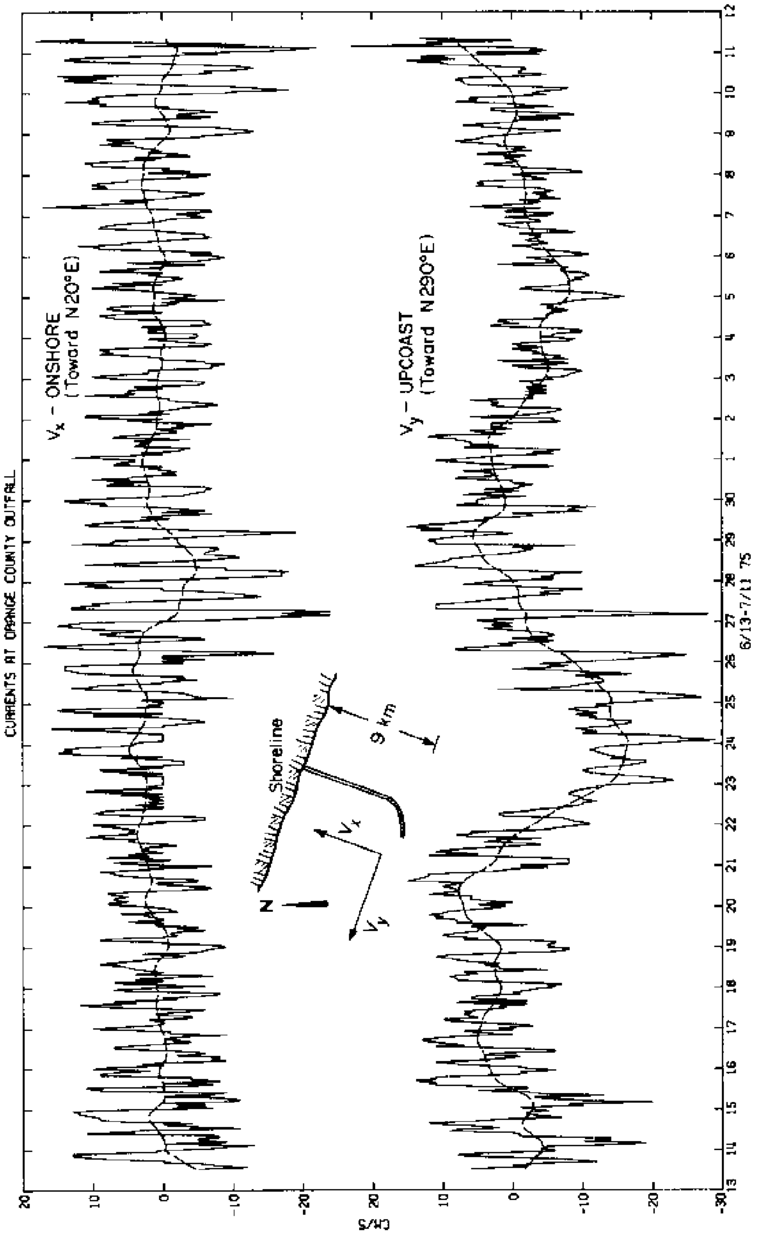


Figure 4.14 Progressive vector diagram for currents shown in Fig. 4.13.

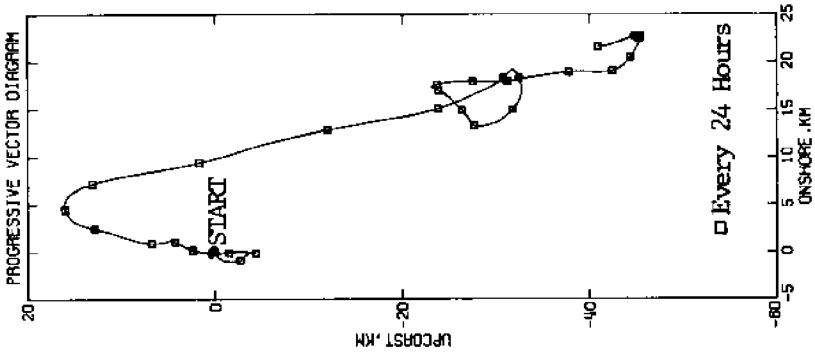
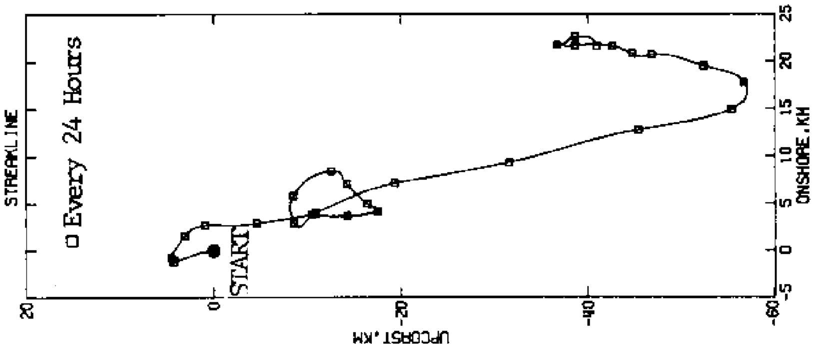


Figure 4.15 Streakline for currents shown in Fig. 4.13.



investigated the effect of an ocean current on the mixing resulting from a long diffuser oriented at various angles to the flow. In all cases, initial dilution is larger when there is a current than when the ambient water is stationary.

In the philosophy of ocean wastewater discharge from outfalls it is implicit that there is sufficient through flow in the region to transport the continuous discharge away from the site. While this may be a good assumption for discharge into open coastal areas, it is by no means clear for discharge into semi-enclosed bodies of water such as estuaries. In these cases, it is important to critically examine the transport and mixing in the zone beyond the initial dilution region, since the diluting water may already contain a certain concentration of waste. Let c_o be the concentration of wastewater in the ambient fluid and let S be the initial dilution. Thus one part of effluent is mixed with S-1 parts of diluting water which iself has a concentration of c_o. The concentration of wastewater in the mixture c is then

$$c = \frac{1 + (S - 1)\,c_o}{S} = \frac{1}{S} + c_o - \frac{c_o}{S}$$

so that the net dilution, interpreted as the inverse of the final concentration is

$$S_{net} = \frac{1}{c} = \frac{1}{\frac{1}{S} + \frac{1}{S_o} - \frac{1}{SS_o}} = \frac{SS_o}{S_o + S - 1}$$

One may call S_{net}, S, and S_o the net initial dilution, the near-field dilution and the far-field dilution, respectively.

SUMMARY

In this chapter, the concept of initial dilution is discussed. It is pointed out that initial dilution is only rather loosely definable, being that part of the dilution resulting from the mixing process dominated by the buoyancy and momentum of the discharge.

Two types of delivery systems are considered in this chapter: outfalls and vessels. Simple results are presented which permit rapid estimation of initial dilutions for simple ambient ocean conditions. The initial dilutions obtainable for typical large outfalls equipped with long multiport diffusers discharging in relatively deep water is on the order of 10^2 to 10^3. For outfalls without diffusers, usually discharging in shallower water, they are often much less, being on the order of ten. For heavier-than-seawater waste discharged instantaneously from barges, the initial dilutions obtainable are sensitive to the size of each individual dump and can vary substantially. If barges are used to transport the waste to deep water and the material released in many smaller dumps instead of a few large ones, the dilution can be increased substantially.

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5

Advection, Diffusion, and Particle Settling

G.T. Csanady

INTRODUCTION

When a wastewater cloud is released in the coastal ocean the method of release usually creates considerable initial turbulence and mixing, whether above a single outfall pipe, over an array of diffusion ports, or in the wake of a barge. A short distance from the releasing device the extra turbulence decays leaving a more or less well-mixed cloud of waste and seawater to be carried away by ocean currents and to be diluted further by natural processes, namely oceanic turbulence and non-uniform currents. This transport and further dilution is the subject of the present chapter, the practical questions of interest being, where and how fast will the waste-seawater mixture go and at what rate will it be further diluted by seawater.

THE COASTAL FLOW ENVIRONMENT

Key flow properties governing the fate of wastewater in the coastal and open ocean are the intensity of turbulence and shear. Several classes of motion, characterized by widely different time scales, contribute importantly to turbulence and/or shear levels: these include surface waves, tidal oscillations, wind-driven longshore currents, and large-scale mean circulation. Most important from a practical viewpoint is the flow environment near a coastal outfall, located 1 to 2 km from the shore, over an "Atlantic" type continental shelf, which remains relatively shallow for considerable distances (order 100 km) from the coast. Problems are generally less critical further from shore or, as discussed later, over "Pacific" shelves, where the depth increases rapidly with distance from shore.

Surface Waves

Surface waves, especially storm waves, are an important source of turbulence and they also enhance certain transfer processes at the air-sea interface and at the seafloor. Although wave motions conform closely to an irrotational (ideal fluid) model, turbulence accompanies them near the surface where smaller waves break, forming whitecaps and sea spray, as well as near the seafloor, where an oscillating turbulent boundary layer develops in shallow water (less then 100 m deep). Sea spray gives rise to some mass transfer at the surface which may be important as a distributed sink for some conservative, or very long-lived, constituents of municipal waste. Wave induced motions and turbulence at the seafloor are important in enhancing bottom shear stress, and hence may lead to resuspension of deposited solid particulate constituents of wastes. Water particles in storm waves have orbital velocities of the order of 1 m sec $^{-1}$ at the surface with a typical period of 10 seconds (sec). Below the surface, the orbital velocity decreases with an e-folding depth scale typically of 20 m, so that at 30 to 40 m depth there are still quite vigorous motions, able to stir up fine particles lying on the bottom.

Tidal Oscillations

In many coastal locations, tidal oscillations contribute most of the kinetic energy of observable motions. Shallow water tides which are long waves propagating shoreward from the edge of the continental shelf occur with great regularity. The typical velocity of tidal motion over Atlantic shelves is 20 centimeters per second (cm sec $^{-1}$), more or less constant over the water column. During a full tidal cycle, individual particles experience elliptical displacements, the major axis of the tidal excursion ellipse being typically several kilometers long. Nearshore, the tidal ellipse is generally oriented parallel to the coastline and the minor axis of the tidal excursion ellipse of course vanishes right at the coast. At 1 or 2 km from the coast, cross-shore tidal excusions remain restricted by the presence of the coast to something less than a kilometer, except near the inlets of coastal ponds and lagoons.

Because tidal displacements are oscillatory, it would seem at first sight that they are of minor importance in the dispersal problem. The most important reason why this is not so is that a fixed outfall does not participate in the tidal excursions. As the coastal waters move past an outfall during tidal oscillations, the water discharged is distributed over a considerable water mass, much as if the waters stood still and the outfall moved over an elliptical path, several kilometers long and about 1 km wide, in the opposite direction to tidal motion.

Over a period that is short compared to the tidal cycle the tidal velocity may be regarded as constant (q), and the diffusion of waste from a fixed outfall treated as a continuous source placed into a uniform current. In this case, waste discharge at the rate of q kg sec^{-1} is distributed over a volume flow rate of uhb m^3 sec^{-1}, where u is tidal velocity, h and b are the depth and breadth of the source (initial mixing) region. The concentration on completion of the initial mixing is thus χ_i = q/uhb, or relatively low for a fairly high tidal velocity. By comparison, the time-average velocity (over at least one full tidal cycle) is much lower and the same argument would give a considerably higher initial concentration, if the effective source breadth b were the same. However, the effect of the tidal excursions is to distribute the waste over the range of these excursions, so that the initial concentration in a time average plume model becomes q/UhB, where U is time-average velocity and B an effective breadth, being roughly equal to actual source breadth, plus twice the cross-shore tidal excursion.

In addition to the above kinematic effects, tides are also responsible for much of the turbulence and shear of a coastal region subject to appreciable tidal motions. At such sites, vertical mixing is always efficient and only little stratification can develop. There is also considerable shear associated with the bottom boundary layer of a strong tidal current, which leads to a larger horizontal shear diffusivity. Furthermore, in somewhat deeper water also internal-mode tidal motions occur, which are associated with relatively large vertical motions of the constant density surfaces and considerable cross-shore mass exchange, by a mechanism similar to that described below for the baroclinic coastal boundary layer.

Wind-driven Longshore Currents

Wind-driven longshore currents dominate the flow field of coastlines with negligible tidal motions. These are generally of the same amplitude as typical tidal currents (30 cm sec^{-1} or so) but occur much less regularly, according to the passage of weather cycles. Although a 100 hr (4-day) periodicity may be statistically shown to be present in wind records, much longer quiescent periods do occur.

Wind-driven currents under well-mixed conditions are generally shore-parallel and do not give rise to the source-extending cross-shore bodily motion of the water column discussed in connection with tides. However, the shear in such currents is generally more intense, at least near the surface, because the wind rarely blows exactly parallel to the coast. The cross-shore component of the wind causes cross-shore water movements near the surface, generally compensated by opposite cross-shore flow at greater depth. Furthermore, the Coriolis force due to the rotation of the earth plays an important role, because wind-driven currents generally persist for a day or two, long enough for such effects to become prominent. Earth rotation effects further enhance shear, especially in the cross-shore direction. Simple frictional models of nearshore flow (so-called Ekman models) show considerable circulation in a cross-shore transect even when driven by longshore directed wind (Figure 5.1 illustrates such a model, from Csanady, 1975).

The most prominent effects of wind are felt in coastal regions deep enough to remain strongly stratified during the summer season (h = order 30 m or more). In such locations the effects of the wind only reach the surface layers, which then move relative to the lower levels both faster and in a more complex fashion than in a well-mixed water column. Figures 5.2 and 5.3 show the appearance of constant temperature, salinity, and density surfaces in a transect off a straight, open coastline, following oppositely directed winds. The change in the appearance of the constant property surfaces is due to massive cross-shore movements (upwelling or downwelling) which follow the arrival of winds of opposing directions. The main uptilt or downtilt of the isolines is confined to a "baroclinic coastal boundary layer" of some 5 to 10 km width. Above the strongest tilted constant density surfaces one finds especially strong longshore currents, "coastal jets" confined to the surface layers alone. These sometimes affect the longshore transport of waste released near shore. However, the most important aspect of the wind induced upwelling-downwelling phenomenon is the massive cross-shore exchange of water associated with

Figure 5.1 Ekman model frictional cross-flow in a coastal zone of variable depth (Csanady, 1975).

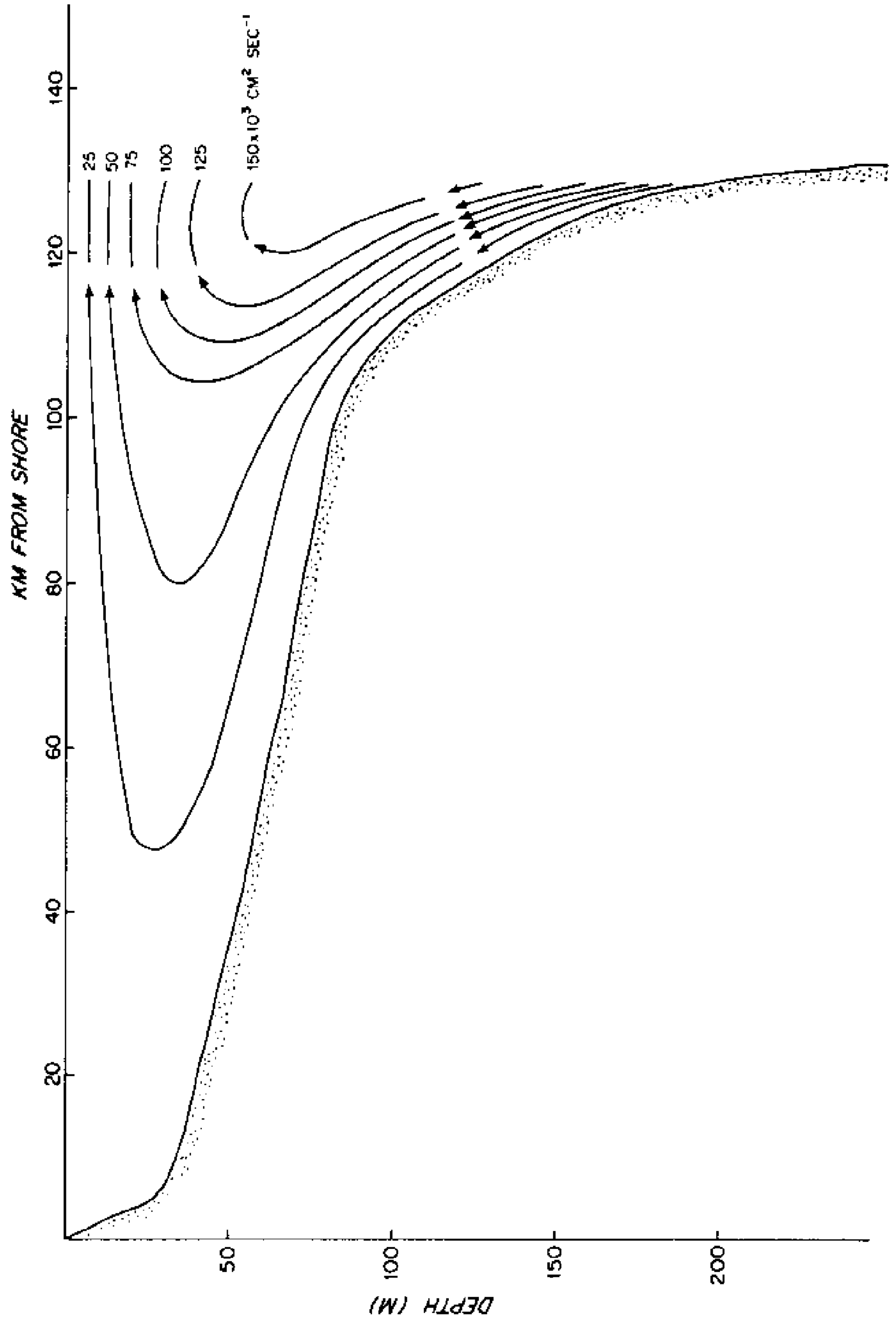
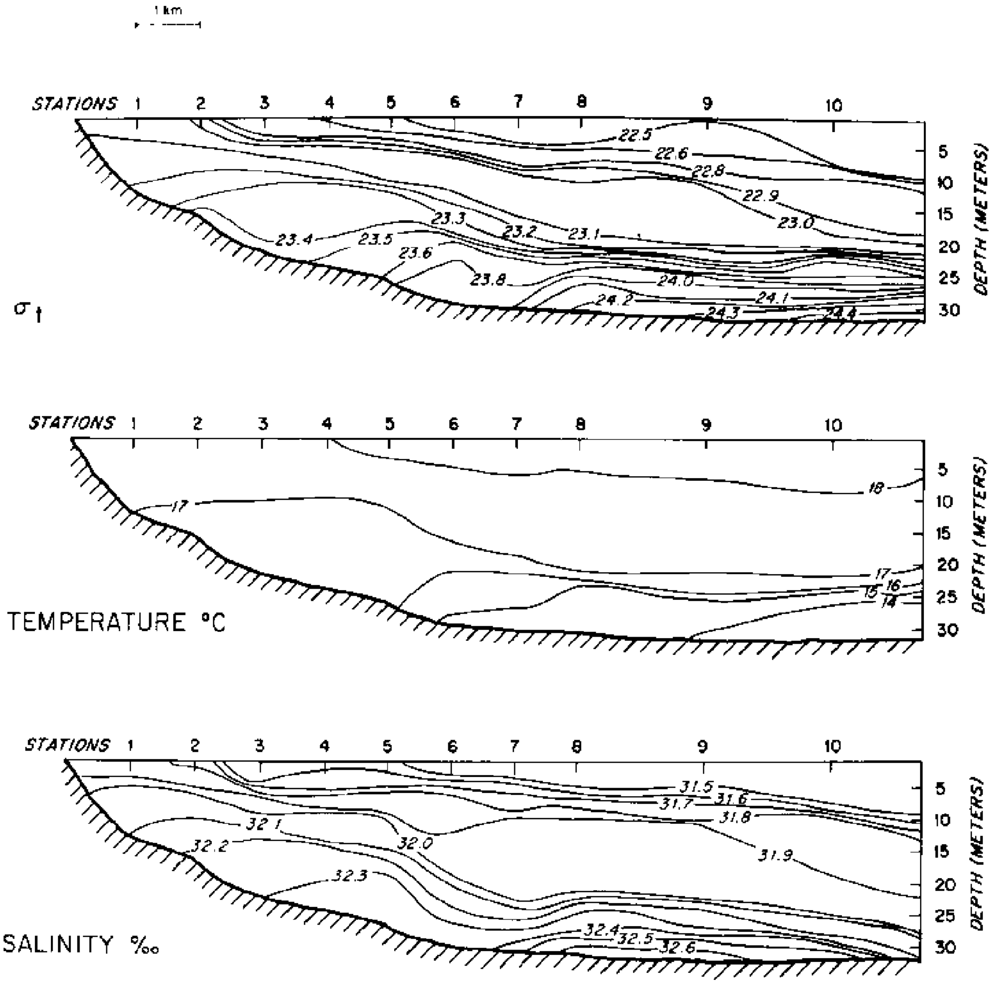


Figure 5.2 Cross sections of temperature, salinity and density across the coastal boundary layer off Long Island, near Shinecock Inlet, illustrating typical upwelling conditions (Scott and Csanady, 1976).

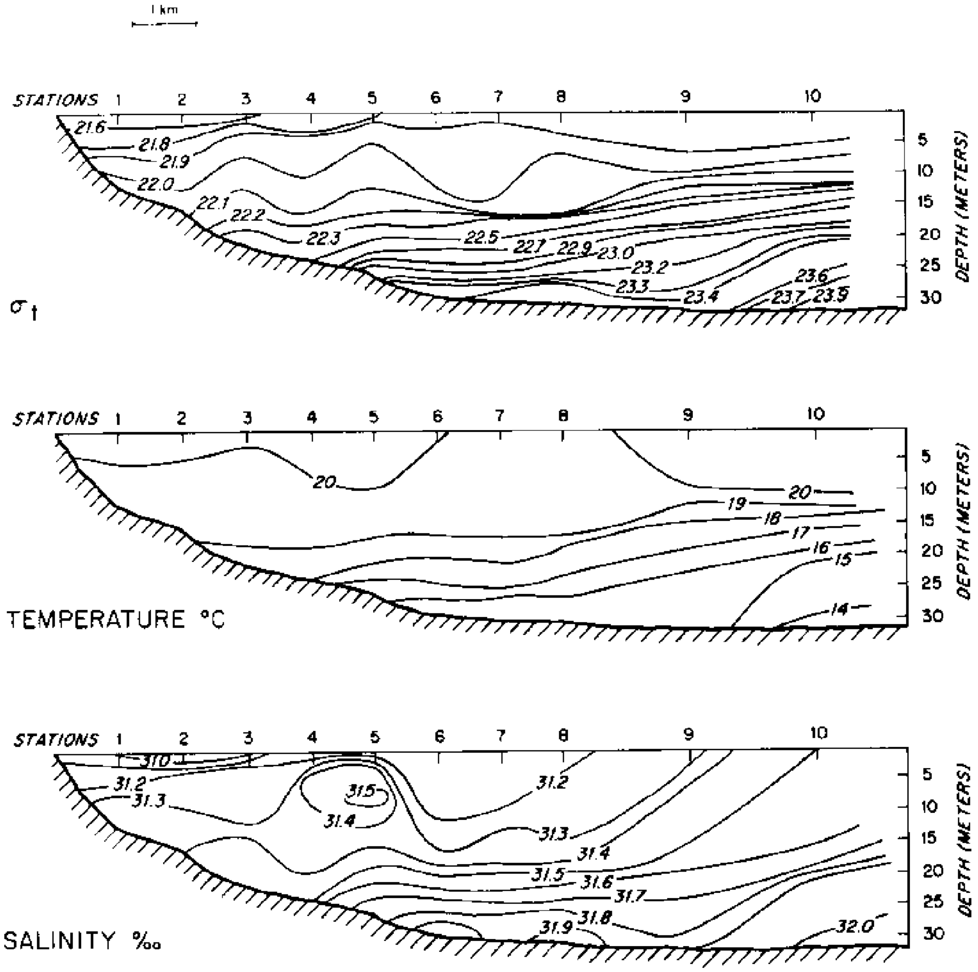


σ_t

TEMPERATURE °C

SALINITY ‰

Figure 5.3 Cross sections of temperature, salinity and density across the coastal boundary layer off Long Island, near Shinecock Inlet, illustrating typical downwelling conditions (Scott and Csanady, 1976).



the up or down movements of the constant property surfaces. The entire water mass is effectively renewed in a nearshore band following the most intense of such episodes.

Particularly intense mass-exchange episodes occur in nontidal waters, not subject to the damping influence of tidal friction. In such locations the sudden changes in the shape of constant property surfaces due to the arrival of strong winds may also propagate along shore as long (Kelvin) waves and cause spontaneously occurring mass-exchange episodes long after the wind event has passed. In coastal regions with strong tidal currents such waves do not seem to be frequent, and even the directly wind induced upwelling and downwelling episodes are relatively less intense. Nevertheless, the phenomenon remains of first-order, practical importance in the waste disposal problem.

The large-scale mean circulation of a coastal shelf region is important in limiting the long-term buildup of long-lived waste constituents, such as heavy metals. Longshore mean velocities are generally of the order of 3 cm sec $^{-1}$ which is enough to "flush" a coastal zone effectively. Another point to remember is that longshore excursions associated with the mean flow can be very large, comparable in some places with continental dimensions. Along the east coast of the United States, for example, the mean flow is southwestward from the Gulf of Maine to Cape Hatteras, northeastward between Cape Hatteras and Miami.

The mean circulation of continental shelf regions is generally a boundary-layer component of the deep oceanic gyres, which impress a longshore sea level slope on the shelf. This large-scale pattern is modified by the mean wind-stress, which "sets up" portions of the shelf according to its topography, especially in semi-enclosed basins such as the Gulf of Maine. The wind-related set up is a pressure field trapped within relatively shallow water, typically within the 50 m depth contour. Where coastal oceanic outfalls are located on Atlantic-type shelves, the water is typically 10 to 30 m deep and the mean wind stress is generally stronger than the gravity force associated with the local longshore mean sea-level slope, so that mean flow is along the mean wind.

There are other flow components in a coastal zone, such as those due to internal tides, inertial oscillations in the internal mode (both of which are accompanied by large vertical movements of constant density surfaces), edge waves and topographic waves, local flows produced by seamounts or canyons, discharges from coastal lagoons, large eddies in the wake of promontories or islands, river plumes and floating lenses of somewhat fresher or warmer water originating from a distant river. While all of these add to the complexity of observable water movements, they are not generally a major factor comparable to those discussed above, except in isolated locations. They can usually be regarded as large-scale turbulence, contributing in the aggregate to mass exchange between a coastal region and the adjacent shelf waters.

A few remarks must also be made here on discharges into relatively deeper waters (greater than 50 m) which are economically feasible over "Pacific" type continental shelves, over which depth increases rapidly with distance from shore. Water motions associated with surface waves or surface tides are of subordinate importance in such locations. However, the stratification of the water mass, and vertical movements of the constant density surfaces become of critical importance.

Effluent released in deep waters below a strong pycnocline tends to be trapped in the bottom layer. Most of the kinetic energy in the bottom layer is provided by motions associated with transient pycnocline movements, such as internal tides, inertial oscillations, and especially important, wind-induced coastal upwelling and downwelling cycles. While such motions tend to advect pollutants away, and also promote mixing by turbulence and shear-diffusion, sometimes they also lead to the exposure of bottom layer waters to the surface, usually very close to shore, in a strong upwelling event. The frequency of such events then becomes an important design consideration. The mean longshore flow over Pacific type shelves is a larger scale phenomenon, behaving more or less as discussed above for Atlantic shelves.

The coastal flow environment is highly variable from one proposed outfall site to another. The "typical" quantitative characteristics of various flow components quoted above do not necessarily apply in any given new location. Reliable estimates of these flow characteristics can only be obtained by specific oceanographic measurements, extending at least over a full year. However, it should not be concluded that such full-scale studies are an essential prerequisite for the design of all outfalls or for the designation of all sludge dump sites. In many locations there is ample general evidence on oceanographic conditions to be certain that waste dispersal will be efficient enough to take care of some limited disposal problem. For example, in an open coastal location, with strong tidal currents, which are usually known to the inhabitants of the sea coast, one can confidently predict effective dispersal over the range of tidal excursions. Long-term buildup of persistent toxic chemicals can be checked using a conservative mean (flushing) velocity. Except for very large sources, the results of such design projections are likely to be satisfactory.

CONSERVATION OF MASS

The quantitative measure of the dilution of a waste in the ocean environment is the concentration of waste per volume of seawater, preferably expressed as fraction of the volume occupied, which is a non-dimensional quantity. Because municipal wastewaters have a density close to 1.0 g cm^{-3}, as has seawater, the concentration of waste released expressed as mass per volume of seawater in cgs units (g cm^{-3}) is very nearly the same as the volume fraction.

Generally speaking, all dilution estimates are based on mass balance, aided by some estimates of a waste cloud's growth. If a given constituent of the waste is stable in the oceanic environment (a "conservative" substance), its total mass Q remains the same as discharged, many hours after release. If the cloud volume has grown to V from an initial V_i, the average concentration of a conservative substance changes from Q/V_i to Q/V, i.e., it is diluted by the factor V/V_i. Rough estimates of this sort are often all that can be made in practical cases and they should in any case always be used to check more sophisticated models. It is particularly important to subject data from diffusion experiments to a mass balance check, because it is easy to lose most of a tracer cloud in the ocean. If only a fraction of the tracer cloud has been sampled, the observed maximum concentration may be much less than what one finds in the densest part of the cloud which may have escaped detection.

Mathematically, one expresses conservation of mass, or lack of it, by writing down a mass balance for an arbitrary volume V of the fluid, fixed in space, limited by a boundary surface A. The total mass of tracer or pollutant within the volume V changes to the extent that there is either net inflow or outflow across the surface A, or growth or decay within the volume V. The inflow or outflow is quantified by the flux $\underset{\sim}{F}$ of the material of interest, i.e., the mass passing elements dA of the surface A per unit area per unit time. Flux is a vector quantity and in a fluid in motion it is given by

$$\underset{\sim}{F} = \underset{\sim}{u}\chi - D\nabla\chi \tag{5.1}$$

where $\underset{\sim}{u}$ is fluid velocity vector, χ the concentration of the substance of interest, and D is (molecular) diffusivity. The second term on the right is flux through molecular exchange down the concentration gradient $\nabla\chi$.

Growth or decay, i.e., a departure from conservation of mass, is important for such waste constituents as bacteria. Effects of this kind may be quantified by a source/sink strength term R (negative for a sink) of the dimension of mass gained or lost per unit volume of V, per unit time. Frequently, this term is adequately represented by a random death law, formally the same as the law of radioactive disintegration:

$$R = -k\chi \tag{5.2}$$

where k is a decay constant of the dimension of $(\text{time})^{-1}$, or reciprocal time scale.

Mass balance for an arbitrary volume (or element) of the fluid is now expressed by:

$$\frac{\partial\chi}{\partial t} = -\nabla\cdot\underset{\sim}{F} + R \tag{5.3}$$

where $\nabla\cdot$ is the divergence operator. Substituting (5.1) and (5.2), and supposing D = constant, one finds the diffusion equation in a moving fluid for a substance subject to the simple decay law of (5.2):

$$\frac{\partial\chi}{\partial t} + \nabla\cdot(\underset{\sim}{u}\chi) = D\nabla^2\chi - k\chi \tag{5.4}$$

This classical equation, identical in form with the equation of heat conduction, underlies most mathematical models of diffusion. In turbulent flow, the equation is of little direct practical use because both $\underset{\sim}{u}$ and χ are random variables, the irregular rapid variations of which, described by (5.4), would be too much to comprehend, even if our computers could simulate them (they can't). However, Eq. (5.4) can be manipulated further to obtain various statistical measures of concentration distribution, which are of value in judging nuisance or hazard.

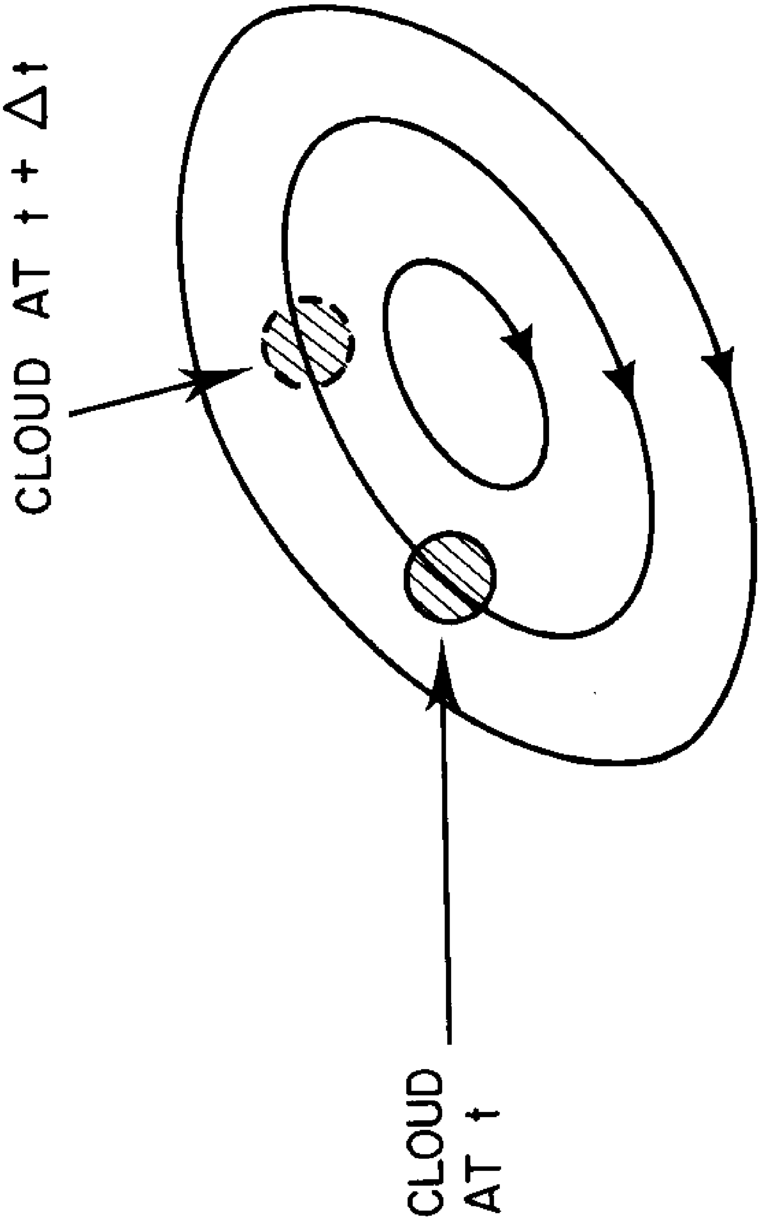
TURBULENT DIFFUSION

In the turbulent natural environment of a coastal discharge the most important mixing process is the advection of concentration by the turbulent velocity fluctuations. Suppose that a quantity of tracer or waste component is introduced into the turbulent fluid in an initial concentration χ_o. The left-hand side of Eq. (5.4) may be interpreted as rate of change of concentration following a parcel of fluid, with its total (fluctuating) velocity. Suppose also that the tracer or waste component is conservative, k = 0, and that its molecular diffusivity D is of the usual low magnitude: 10^{-3} cm^2 sec^{-1} or less. The right-hand side of (5.4) will then be negligible except where very sharp concentration gradients occur. Most of the initial cloud of concentration χ_o will simply be advected by the turbulent velocities. In time, these turbulent motions stretch and contort this initial cloud into a very complex shape, and generate more and more regions of high concentration gradient, where molecular diffusion <u>is</u> important. However, the primary physical factor distributing tracer or waste material over a larger region of space than occupied initially is the random advection by turbulent eddies.

The physics of the turbulent diffusion process are treated in standard texts (e.g., Sutton, 1953; Csanady, 1973). Here, key physical facts and basic equations will be sketched without producing all the necessary supporting evidence.

Turbulent fluid motion may be thought of as consisting of many eddies of different sizes, or more or less closed-flow structures qualitatively similar to vortices of different diameters. Eddies of different sizes act on a diffusing cloud of tracer or waste component differently, according to the size of the diffusing cloud. Consider a large eddy acting on a small diffusing cloud, Figure 5.4. Over the cloud diameter the eddy velocity distribution is more or less uniform so that advection by these velocities results mainly in a bodily displacement of the cloud,

Figure 5.4   Effect of large eddy on small diffusing cloud.



and very little distortion. The result is important for estimating probability of high concentrations at fixed points, but not from the point of view of dilution produced, or concentrations in a frame of reference moving with the center of gravity of the cloud.

Take now the opposite extreme of a large cloud, acted upon by a much smaller eddy, Figure 5.5. The eddy clearly tends to extend the boundary of the cloud outward, and to transport ambient fluid into the cloud, thus certainly contributing to dilution. However, the effect is limited to a small region of the cloud and is in many ways similar to molecular agitation, which acts over the range of the molecular mean free path, i.e., a small distance compared to ordinary cloud diameters. An array of small eddies does not perceptibly alter the position of the center of gravity of a large diffusing cloud, but it produces some slow mixing, much as molecular agitation.

Consider finally the situation illustrated in Figure 5.6, where the cloud interacts with an eddy of roughly similar size. A major distortion of cloud shape is produced, radically increasing the contact surface between tracer and ambient fluid, and rapidly increasing the region of space over which the tracer is distributed.

The net conclusion is that the presence of eddies similar in size to a diffusing cloud leads to rapid cloud growth and dilution. Parenthetically, one should also note that concentration fluctuations are also relatively larger under these rapid-growth conditions than either of the previous two cases.

When waste is released continuously into an idealized steady and uniform current, tracer clouds are serially generated, forming a continuous plume in the direction of the current (Figure 5.7). As one tows an instrument across such a plume at a given distance from the source, it records a tracer concentration irregular in shape, and varying from transect to transect. See Figure 5.8 for an actual example. It should be noted also that the origin along the abscissa in Figure 5.8 is arbitrary: not only is the plume cross section irregular, but its centerline also meanders back and forth around a mean position, the actual instantaneous shape of the plume being a sinuous curve of continually changing shape (instead of the idealized straight line in Figure 5.7), even when a current is more or less steady and

Figure 5.5 Small eddy mixing edge of large cloud.

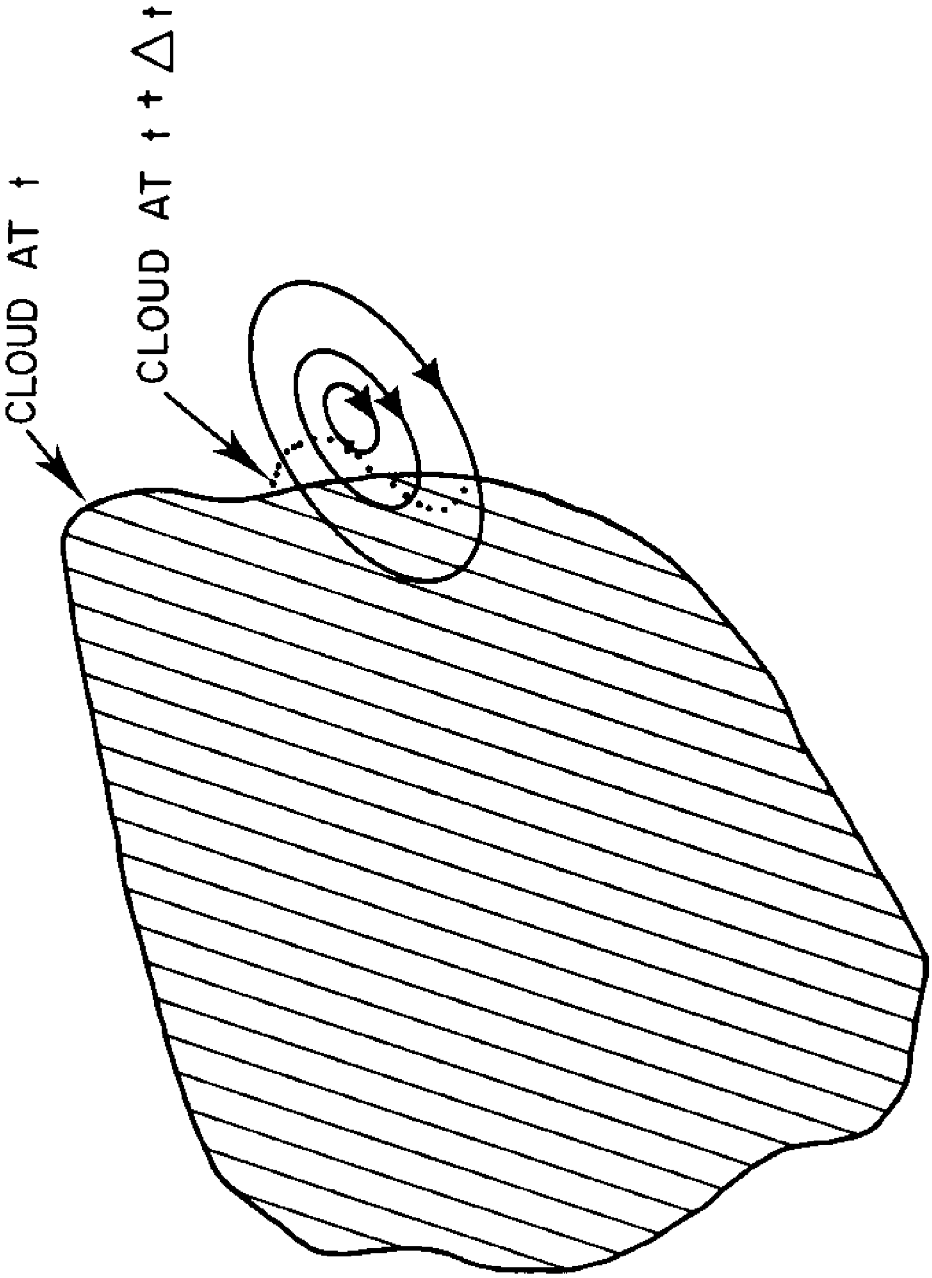


Figure 5.6 Encounter between diffusing cloud and eddy of similar size.

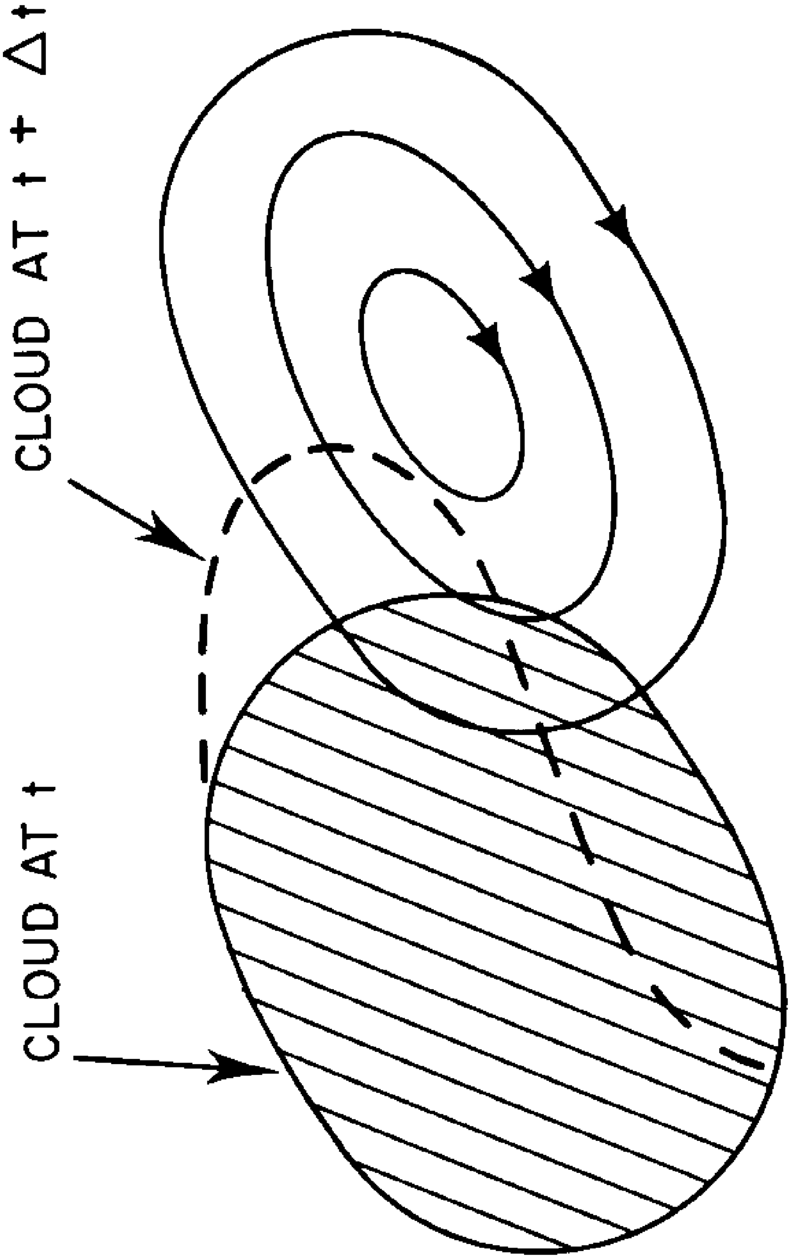


Figure 5.7 Schematic illustration of waste plume formed in a coastal current from a succession of serially released puffs.

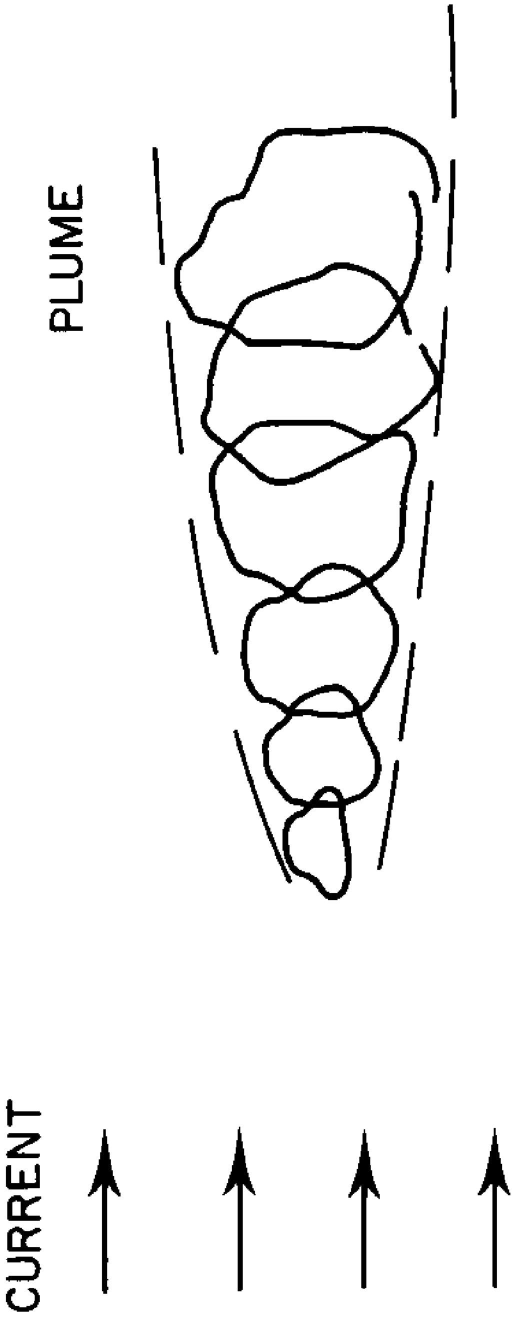
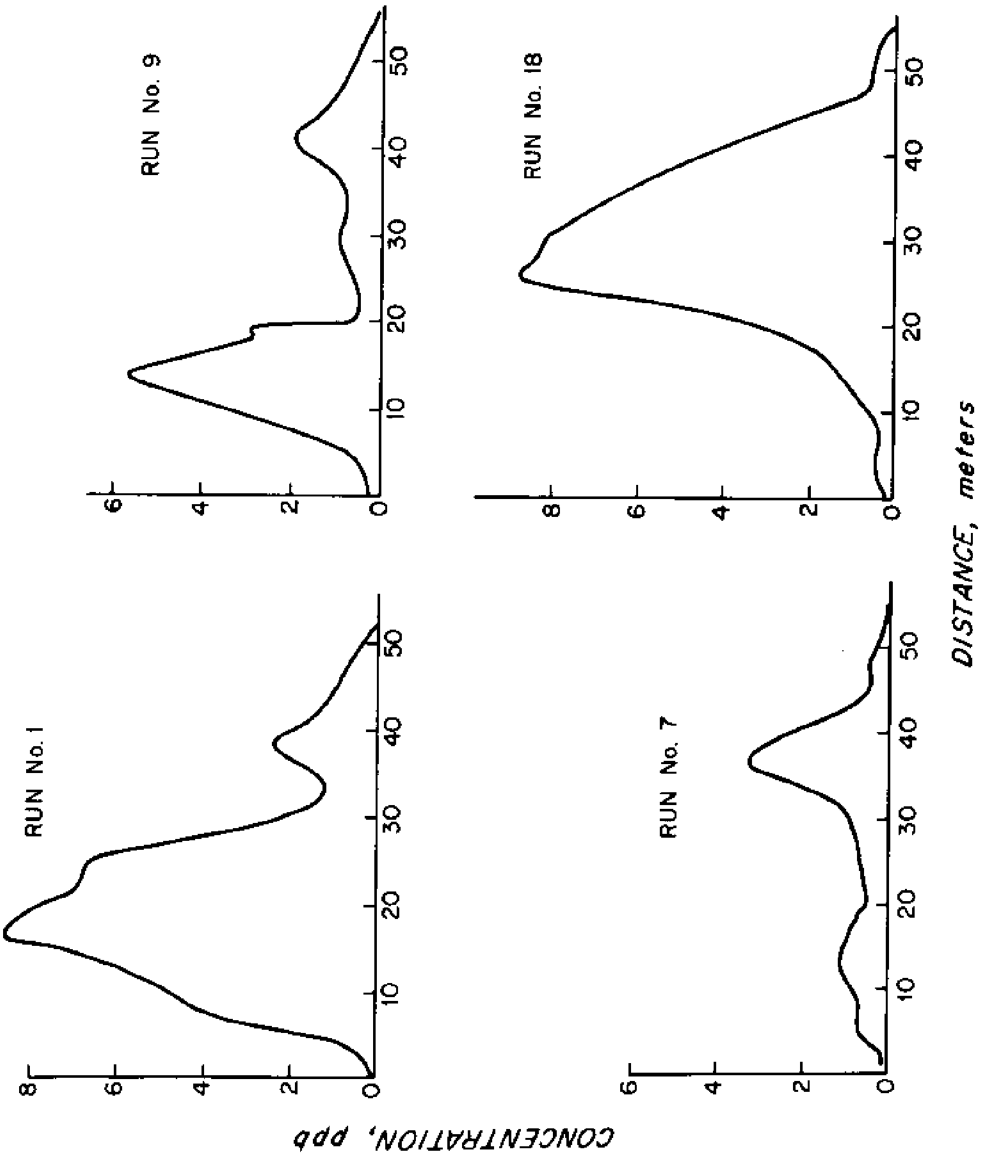


Figure 5.8 Examples of tracer concentration profiles observed across a diffusing plume.



uniform in the mean. In tidal waters the current vector is also subject to substantial non-random changes semidiurnally and diurnally.

It is not at once evident, how to quantify the dilution reached in a given waste cloud or plume if concentration is a random variable. What degree of statistical detail is necessary for a satisfactory assessment of nuisance or hazard? The answer to this question depends to some extent on the biological and other effects of waste external to physical considerations, which are outside the scope of the present chapter. However, it is possible to pose some general questions regarding external effects in physical terms. If it is simply the maximum concentration of some waste constituent that is of concern, one would like to know over what neighborhood of the source a given threshold concentration is exceeded with given probability. If, on the other hand, conditions at some fixed point are of primary interest (e.g., at a nearby water intake), one would be content to know the probability of exceeding prescribed threshold concentrations at that point. It is clear that the irregular meandering of a plume strongly affects the answer to the second question, but is unimportant if one simply wants to know the areal extent of concentrations higher than so high.

The question of how to extract useful statistics from observed concentration distributions, while apparently trivial, leads to important distinctions between different theoretical models of turbulent diffusion. If, as in deriving the classical diffusion equation earlier, attention is directed to a sample volume fixed in space, one may determine the usual statistics, such as mean concentration, mean square fluctuation, or the entire probability distribution of concentration at that fixed sample volume. When the sample volume is small, one speaks of concentration at a fixed "point", and its probability distribution. Such a distribution can be determined approximately from an ensemble of experiments carried out under identical ambient conditions -- e.g., while the "mean" current remains the same in speed and direction at the locations of interest. Although this is never strictly the case in the coastal ocean, the idealization is useful.

The variability of concentration at a fixed point is often mainly due to the irregular bodily wandering about of a diffusing patch or plume. Of an ensemble of experiments under identical ambient conditions, some will result in the plume or patch passing over the sampling volume of interest, while in other experiments the cloud will miss the sampling location. When a cloud is small compared to the characteristic size of the eddies present, its bodily excursions will be much larger than its diameter, so that it will only rarely hit a small sample volume. Under these conditions the observed concentration will be high in some experiments, negligible in others. In the case of a larger cloud the fluctuations will not be quite so extreme, but it remains true that fixed-point statistics are affected by the bodily motion of clouds as well as by their dilution.

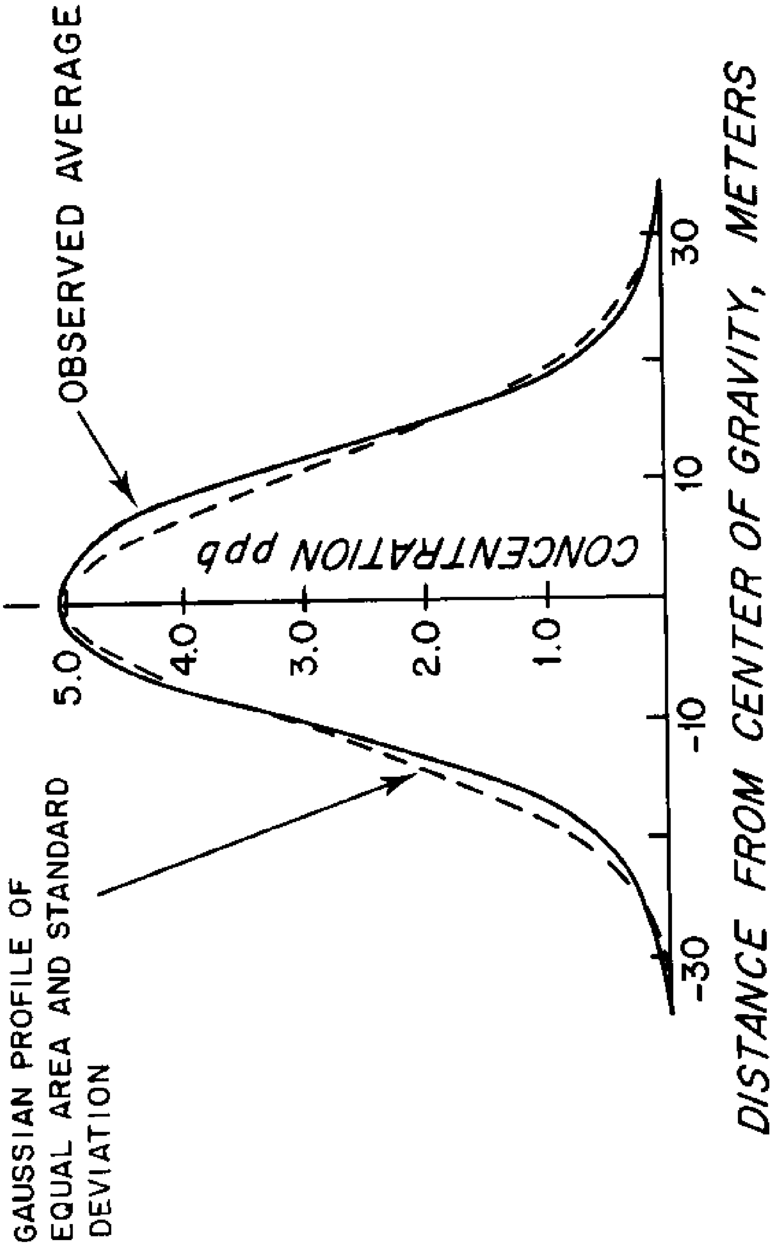
If one's concern is not with concentration at a fixed point, but the minimum dilution achieved at a given time after release, regardless of a cloud's position, the bodily movement of a cloud is an irrelevant detail. To form appropriate statistics, one best refers distances then to the center of gravity of a patch or plume. In the case of the plume concentration profiles shown in Figure 5.8, for example, one would overlap the profiles obtained in an ensemble of experiments so that their centers of gravity coincide. Ideally, one would then be able to determine the probability distribution of concentration at given distances from the center of gravity. In practice, from an ensemble of limited size, one may calculate reasonable estimates of first and perhaps second moments of the probability distribution (i.e., the mean concentration and the mean square fluctuation). Examples from an ensemble of 25 experiments (of which 4 were shown in Figure 5.8), of the mean concentration and of the mean square concentration fluctuation distribution versus distance from the plume center are shown in Figure 5.9 (from Csanady, 1966b).

MEAN CONCENTRATION DISTRIBUTION

An individual element of tracer or waste cloud executes a succession of random movements in a turbulent fluid. Its position vector $\underset{\sim}{x}$ at time t relative to its point of release (in a fixed or a moving frame of reference) is a random variable. A probability density distribution P $(\underset{\sim}{x}, t)$ may be defined, such that P $d\underset{\sim}{x}$ is the probability of a particle's displacement vector ending in the volume element $d\underset{\sim}{x}$ around the point $\underset{\sim}{x}$, at time t after release. The stochastic <u>mean</u> concentration $\overline{\chi}$ of tracer particles at $(\underset{\sim}{x}, t)$ is then clearly

$$\overline{\chi}(\underset{\sim}{x},t) = QP\,(\underset{\sim}{x},t) \tag{5.7}$$

Figure 5.9 Tracer concentration averaged for 25 cross sections similar to those in Figure 5.8, with centers of gravity overlapped.



where Q is the total amount of tracer present. In virtue of this fundamental relationship, a number of results relating to the stochastic mean concentration field may be arrived at by analyzing the kinematics of particle movements.

If the particles of the tracer or pollutant have executed a large number of independent "steps", the probability density P is a result of a random walk process. In spatially homogeneous turbulence, particles may be expected to move away from their point of release at the same rate in all directions, so that a diffusing cloud is isotropic. A classical result in probability theory is that the distribution P resulting from an isotropic random walk process is asymptotically normal or Gaussian. Under the ideally simple conditions of spatial homogeneity the particle displacement probability density becomes then

$$P = \frac{1}{(\sqrt{2\pi}\,\sigma)^3} \exp\left(-\frac{r^2}{2\sigma^2}\right) \tag{5.8}$$

where r is distance from the point of release and σ is the root-mean-square distance reached by an assembly of particles.

As a model of diffusion in coastal waters, Eq. (5.8) is somewhat overidealized, because particle step lengths generally differ according to spatial direction, vertical motion in particular being generally more sluggish than horizontal motion. A suitable modification of (5.8) is for this case

$$P = \frac{1}{(2\pi)^{3/2}\sigma_x\,\sigma_y\,\sigma_z} \exp\left(-\frac{x^2}{2\sigma_x^2} - \frac{y^2}{2\sigma_y^2} - \frac{z^2}{2\sigma_z^2}\right) \tag{5.9}$$

where the three standard deviations are now not equal and especially $\sigma_z \ll \sigma_x$ or σ_y, if z is chosen to be the vertical axis, as usual. The result as written down is valid provided that (x,y,z) are the principal axes of ellipsoidal surfaces describing constant P. This formulation is adequate for most practical applications.

Together with Eq. (5.7), this result now describes the stochastic mean concentration field of an instantaneous point source. The result must also satisfy the averaged diffusion equation, (5.4). Writing $\chi = \overline{\chi} + \chi'$, $\underset{\sim}{u} = \overline{\underset{\sim}{u}} + \underset{\sim}{u}'$, etc, to denote means and fluctuations the averaged form of (5.4) becomes

$$\frac{\partial \bar{\chi}}{\partial t} + \nabla \cdot (\bar{\underset{\sim}{u}}\bar{\chi}) = - \nabla \cdot (\overline{\underset{\sim}{u}'\chi'}) + D\nabla^2\bar{\chi} - k\bar{\chi} \qquad (5.10)$$

where overbars denote stochastic (ensemble) averages, primes departures from these averages in individual trials. This equation may be thought to apply to either the mean concentration field at fixed points, or that in a frame of reference attached to the center of gravity. In the latter case, velocities $\underset{\sim}{u}$ must be interpreted as velocities relative to the center of gravity.

The major difficulty with Eq. (5.10) arises from the randomness of both fluid velocity and concentration, which results in the appearance of the covariance $\overline{u'\chi'}$ in this equation. Physically, this term represents mean flux of the diffusing quantity due to turbulent movements and is of key importance in the dilution problem.

Eq. (5.9 with 5.7) constitutes a solution of (5.10) with $\bar{\underset{\sim}{u}} = 0$ and k = 0. Substitution shows that the turbulent flux terms in homogeneous turbulence are

$$\overline{u'\chi'} = -\frac{1}{2}\frac{d\sigma_x^2}{dt}\frac{\partial\bar{\chi}}{\partial x}$$

$$\overline{v'\chi'} = -\frac{1}{2}\frac{d\sigma_y^2}{dt}\frac{\partial\bar{\chi}}{\partial y} \qquad (5.11)$$

$$\overline{w'\chi'} = -\frac{1}{2}\frac{d\sigma_z^2}{dt}\frac{\partial\bar{\chi}}{\partial z}$$

This is exactly the same relationship as applies to flux by molecular diffusion, except that eddy diffusivities K_x, K_y, K_z enter in place of molecular diffusivity D. The eddy diffusivities are seen to be different along the three coordinate axes and to be defined by

$$K_x = \frac{1}{2}\frac{d\sigma_x^2}{dt}$$

$$K_y = \frac{1}{2}\frac{d\sigma_y^{\,2}}{dt} \qquad (5.12)$$

$$K_z = \frac{1}{2}\frac{d\sigma_z^{\,2}}{dt}$$

Further kinematic analysis shows that these eddy diffusivities may be expressed as the product of an average step length and root mean square velocity, much as molecular diffusivity is a product of mean free path and radian means per second (rms) molecular velocity.

Although this result was derived for homogeneous turbulence, it may be generalized to the case of more complex situations where turbulence intensity and eddy length scale vary in space. Provided that the variation is suitably slow, i.e., that the turbulence is nearly homogeneous over at least two or more eddy diameters, the same relationships may be locally applied. On the other hand, the extension of the eddy diffusivity concept to cases with abrupt variation of turbulence properties (such as found near density fronts) is not readily justified. Such fronts are more realistically idealized as internal boundary surfaces.

For quasi-homogeneous turbulence, however, Eqs. (5.11) and (5.12) are realistic and may be used to write down a differential equation for the mean concentration. Noting that $\nabla \underset{\sim}{u} = 0$ for incompressible fluid, and substituting (5.11) and (5.12) into (5.10) there results

$$\frac{\partial\bar{\chi}}{\partial t} + \underset{\sim}{\bar{u}} \cdot \nabla\bar{\chi} = \frac{\partial}{\partial x}\left(K_x \frac{\partial\bar{\chi}}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial\bar{\chi}}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial\bar{\chi}}{\partial z}\right) + D\nabla\bar{\chi} - k\bar{\chi} \qquad (5.13)$$

In most practical applications the molecular diffusivity D is small compared to eddy diffusivity K and may be neglected. The left-hand side of this equation expresses rate of change of concentration following a parcel of fluid with the local <u>mean</u> velocity. The right-hand side contains the flux divergence term, which expresses the tendency of diffusion to fill in the hollows and level the peaks, and also any sink or source terms, represented here by a linear decay term.

This equation may be solved for the mean concentration field, if initial and boundary conditions are prescribed. Initial conditions usually express the method of release of a tracer or contaminant. Boundary conditions at solid surfaces may be usually written as

$$-K_n \underset{\sim}{n} \cdot \nabla\overline{\chi} = v_d\overline{\chi} \tag{5.14}$$

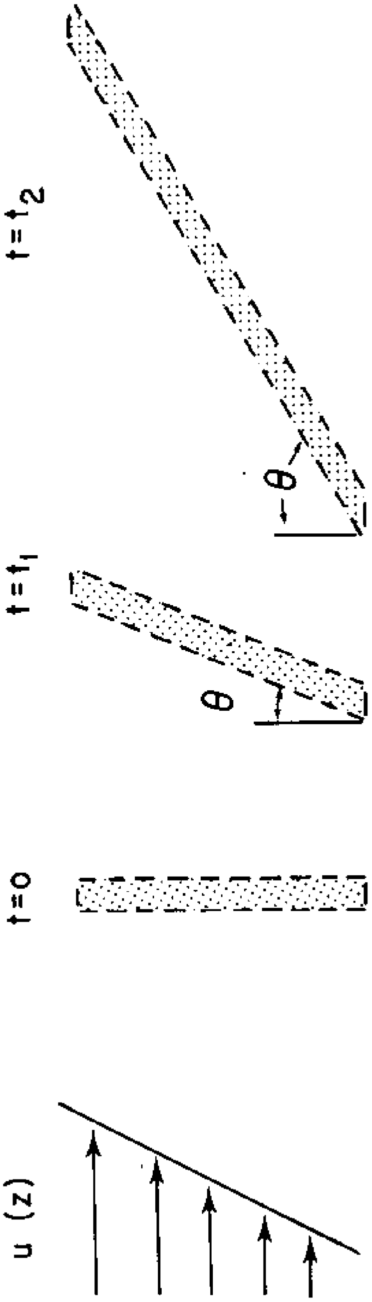
where $\underset{\sim}{n}$ is local surface normal, K_n diffusivity along $\underset{\sim}{n}$, and v_d is a "deposition velocity." The flux normal to the boundary surface is the deposition velocity v_d times mean concentration. Should the deposition velocity be zero, the boundary surface is said to be reflective, in which case the normal gradient of mean concentration vanishes. With v_d non-zero the task of finding solutions to (5.13) becomes rather more complicated. With reflective boundaries the "method of images" (see e.g., Carslaw and Jaeger, 1959) allows solutions for concentrated sources to be written down relatively easily in simple flow fields. In any event, however, one must remember that all that Eq. (5.13) describes is the field of stochastic mean concentration, which may be an inadequate basis for judging nuisance or hazard due to a contaminant.

SHEAR DISPERSION

In much of the above discussion the mean flow has been assumed, tacitly or explicitly, to have the same velocity over the region of interest. The necessity for this restriction arises from the fact that a spatially non-uniform, "sheared", mean flow itself contributes to the dispersal of a cloud of tracer or pollutant and is thus important in the municipal waste dispersal problem.

The physical effect of shear flow on diffusion is easily understood by means of a simple illustration, Figure 5.10. Let the velocity component along the x-axis be non-uniform in the vertical, $u = u(z)$. Constant shear, $\partial u/\partial z$ = constant, is an adequate model. A column of tracer vertical at $t = 0$ becomes tilted at an angle θ against the vertical a short time later due to differential advection between top and bottom. The tangent of this angle increases linearly in time in this simple example. Tracer within the column diffuses forward and backward across the faces of the column which are initially vertical. As the shear flow tilts the column, the lengths of

Figure 5.10 Effect of shear flow on a waste filament.



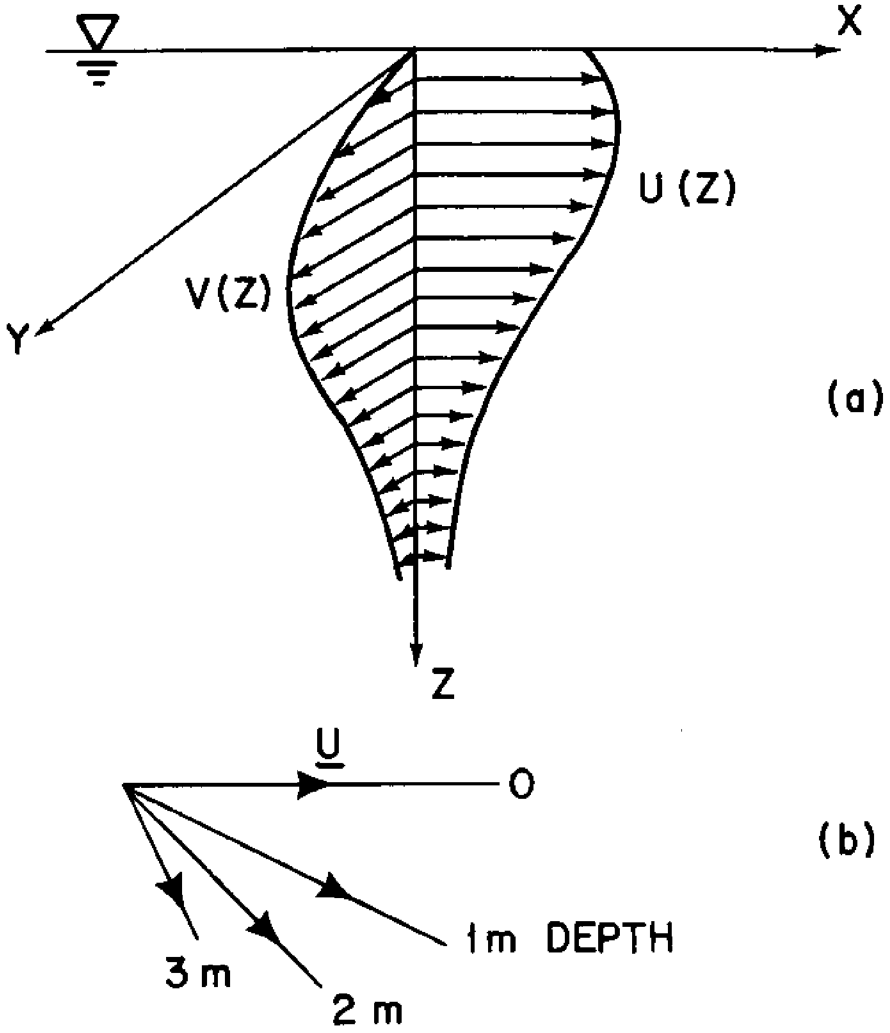
these forward and backward faces increase with sec θ. If the rate of diffusion across these faces (the flux) remains constant, the rate of dilution increases also as sec θ. Simply put, mean shear increases the contact surface between tracer and ambient fluid and leads to increased dilution. The effect is fundamentally much the same as the stretching and straining influence of random eddies, but it is more persistent when due to mean flow and potentially more important.

In the simple example, illustrated in Figure 5.10, enhanced cloud growth in the x-direction is produced by an interaction of velocity differences along x and vertical mixing. In the coastal ocean, non-uniformities along the vertical of both horizontal velocity components are important. Such "skewed shear flow" typical of the coastal ocean is illustrated schematically in Figure 5.11 by velocity profiles u(z) and v(z), as well as a hodograph of the velocity vector $\underset{\sim}{u}(z)$. In situations like this, the cloud growth along both horizontal axes is augmented by mean shear. A plume of tracer or pollutant will take a path along some intermediate mean velocity vector, and its lateral growth will be affected by the non-uniformity of the velocity in the direction normal to plume axis.

Shear flow non-uniformity affects diffusion in all realizations of an experiment in about the same way. The behavior of the stochastic mean concentration field therefore reflects the quantitative effects of shear quite well. This may be described using the mean concentration equation (5.13). With arbitrarily distributed $\underset{\sim}{u}(z)$ and K(z) the mean concentration equation is difficult to solve. However, it is possible to derive somewhat simpler equations for the spatial moments of the concentration distribution, which characterize the motion of the center of gravity of a cloud or plume, and its growth.

A number of important theoretical investigations of shear dispersion have been carried out since the pioneering work of Taylor (1954). They revealed a fundamental difference in diffusing cloud growth rates according to whether the sheared region of flow is all occupied by a diffusing cloud or not. In the former case a (constant) "shear diffusivity" may be calculated, the cloud size growing asymptotically as $t^{1/2}$. In the case of a cloud expanding vertically into a previously unoccupied region of shear, the cloud growth is more rapid because a greater and

Figure 5.11 Typical skewed shear flow velocity distribution in oceanic surface layer (Csanady, 1966).



greater velocity difference comes into play to distort the cloud. The effect is fundamentially very similar to the influence of bigger and bigger eddies acting on a growing cloud: sheared mean flow in this context is merely a particularly persistent large eddy.

The results of a simple example of shear dispersion in a depth-limited field will illustrate the importance of this phenomenon. Consider the instantaneous release of tracer cloud into some limited region of a flow field of constant depth h. Suppose that the tracer substance is conservative and that the surfaces z = 0, -h are reflective. After some initial period in which the cloud is able to grow vertically, it comes to fill the entire depth. In this asymptotic phase it will be carried along by the mean flow with some mean velocity (U,V), while it will continue to grow in the x and y directions. In the simple example where K_z = constant and the x-wise velocity varies linearly from zero at the bottom to 2U at the surface, the center of gravity of the cloud at a given level is located at

$$c_x = Ut + h[\frac{Uh}{12K_z}(1 - \frac{6z^2}{h^2} - \frac{4z^3}{h^3})] \tag{5.15}$$

The square bracketed term is non-dimensional and it varies between $\pm Uh/12K_z$, which in typical cases is of order ± 50. The line connecting the centers of gravity at each level is thus heavily tilted, its average angle against the horizontal being about 1/100. Referring back to Figure 5.10 one may interpret the present result as showing that an equilibrium between the shearing action of the mean flow and the smearing action of mixing comes to be established once a cloud is tilted at a sufficiently small angle against the horizontal. In oceanic diffusion experiments, the relative displacement of the cloud center at different levels is often conspicuous, vividly demonstrating the influence of shear.

In this same example, the standard deviation of the cloud, σ_x, is also variable level from level, and is given by

$$\sigma_x^2 = 2D_x(t-t_o) + \frac{U^2h^4}{K_z^2} f(\frac{z}{h}) \tag{5.16}$$

where f(z/h) is a 6th degree polynomial:

$$f(\zeta) = \frac{\zeta^2}{45} (\zeta + 1) (\zeta^3 + 2\zeta^2 + \frac{9 - \zeta}{8}) \qquad (5.17)$$

and D_x is "shear diffusivity":

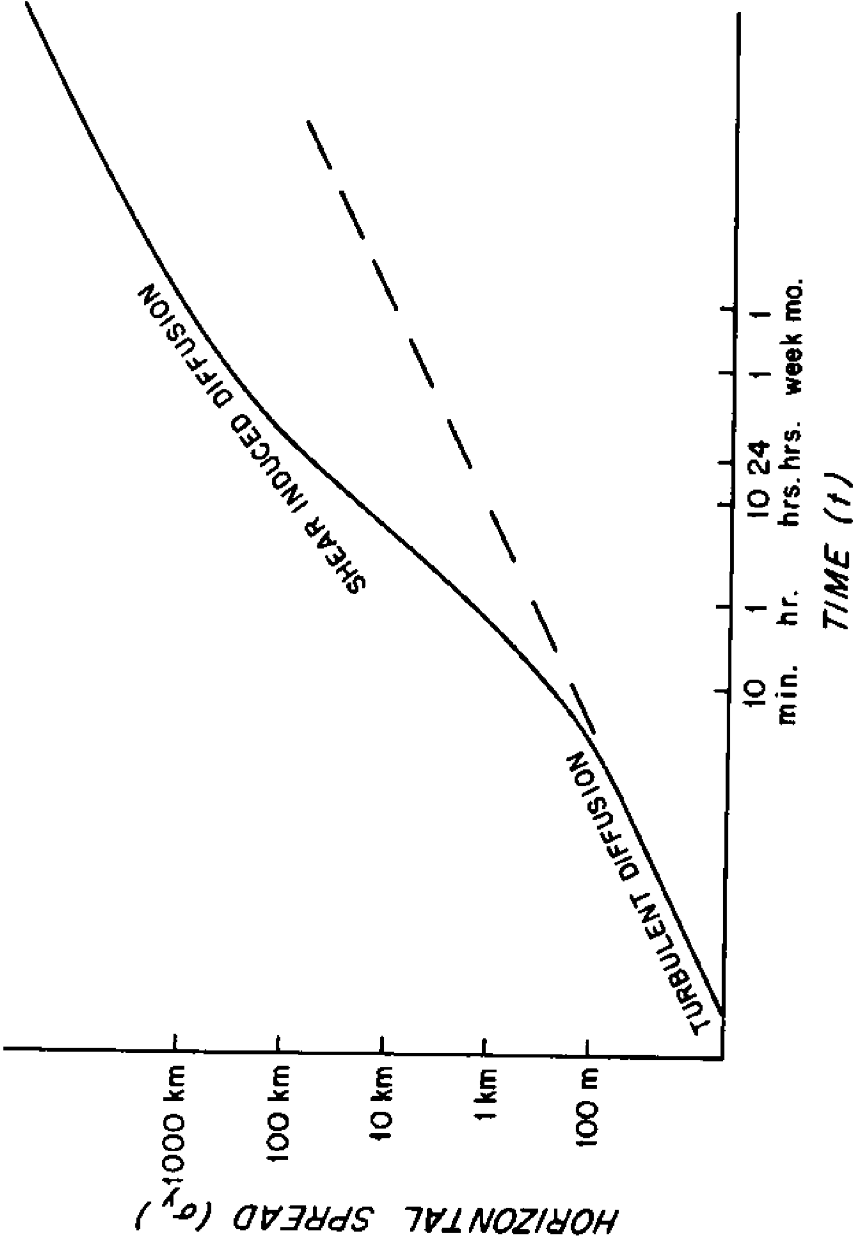
$$D_x = K_x + \frac{U^2 h^2}{30K_z} \qquad (5.18)$$

The function $f(\zeta)$ vanishes at both $\zeta = 1$ and $\zeta = -1$, i.e., at the top and bottom of the water column, but is positive in between and peaks at $\zeta = -1/2$, where $f(\zeta) = 5/1152 = 0.00434$. Thus even if the D_x term in Eq. (5.16), i.e., the cloud at $z = 0$ and $-h$, were small (an unlikely eventuality), σ_x at the center of the water column would be at least 40 h (with $Uh/k_z \cong 600$). The observable cloud size is about $4\sigma_x$ or greater than 160 h, which even with h = 10 m equals 1.6 km. The above asymptotic results are therefore seen to apply to clouds that have become strongly tilted and large at any level.

The physical interpretation of the quantity D_x is effective diffusivity along x, because it is related to cloud growth again by a relationship similar to (5.12). Asymptotically, the cloud grows as $t^{1/2}$, with diffusivity D_x. The typical value of Uh/K_z being about 600, D_x exceeds K_z by a factor of order 10^4. The eddy diffusivity along x, K_x, although substantially greater than K_z, is typically one or two orders of magnitude smaller, so that K_x in (5.18) is a negligible quantity. Typical orders of magnitude in coastal zone applications are $K_z = 10$, $K_x = 10^3$, $D_x = 10^5$, all in $cm^2 sec^{-1}$.

Unfortunately, analytical expressions for cloud growth due to shear dispersion before a cloud occupies the available depth become so unwieldy as to be almost useless. However, the various simple models investigated analytically or numerically all show very similar transitional behavior, exemplified by Figure 5.12. In the log-log plot of this illustration the cloud size σ_y grows as two parallel straight lines (proportional to $t^{1/2}$) in the initial and in the asymptotic phases, corresponding respectively to eddy diffusion and shear diffusion. In between, the $\sigma_y(t)$ curve has an inflection point, so that a straight line fit to the intermediate phase immediately suggests itself. A straight line in a log-log plot corresponds to a power law, $\sigma_y \sim t^n$. The value of the exponent of best fit in several similar models is close to n = 1.15, which is not very different from n = 1. Thus one arrives at a

Figure 5.12 Typical theoretical model result for growth of cloud in shear flow. Initially, cloud is extended by turbulent eddies, asymptotically by an interplay of shear and vertical mixing in equilibrium. In between, a phase of accelerated diffusion occurs, characterized by rapidly increasing effective diffusivity (Csanady, 1969).



quasi-theoretical result representing intermediate phase (or "accelerated") diffusion in shear flow described by $\sigma_y \sim \text{Constant} \cdot t$. Extending this to two dimensions one writes:

$$\frac{d\sigma_x}{dt} = \omega_x \qquad (5.19)$$

$$\frac{d\sigma_y}{dt} = \omega_y$$

The parameters ω_x, ω_y are horizontal "diffusion velocities." They have been introduced into the literature on an empirical basis to represent observations of cloud growth, e.g., by Pritchard and Okubo (1969).

From the analytical models one may also deduce a crude formula for the diffusion velocity:

$$\omega_x = \frac{U}{4} \qquad\qquad \omega_y = \frac{V}{4}$$

where U and V are characteristic velocities associated with the shear along x and y respectively. "Typical" values of ω_x or ω_y are 0.1 to 1 cm sec $^{-1}$.

Experimental evidence on diffusion experiments in coastal regions shows that the "intermediate" phase of diffusion characterized by (5.19) is usually dominant in the diffusion time range of a few hours to a few days.

VERTICAL MIXING

While it is reasonable to ascribe the horizontal dispersion of a tracer or pollutant in the sea mainly to skewed shear flow, vertical mixing is certainly effected by turbulent eddies. The most important demonstration that this is so comes from strongly stratified layers in a thermocline or halocline, where vertical diffusion becomes negligible, on the time scales of interest in waste dispersal. In a sharp vertical density gradient the force of gravity suppresses turbulence, arresting turbulent diffusion altogether. The result is that such a sharp density gradient -- often effectively an interface between two turbulent fluids of slightly different density -- acts as a diffusion floor or ceiling for a cloud which is released above or below the interface.

In shallow coastal waters, from late fall to spring, cooling and mechanical stirring of the surface by strong winds combine to produce a well-mixed water column. In this case, turbulent eddies behave much as in channel flow, well studied in the laboratory. The length scale of turbulence in the middle of the water column is a fairly large fraction of the depth h, while the velocity scale is proportional to $u*$, or friction velocity $u* = \sqrt{\tau/\rho}$, where τ is the larger of the surface or bottom shear stress and ρ is water density. A crude formula for the vertical exchange coefficient in such a well-mixed water column is:

$$K_z = \frac{u_* h}{20} \tag{5.20}$$

A typical value of the wind stress is 1 dyne cm^{-2}, giving rise to $u* = 1$ cm sec^{-1}. Bottom stress is of a similar order of magnitude. For h = 10 m, (5.20) yields the typical value of $K_z = 50$ cm^2 sec^{-1}.

The constant value of K_z given by (5.20) applies to the central portion of the water column, exclusive of "wall layers" at the surface and bottom, which are typically h/10 or so thick, i.e., of the order of 1 m near coastal outfalls. Within wall layers the exchange coefficient varies linearly with distance from the boundary, bottom or free surface:

$$K_z = 0.4\, u_* |z| \tag{5.21}$$

where $|z|$ has to be replaced by z + h near the bottom. Wall layers are mainly important in the horizontal dispersion problem because they harbor strong shear.

The above results, especially (5.20) are importantly modified even by weak stratification. If the surface layers have a density defect $\Delta\rho$ relative to the bottom layers, they are subject to a buoyant acceleration $b = (\Delta\rho/\rho)g$. The relative importance of buoyancy compared to mechanical stirring by surface or bottom shear stress is measured by the bulk Richardson number:

$$R_i = \frac{bh}{u_*^2} \tag{5.22}$$

When the value of R_i exceeds 10^3 or so, a sharp pycnocline forms within the water column some distance above or below the stirred boundary. The vertical exchange coefficient within a sharp pycnocline does not usually vanish completely owing to the breaking of internal waves, etc., but it ranges from K_z = 0.1 to 1.0 cm^2 sec^{-1}. When R_i becomes 10 or less, the water column behaves as if well mixed, i.e., (5.20) may be taken to apply. Around R_i = 100 a weak and diffuse pycnocline is found to occupy much of the water column and the vertical exchange coefficient is in the range K_z = 1-10 cm^2 sec^{-1}. In water about 10 m deep, R_i = 10^3 corresponds to a density defect of 1 part in one thousand, at a typical u_* = 1 cm sec^{-1}.

In such shallow water, the initial mixing produced by a well-designed diffuser distributes the waste over the entire water column. One might think that there is then no further vertical diffusion, unless the mixture is buoyant enough to reform in a surface lens. In any case, however, vertical concentration differences are rapidly created again by differential advection of top and bottom layers, as by the mechanism illustrated before in Figure 5.10. The value of K_z remains therefore important in determining the effective horizontal dispersion coefficient, as should be evident from some earlier remarks.

When the waste is released into the surface or the bottom layer of a deeper water column (e.g., h = order 100 m) it often remains confined to a fraction of the water column above or below a sharp pycnocline. This occurs when the pycnocline is far enough above or below the release point to escape mechanical stirring due to the method of release. In the case of bottom release, the buoyancy of the effluent-seawater mixture produced by initial mixing might still be high enough to pass through a relatively weak pycnocline, while a stronger one will arrest the rising waste plume (see Chapter 4). The entire waste cloud is then trapped beneath the interface and disperses there, as governed by the shear and turbulence in the bottom layer. The absence of waste in the surface layer certainly tends to minimize any environmental impact under these circumstances. However, dispersion may be slow in the bottom layer which is effectively insulated from the influence of wind stress at the surface: there is, for example, less reason for cross-flow shear to develop. A relatively concentrated cloud present in the bottom layer may subsequently be brought to the surface very close to shore in an upwelling event caused by offshore wind or a longshore wind leaving the coast to the left.

When the waste cloud ends up in the mixed layer above a density interface, its dispersal is governed by the near-surface shear and the shear just above the interface, both generally quite strong. Bulk shoreward motion is also possible in this case, due, for example, to a wind-induced downwelling event, but owing to efficient mixing, this is a somewhat less serious problem than the upwelling of a bottom-trapped waste cloud near shore.

All in all, the density distribution in a deeper water column (h = 30 m or more, say) is a very important parameter in determining the behavior of waste released either near the surface or near the bottom. Nearshore, one of the main problems is that under stratified conditions the surface or bottom layers slide relatively easily shoreward in upwelling or downwelling events. In other words, the coastal flow environment becomes in these cases of crucial importance in determining the environmental impact of waste.

BEHAVIOR OF PARTICULATE AND FLOATABLE CONSTITUENTS

Sewage and especially sewage sludge contains particulate and other materials of densities both greater and smaller than seawater. Many heavy metals and other toxic components of domestic wastes are present in these fractions (see Chapter 6) so that their dynamic behavior in the ocean environment is of great importance.

SETTLING OF HEAVY PARTICLES

Heavy particles sink and tend to settle out on the seafloor. In the present context their most important characteristic is their settling velocity, w_s. The median settling velocity of particulate material in sewage is typically 10^{-3}cm sec^{-1}, which is very slow. However, in any given batch of sewage there is a considerable range of particles with widely differing settling velocities (by a factor of about 10^2, either side of the median settling velocity). The median size of the typical sewage particle is of the order of 100 μ (10^{-2} cm) but this is a difficult variable to observe under natural conditions, and there is of course again a considerable spread about the median.

The density of sewage particles may be inferred from their size and settling velocity. At the slow settling velocities in question Stokes' formula is likely to be a reasonable approximation:

$$w_s = \frac{g}{18}\frac{\Delta\rho}{\rho\nu}\, d^2 \tag{5.22}$$

where $\Delta\rho$ is the excess density of the particle over the surrounding fluid, the density of which is ρ, ν is fluid kinematic viscosity, and d is particle diameter. Putting $d = 10^{-2}$cm, $w_s = 10^{-3}$cm $\sec^{-1}$, into this formula, one finds for the "typical" proportionate density excess of the particles

$$\frac{\Delta\rho}{\rho} = 1.8 \cdot 10^{-3} \tag{5.23}$$

This is of the same order as the density differences existing in a stratified water column in the ocean, between a surface mixed layer and the somewhat denser water below. One immmediately infers that as such a particle falls from a lighter to a denser fluid environment, its settling velocity reduces considerably, and even vanishes, at least until thermal and chemical equilibrium is established between the water content of the particle (making up most of its mass) and the surrounding water. In the course of the barged disposal of sludge the waste is initially distributed over a wake some 10 m deep. Under stratified conditions, a fraction of the particles released may be expected to accumulate at the thermocline, where their settling velocity becomes small. This has in fact been observed by acoustical tracking of particulate material (Orr and Hess, 1978).

An important question is, at what rate heavy particles deposit on the seafloor. Under quiescent conditions (as in laboratory experiments carried out for the purpose of determining settling velocity) the particles simply settle on the bottom as they arrive, so that their rate of deposition is concentration times settling velocity:

$$-F_b = w_s\, \chi_b \tag{5.24}$$

where F_b, χ_b are vertical flux and concentration of the particles in question at the bottom.

Under turbulent conditions, particles of a density much higher than water would be projected across the viscous sublayer at the bottom so that their deposition velocity could be higher than w_s. The same would be true of particles having some chemical affinity for the bottom surface. However, their physico-chemical properties, size and density range put the sewage particles into the class of naturally occurring fine organic suspended particles, which are not subject to influences increasing deposition velocity. On the contrary, such very fine organic particulates deposit only under quiescent conditions. With turbulence present, the probability of deposition for each such particle diminishes from unity, so that the deposition rate may be written

$$-F_b = w_s \chi_b p \qquad (5.25)$$

where p is the probability of deposition, or, if one prefers to think of it that way, (1-p) the probability of resuspension.

A formula for the probability of deposition (due to Einstein and Krone, 1962, see also McCave, 1972) is

$$p = 1 - \frac{\tau_o}{\tau_l} \qquad (5.26)$$

where τ_o is the actual shear stress at the bottom and τ_l is a limiting shear stress (for material of given physical characteristics) above which no deposition occurs. For natural organic suspended materials τ_l is of the order 0.5 dyne cm^{-2}. Steady flow of a velocity of 15 cm sec^{-1} (measured a meter or two above the bottom) produces about this shear stress over a smooth floor.

Bottom shear stress substantially higher than τ_l leads to resuspension of previously deposited material. In an open coastal environment the bottom stress exceeds τ_l most of the time, so that fine organic particles do not settle permanently. Where they do settle, they form mud patches. Presumably, sewage particles behave in much the same way and ultimately become part of mud deposits at such locations on the continental shelf and slope where flow conditions allow the accumulation of fine deposit. Elsewhere, they must be considered mobile. This is certainly the case in an active shallow coastal region subject to tides and wind-driven currents.

DIFFUSION OF HEAVY PARTICLES

Owing to the small excess mass of sewage and sludge particles, relative motion due to inertial effects is unimportant, and the particles follow water movements, except that a certain settling velocity is superimposed. The advection and diffusion of a cloud of particles of constant settling velocity is therefore subject to the diffusion equation (5.5), with one additional term on the left expressing advection by the settling velocity. In the simple case where horizontal variations of concentration vanish, this equation becomes

$$\frac{\partial \chi}{\partial t} - \frac{\partial}{\partial z} (w_s \chi) = \frac{\partial}{\partial z} (K_z \frac{\partial \chi}{\partial z}) \tag{5.27}$$

Some simple solutions of this equation (or of a more complex form, with horizontal variations included as in 5.5) will illuminate the behavior of a diffusing cloud of "heavy" particles.

Well-stirred Water Column

A time-independent first integral of (5.27) is:

$$-F_z = w_s \chi + K_z \frac{\partial \chi}{\partial z} = \text{constant} \tag{5.28}$$

the physical interpretation of $-F_z$ being vertical flux along negative z, i.e., downward. If this flux at the free surface is zero, it is zero everywhere, including the bottom. Under these conditions (5.28) shows that the "settling" flux $-w_s \chi$ is equal and opposite to the "stirring" flux $-K_z(\partial\chi/\partial z)$. A zero-flux (no deposition) boundary condition at the seafloor is consistent with the physics of the problem discussed above if the flow velocity is high enough to cause bottom stress in excess of τ_1, i.e., a deposition probability p of zero. Turbulence is then able to counteract the settling tendency of heavy particles everywhere (including the bottom) and thus keeps them in suspension.

A second integral of (5.28) is

$$\chi = \chi_b \exp \left(- \int_{-h}^{z} \frac{w_s}{K_z} dz \right) \tag{5.29}$$

where χ_b is the concentration at the bottom, $z = -h$. This may be determined, e.g., if the total amount in suspension is known. In a well-stirred water column, to which this model applies, it is reasonable to regard w_s, K_z as constant. The surface to bottom concentration ratio is then

$$\frac{\chi_s}{\chi_b} = \exp \left(- \frac{w_s h}{K_z}\right) \tag{5.30}$$

Using the formula (5.20) for vertical eddy diffusivity, the factor in the exponential is seen to be 20 w_s/u_*, where u_* is bottom friction velocity. As the bottom stress was already supposed to exceed τ_1, u_* may be taken to be of order 1 cm sec $^{-1}$, or 3 orders of magnitude larger than the "typical" value of w_s. For such a particle fraction the exponent in (5.30) is small and χ_s/χ_b is near unity (0.98, given the typical data). It should be remembered, however, that in addition to fractions near the median settling velocity, sewage or sludge also contains some particles of a much higher settling velocity. With $w_s = 10^{-1}$cm sec^{-1} the exponent in (5.30) becomes -2 and the χ_s/χ_b ratio 0.14, for $u_* = 1$ cm sec^{-1}. Only the largest fractions concentrate near the bottom in this manner, most of the rest of the particulate sewage constituents being nearly uniformly distributed over a well-stirred water column.

Two Stirred Layers

The boundary condition of zero deposition rate at the bottom is realistic also in a stratified fluid, if the layer nearest the bottom is in fast enough motion to give rise to bottom stress in excess of τ_1. The solution (5.29) remains valid for this case, and w_s and K_z are not now constant with depth.

The typical distribution of the eddy diffusivity characterizing such cases is a fairly high, nearly constant value within a wind-mixed surface layer, a much lower value in the pycnocline, and a high value again in a mixed layer above the seafloor, stirred by bottom shear. Correspondingly, w_s/K_z has a maximum within the upper pycnocline. As discussed above, w_s is also likely to change with depth, reducing in the denser water of the lower layers. The net effect may be fairly complex, but the concentration distribution should be characterized by a sharp concentration gradient in the upper pycnocline.

The Traffic Jam Problem

Consider the release (e.g., from a barge) of a quantity of particles of constant $w_s = w_{so}$, distributed initially over a surface mixed layer above a well-defined pycnocline, in a concentration χ_o. The cloud starts to descend as a plug, but runs into a traffic jam in the pycnocline, where w_s decreases. Conditions in this region are fairly satisfactorily modelled in a simple way by prescribing constant flux some distance above the pycnocline and finding a steady-state solution.

Eq. (5.28) applies to this case, but with $F_z \neq 0$:

$$w_s \chi + K_z \frac{\partial \chi}{\partial z} = w_{so} \chi_o \tag{5.31}$$

As w_s decreases to w_{s1} (say), the concentration tends to increase to maintain the settling flux at its original value. Without vertical diffusion the value of the concentration would increase to

$$\chi_1 = \chi_o \frac{w_{so}}{w_{s1}} \tag{5.32}$$

Vertical diffusion tends to smooth out any sharp gradients over the diffusion depth scale K_z/ω_s, but this is not a very important effect: the concentration increases sharply in the upper thermocline.

Trajectory of Heavy Cloud

So far, horizontal displacements of a cloud of heavy particles have not been considered in this section. Typical horizontal velocities, however, are large in comparison with typical settling velocities. A small cloud of heavy particles, released near the surface (say) falls through the water column and samples horizontal velocities at all levels by the time it reaches the bottom.

The trajectory of a small cloud of heavy particles is described by

$$\frac{dz}{dx} = \frac{w_s}{u} \qquad\qquad \frac{dz}{dy} = \frac{w_s}{v} \tag{5.33}$$

If the horizontal fluid velocities u, v, and the settling velocity w_s are functions of depth only, these equations are easily integrated to give

$$x = \int_z^o \frac{u}{w_s}\, dz \qquad\qquad y = \int_z^o \frac{v}{w_s}\, dz \tag{5.34}$$

the horizontal displacements x, y being measured from the release point. By the time the cloud hits bottom, it has been displaced by horizontal distances of, for w_s = constant:

$$x_b = \frac{U}{w_s} h \qquad y_b = \frac{V}{w_s} h \tag{5.35}$$

where U, V are depth-average velocities. For non-constant w_s, a suitable effective value has to be substituted in this formula.

Typical values of U(longshore) are 10 cm $\sec^{-1}$, so that with $w_s = 10^{-3}$ cm $\sec^{-1}$ the horizontal displacement x_b is 10^4 times depth or 100 km for 10 m depth. Thus typical sewage particles travel very long distances before they even tend to deposit. Of course they will not deposit, as already discussed at some length, unless the bottom stress is low. Even if they do deposit, they will be resuspended (and stirred right through the water column) by storms, while in shallow water. They will then be subject to further long displacements before most of them can redeposit again.

In Chapter 6, Morel has argued that the fate, and especially deposition, of particles with an appreciable free fall velocity depends critically on their tendency to coagulate. Morel has there reinterpreted some standard observed results on sedimentation rates. Clearly the precise behavior of the waste particles in this regard determines what conclusions one may draw from calculations of the kind presented in this chapter. If there is, in fact, an essentially one-way tendency for particles to coagulate and become heavier and heavier, eventually their free fall velocity must become large enough to cause rapid deposition and perhaps adhesion to the sediments. Morel also makes clear that current knowledge of the physico-chemical behavior of sewage particles is inadequate to decide such questions conclusively and quantitatively. The question whether a significant proportion of originally small particulate constituents of domestic waste coagulate to large enough size to form stable organic deposits remains open, but also somewhat unlikely, in view of the well-established behavior of naturally occurring organic particulates.

FATE OF FLOATABLES

Municipal waste contains a certain fraction of material which is positively buoyant and which, after the turbulence of the initial mixing dies down, comes to float on the surface. One of the most important goals of sewage treatment plants is to eliminate floatables as far as possible. However, even if the efficiency of removal in the treatment plant is 100 percent, a new floating fraction is formed on release into seawater, which is considerably heavier than the treated wastewater, and in which various chemical and biological changes take place.

The horizontal dispersion of buoyant pollutants exhibits certin peculiarities, on account of the fact that these are confined to a two-dimensional boundary of a three-dimensionally turbulent medium. At such a boundary, convergent and divergent zones usually occur. Non-buoyant fluid wells up in divergences and dives down in convergences; floating particles are prohibited by their buoyancy from participating in vertical motions, with the result that they congregate in convergences, thin out in divergences. The transport, turbulent diffusion, and beach deposition of such floating particles has received very little systematic attention in the literature so far.

When a moderately strong wind blows over a water surface, it generates a characteristic big-eddy field in the wind-driven current consisting of "Langmuir circulations" which are marked by long parallel lines of foam ("windrows"). Such flow structures have been the subject of a number of studies since the pioneering investigation of Langmuir (1938). The windrows are known to form at lines of confluence parallel with the wind, where the water sinks. They have characteristic spacings of several meters to several tens of meters. They collect not only foam, but also other buoyant particles, such as those present in municipal waste, globules of fat, etc.

Langmuir circulations are the big eddies of near-surface, wind-driven shear flow and they decay and reform in new locations at periods roughly of the order of 10^3 sec (1/4 hr). Thus they do not interfere with the horizontal diffusion of floatables on a larger time scale, because a given buoyant particle becomes successively caught up in a number of eddies, which take it through a classical random walk. A practically important effect which remains is, however, that where such particles approach the shoreline, they are not evenly distributed but come in groups concentrated in windrows. Thus their apparent concentration is higher and they tend to be more noticeable on beaches.

Close to a coastline, and often more or less parallel to it, there are also other, more permanent confluences, which only disappear and reform on a change of wind, or on a major current reversal unrelated to wind, e.g., in every tidal cycle. Owing to their longer lifetime, such quasi-permanent confluences collect a greater quantity of floatables. On a change of wind or current, these may find their way toward the beaches.

The last few hundred meters in front of a beach are crossed by floating particles according to the action of wind, waves and the rip-current system generated by the waves on the particular shoreline configuration. There are a few preferred locations for flotsam to accumulate on beaches: this is where waves transport it shoreward. Deposition occurs apparently when waves decay in amplitude. Groups of floating particles thrown high on the beach by a large wave are then not washed up again by the next slightly smaller wave.

Quantitatively, the long-term horizontal diffusion of floating particles may be described by a two-dimensional diffusion equation, with a horizontal diffusivity of the order of 10^6 cm^2 sec^{-1} (judged by the length-scale and decay period of windrows). As a shore boundary condition, a horizontal deposition velocity v_s may be introduced, such that the deposition rate is

$$I = v_s \chi_s \tag{5.36}$$

with χ_s being surface concentration at the shore (g/cm^2 or equivalent units). The order of magnitude of v_s appears to be 0.1 - 1.0 cm sec^{-1}. However, it should be kept in mind that such an approach glosses over the details of the concentration field. In reality, floating particles arrive on the beach in groups with a concentration one or two orders of magnitude greater than the long-term, spatially smooth average model of the diffusion equation yields.

Floating particles composed of fatty acids, etc. are exposed to particularly rapid weathering at the sea surface and their decay rate must be considerable. There does not appear to be any quantitative information on this point, but it should be clear that such particles are not likely to constitute a nuisance after being exposed to sun and wind for a longer period.

THE USE OF MODELS

Previous sections of this chapter have dealt with the fundamentals of turbulent diffusion and shear-flow dispersion, as well as with environmental conditions and key environmental parameters which affect the diffusion-dispersal process. The following discusses several quantitative diffusion models and the practical conclusions that may be drawn from these models.

Box Model

The simplest possible conceptualization of the nearshore waste disposal problem leads one to a so-called "box model." This exhibits the important mass balances with particular clarity. From a practical point of view, its main function is to verify that no long-term buildup in the concentration of persistent waste components need be feared in a given coastal location. Over shallow Atlantic-type shelves, at least, it is not immediately obvious that the continuous release of a waste constituent with a very long lifetime in the ocean environment will not lead to an undesirable long-term rise of background concentration levels near the discharge.

Over the long term the concentration of a given long-lived waste component in the coastal region adjacent to the release point is limited by the rate at which that waste component can be transferred to the larger mass of the atmosphere-ocean system. One may conceptualize the process in two steps. The tidal water movements and other short-term flow components first efficiently distribute the released waste over an "extended source region." This may be taken to have longshore dimension X, cross-shore dimension Y, roughly equal to twice the tidal excursions, as discussed earlier. In non-tidal waters the dimensions of the extended source region are mainly governed by the method of discharge.

Longshore advection, surface mass transfer to the atmosphere and cross-shore mass exchange to the rest of the ocean remove a persistent waste constituent of interest at the same combined rate at which it is introduced by the outfall into the extended source region. The average concentration of the waste constituent in that region increases to χ_i in order to allow its steady state transfer to the atmosphere-ocean system.

Figure 5.13 illustrates the simple box model of the extended source region. If the volume flow rate through the outfall is Q_v, and if the concentration in the outfall is χ_o, a given waste species is released at the rate

$$q = \chi_o Q_v \tag{5.37}$$

Several mechanisms combine to remove the waste species from the extended source region: chemical and biological decay, longshore advection, cross-shore mass-exchange, and surface mass transfer. Decay may be represented by a linear law of the form (5.2) integrated over the volume of the extended source region:

$$q_d = k\chi_o XYH \tag{5.38}$$

where H is the average depth and k a reciprocal time-scale of decay. For the long-lived species of principal interest in a box-model calculation, k is vanishingly small.

Longshore advection or "flushing" removes the waste constituent of interest because the concentration in the water leaving the extended source region is higher by χ_i than in the water entering it. The rate of flushing is then

$$q_f = UHY \chi_i \tag{5.39}$$

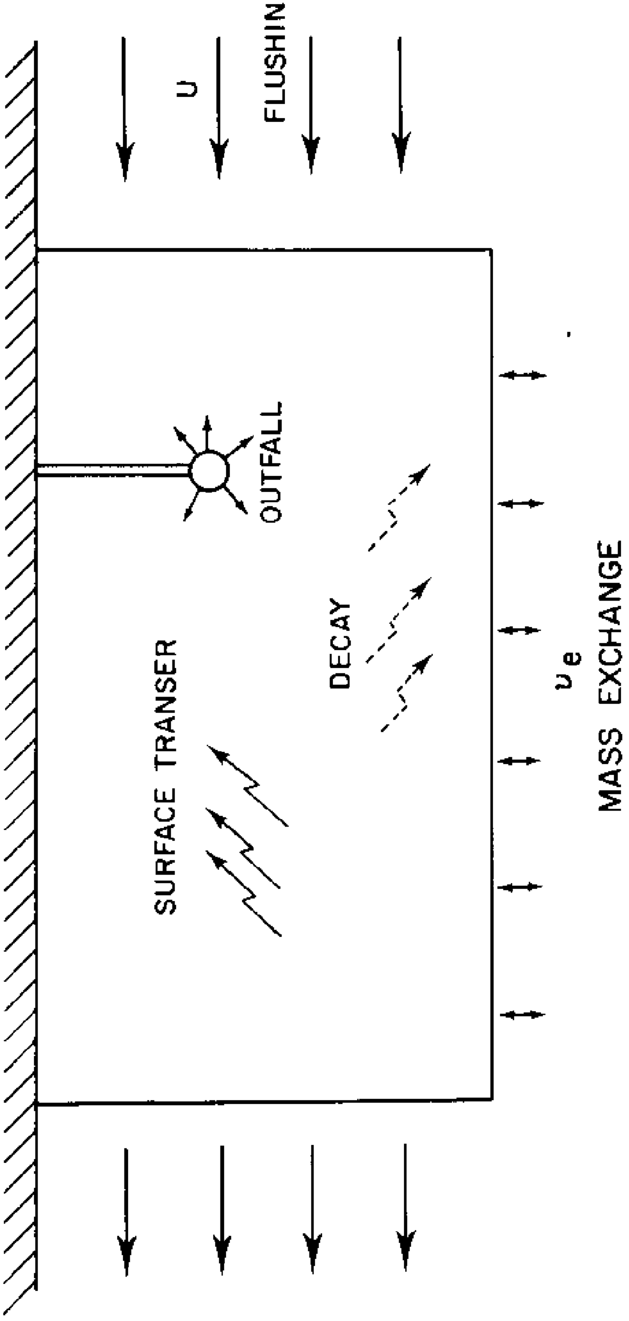
where U is average longshore velocity (average over a long period and over a cross-shore transect across the extended source region).

Across the seaward edge of the extended source region there is no net water transport, but as explained above, there is vigorous exchange associated with wind impulses, internal tides, etc. This may be parameterized in terms of a mass-transfer velocity v_e, such that the cross-shore exchange rate is

$$q_e = v_e HX \chi_i \tag{5.40}$$

Mass transfer to the atmosphere, if significant, may be taken into account in a similar manner, introducing a surface mass transfer velocity v_s:

Figure 5.13 Schematic illustration of box model used to check long-term concentration buildup near outfall.



$$q_s = v_s XY \chi_i \tag{5.41}$$

If permanent deposition of the waste species is occurring, a similar equation may be written down for the total rate of deposition. However, for reasons explained earlier, this is not likely to be significant.

Steady state balance between release and removal of the waste constituent of interest is now expressed by

$$q = q_d + q_f + q_e + q_s \tag{5.42}$$

Because all terms on the right are proportional to χ_i, an expression for the concentration in the extended source region is easily obtained:

$$\chi_i = \chi_o \frac{Q_v}{kHYX + UHY + v_e HX + v_s YX} \tag{5.43}$$

The quantity multiplying the release concentration χ_o may be viewed as a reciprocal impedance: The long term buildup of concentration in the extended source region is release concentration divided by the impedance. Alternatively, and more in accord with earlier discussion, the impedance is a dilution factor characterizing the long-term concentration in the extended source region. This is seen to be the sum of contributions due to decay, advection, mass exchange and surface loss:

$$D_i = \frac{kHYX}{Q_v} + \frac{UHY}{Q_v} + \frac{v_e HX}{Q_v} + \frac{v_s YX}{Q_v} \tag{5.44}$$

Typical physical parameters characterizing a large outfall in shallow coastal waters (over an Atlantic-type shelf) are listed in Table 5.1. Dilution factors calculated with their aid are listed in Table 5.2. Note that neither surface loss nor decay affect the resultant dilution factor very much, the main factors governing long-term concentration buildup being longshore advection or flushing and cross-shore mass-exchange. This is true of an "active" shallow coastal zone where both U and v_e are relatively high. A much greater degree of buildup may be expected in a less active region, where U and

Table 5.1 Physical Parameters Typically Affecting Large Coastal Outfall

Volume flow rate, Q_v	1 m^3 sec^{-1}
Extended source region depth, H	10 m
Extended source region width, Y	1000 m
Extended source region length, x	3000 m
Longshore mean velocity, U	0.1 m sec^{-1}
Cross-shore velocity, v_e	0.03 m sec^{-1}
Surface mass transfer velocity, v_s	10^{-5} m sec^{-1}
Decay constant, k: short-lived constituent	10^{-5} sec^{-1}
long-lived constituent	10^{-7} sec^{-1}

Table 5.2 Component Dilution Factors for Typical Large Coastal Outfall

Dilution due to	Short-lived Constituent	Long-lived Constituent
Longshore flushing	1000	1000
Cross-shore exchange	900	900
Surface loss	30	30
Decay	100	1
Total Dilution	2030	1931

v_e are low. Simply put, the volume of water available for diluting the waste is limited in a shallow coastal location and this determines how much dilution is possible. Where the total dilution available is uncomfortably low, barging of sewage sludge to an offshore site should be considered. An offshore site generally offers a larger total volume (X, Y and H) of the extended source region, as well as higher flushing and mass-exchange velocities. Over Pacific-type continental shelves the depth available for nearshore mixing is as much as an order of magnitude larger, so that the limits on dilution are more favorable.

Classical Straight Plume Diffusion Model

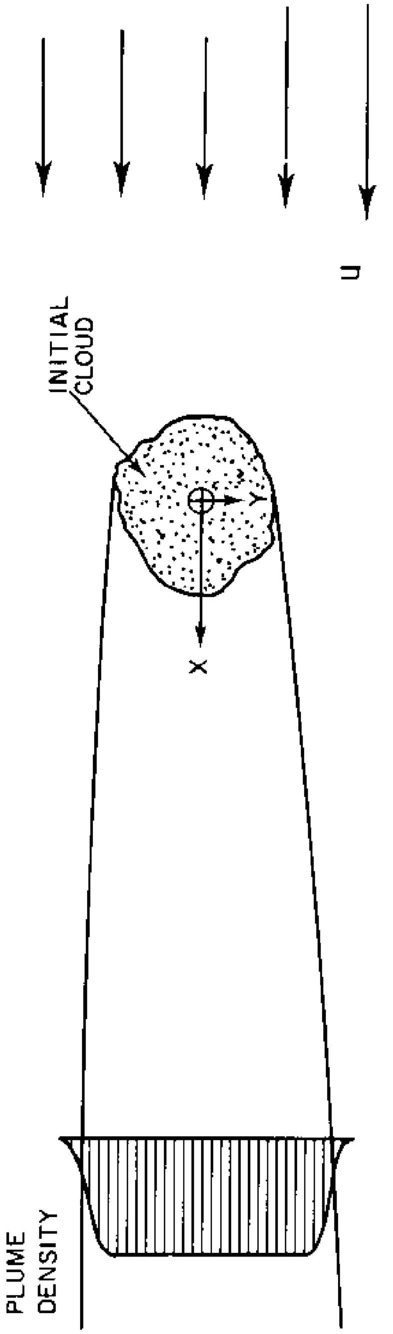
For the short term, i.e., a period of one or two hours, tidal currents are approximately steady and spatially uniform. The diffusion of effluent discharged into such a simple flow environment is well described by the classical straight-plume model developed by Brooks (1960) and others. Because this has been used extensively in the past, only a brief account is given here.

Above a single- or multi-port diffuser located in coastal waters the waste "boils" to the surface or to a level of neutral buoyancy as discussed by Koh in Chapter 4, and mixes effectively with a fairly large volume of seawater. Further dilution with seawater is then primarily due to mixing at the edges of the waste plume which forms downstream of the initial mixing zone. In other words, diffusion is a one-dimensional process, taking place in the cross-plume direction only. For this situation, further dilution (and decay, if appropriate) of any waste species may be approximated by a Gaussian plume model (Csanady, 1973), leading to the following formula, valid for release far from shore:

$$\chi(x,y) = \frac{1}{2}\ \chi_i e^{-kx/U}\left[\mathrm{erf}\left(\frac{b+2y}{2\sqrt{2}\ \sigma_y}\right) + \mathrm{erf}\left(\frac{b-2y}{2\sqrt{2}\ \sigma_y}\right)\right] \tag{5.45}$$

This classical model is illustrated in Figure 5.14. In Equation (5.45) x is distance along plume axis, k the decay constant, and σ_y is standard deviation along the crossplume direction, the growth of the plume being due to eddy or shear diffusion. In the usual case shear diffusion dominates and the growth of the plume may be described by a diffusion velocity ω_y (5.19). Writing t = x/u for diffusion time:

Figure 5.14 Classical diffusion model of waste plume in a steady and uniform current.



$$\sigma_y = \frac{\omega_y x}{U} \tag{5.46}$$

In the classical model the initial concentration χ_i (after jet diffuser mixing) is multiplied by a factor expressing decay and another factor describing dilution due to lateral mixing. At the centerline of the plume, y = 0, the dilution factor due to lateral mixing is

$$\mathrm{erf}\left(\frac{b}{2\sqrt{2}\ \sigma_y}\right)$$

The argument of the error function decreases with increasing distance from the source, being very large close to the source. The value of the error function is, correspondingly, very close to its asymptotic value of 1.0 at short distances x, expressing absence of dilution through lateral mixing. Physically, the center concentration is only affected when mixing at the edges of the cloud has been in progress long enough to "bite" into the cloud substantially. This occurs when the argument of the error function drops below 2, i.e., when

$$\sigma_y \geq \frac{b}{4\sqrt{2}} = 0.177b \tag{5.47}$$

Taking b = 300 m, ω_y = 0.5 cm $\sec^{-1}$, this criterion is satisfied for diffusion times in excess of 10^4 sec, i.e., some 3 hr. With u = 30 cm/sec, the plume length over which the center concentration remains unaffected by mixing is about 3 km. In other words, for plumes of this relatively large initial width, lateral mixing is entirely ineffective in reducing the maximum concentration over the whole range of validity of a classical straight plume diffusion model. For periods longer than three hours the temporal variation of tidal velocity must be taken into account. Physically, the efficient initial (jet/diffuser) mixing of a well-designed diffuser in effect preempts further dilution by natural processes for several hours.

The decay factor in (5.45) is similarly inconsequential if the decay constant is of order 10^{-5} $\sec^{-1}$ (a realistic value for bacterial die-off, for example) or less and the maximum diffusion time x/u of interest is 10^4 sec. The classical model under these circumstances merely describes the rather trivial transition from a more or less uniform distribution in the well-mixed initial cloud to the bell-shaped (Gaussian) distribution characteristic of diffusing clouds generated by concentrated sources.

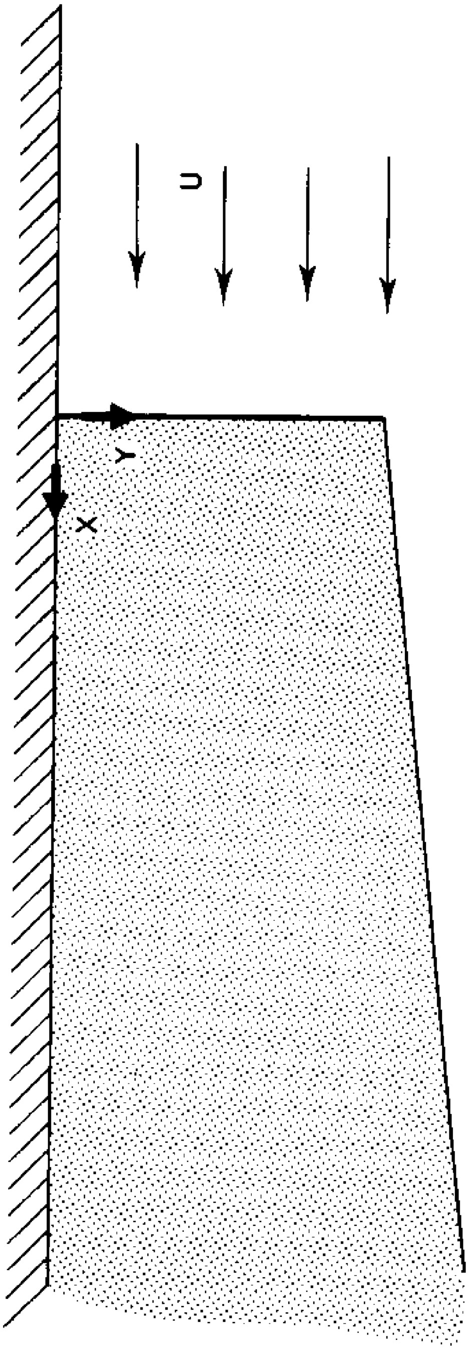
Effectively the same model can also be applied as a more sophisticated alternative to the box model described in the previous section for representing long-term diffusion. Consider now that the "initial" mixing extends at least over a full tidal cycle, during which the waste is effectively distributed over the range of tidal excursions, i.e., the "extended source" region defined previously. Because these usually take the waste close to the shore, the presence of a shoreline can no longer be ignored. An appropriate simple model of the same kind as the box model of Figure 5.14 is one in which the extended source region extends from the shore $y = 0$ to $y = b/2$, see Figure 5.15. This is effectively <u>half</u> a plume of the classical model wherein the zero cross-shore flux condition at the coast is satisfied by symmetry. The solution Eq. (5.45) remains valid, although only $y \geq 0$ is physically real and the interpretation of χ_i and b changes somewhat. For the source extension b/2 one must substitute something comparable to twice the cross-shore tidal excursion, while χ_i is determined from

$$\chi_i \frac{b}{2} UH = \chi_o Q_v \tag{5.48}$$

where U is now <u>long-term</u> flushing velocity and H is average depth over the range $y = 0$ to $y = b/2$. For typical values $b = 1$ km, $U = 0.1$ m sec^{-1}, $H = 10$ m one finds an extended source dilution χ_o/χ_i of 1000, pretty much as Table 5.2 shows for dilution due to flushing in a box model.

A more detailed comparison of this model with the simpler box model discussed earlier is as follows. The dilution due to flushing is represented as initial dilution, and the concentration in the model rises abruptly to χ_i at $x = 0$. Decay <u>and</u> surface loss of waste species to the atmosphere may be taken to be represented by the exponential term if one writes $k^* = k + v_s/H$ in place of the exponent k in (5.45). The e-folding length scale of this distribution is then U/k^* which is typically tens of kilometers or more. As in the box model, this term is not very significant in reducing concentrations near the source. What was labelled as cross-shore mass exchange in the box model is now represented as horizontal diffusion. For the long-term diffusion problem, an effective diffusivity D_y should be introduced. This yields the plume size

Figure 5.15 Extended source steady plume diffusion model.



$$\sigma_y = \sqrt{2D_y\ x/U} \tag{5.49}$$

The concentration drops substantially due to horizontal diffusion when $\sigma_y = 3\frac{b}{2}$ or so, i.e., when

$$x \simeq \frac{Ub^2}{D_y} \tag{5.50}$$

A realistic value of D_y for long-term coastal diffusion is 10^5 $cm^2\ sec^{-1}$, which gives with $U = 10$ cm sec^{-1}, b = 1 km, x = 10 km. In other words, there is a moderately long influence zone downstream of the discharge over which the mean concentration is not much less than X_1. This corresponds to the longshore dimension of the extended source region in the box model.

Meandering Plume-Statistical Model

Although short- and long-term diffusion limits have been adequately highlighted by the discussion in the previous sections, it is clear that the simple models used give only a very limited picture of nuisance or hazard associated with waste release in the coastal environment. On the one side, a calculation of long-term mean dilution rates is not likely to exhibit the worst effects of a waste plume. On the other side, the representation of onshore-offshore mass exchange by a mass exchange velocity does not do justice to the vigorous natural phenomena associated with upwelling-downwelling cycles, which sometimes remove contaminated waters from the coastal zone in one fell swoop. In order to come to grips with the problem in a more effective way, it is necessary to consider the bodily displacements of puffs or plume elements of the waste due to tidal- and wind-driven currents, as well as mean flow and exchange processes. The general problem is that of an arbitrarily meandering plume generated in variable currents by a continuous source, a problem not so far treated in the open literature, so that it will be discussed here in some detail, following an unpublished report (EG&G, 1976).

Instantaneously observable plumes generated by continuous point-sources are almost always long and slender, so that the concentration varies in them much more slowly in a direction parallel to the local plume axis than perpendicular to it. It is therefore convenient to describe the concentration distribution in plane cross-sections of the plume, perpendicular to the axis. Statistics may then be calculated at fixed distances p from the plume centerline in such a cross section, where p is a <u>two-dimensional</u> vector. Such statistics describe the relative diffusion process in a continuous plume. Because the plume width grows slowly along the axis, concentrations decrease slowly with distance from the source. It is therefore also necessary to prescribe at what specific locations the individual cross-sections are taken, to make up a population determining concentration probabilities at fixed p. Physically the soundest procedure would be perhaps to compare cross sections taken all at a fixed distance ℓ (measured along the arc of the plume-axis) from the source. It is, however, experimentally quite difficult to carry out concentration surveys in sections at fixed ℓ, when plumes are curved and vary their shape in time. It is easier to collect sections, the planes of which all pass through a fixed point x (in the sea such a point may be marked by an anchored buoy). It turns out that it is also most convenient from a theoretical point of view to think of many cross sections of a plume, which all pass through a fixed point x.

In the continuous release case, meandering manifests itself in irregular displacements of the plume centerline. At a fixed point x, large changes in instantaneous concentration occur according to whether a plume is close-by or not. One may define as $\Pi(p,x)dp$ the probability that the plume centerline is at a perpendicular distance p from the fixed point x, within the area element dp of the plane normal to the local plume axis. Owing to the slenderness of the plume only relatively small distances $|p|$ have any practical significance, so that one can safely ignore possible complications, such as the existence of two or more perpendicular distances from the point x where a given plume-realization may be found (the radius of curvature of a plume may always be safely assumed large compared to its width).

The conceptual experiment defining the probability density $\Pi(p,x)$ is as follows. Suppose that a large number of plume-centerline realizations are observed, a fraction of which pass close enough to the point x to have some measurable influence on the realized concentrations at x. Cross sections are laid to these plumes through the point x, and the position of the plume centerline is marked by a dot. Turning the cross sections all into a single common plane, e.g., one perpendicular to the radius vector $\underset{\sim}{x}$, the density of the dots per unit area in this common plane determines $\Pi(\underset{\sim}{p},\underset{\sim}{x})$.

An infinitesimal length of arc along the plume centerline consists of a series of puffs released over an infinitesimal time interval. If the fluid velocity perpendicular to the plume section is $\underset{\sim}{V}_p$, puff centers within the volume $\underset{\sim}{V}_p\, dt\, d\underset{\sim}{p}$ contribute to the probability distribution $\Pi(\underset{\sim}{p},\underset{\sim}{x})$. Since puffs of all "ages" may be present (in principle) at $\underset{\sim}{x} + \underset{\sim}{p}$, one has the relationship:

$$\Pi(\underset{\sim}{p},\underset{\sim}{x}) = \int_0^\infty P(\underset{\sim}{x} + \underset{\sim}{p},t)\, |\underset{\sim}{V}_p|\, dt \tag{5.51}$$

A simplified form of this result is valid for plumes so <u>slender</u> that $P(\underset{\sim}{x} + \underset{\sim}{p}, t)$ is independent of $\underset{\sim}{p}$ for all distances $\underset{\sim}{p}$ for which significant effects are produced at the fixed point $\underset{\sim}{x}$. At all $\underset{\sim}{p}$ of interest, then $\Pi(\underset{\sim}{p},\underset{\sim}{x}) \cong \Pi(o,\underset{\sim}{x})$ and

$$\Pi(o,\underset{\sim}{x}) = V_p \int_0^\infty P(\underset{\sim}{x},t)\, dt \tag{5.52}$$

where V_p is a weighted average fluid velocity magnitude along the plume axis. Physically, V_p is a measure of how densely the waste is distributed along the plume axis, a higher V_p meaning that the material released during dt is stretched out over a longer distance.

In a complex velocity field V_p might well vary significantly with position $\underset{\sim}{x}$: nearshore, for example, cross-shore velocities are generally lower than longshore ones, so that points seaward of the source may be characterized by lower plume-transport velocities than points situated at the same distance from shore, displaced longshore, however. On the whole, the fact that V_p is a weighted average should ensure that it has only a relatively modest range of variation. In a simple model it is not too unreasonable to regard V_p as constant. The determination of the distribution $\Pi(o,\underset{\sim}{x})$ resolves itself to finding a suitable statistical model of puff center displacements $P(\underset{\sim}{x},t)$.

The problem is then to describe the statistical distribution of the position vector $\underset{\sim}{c}(t)$ of the center of gravity of meandering puffs of waste. Reserving the symbol χ for stochastic mean concentration, let the <u>realized</u> concentration distribution in a single puff be designated $N(\underset{\sim}{x},t)$. The total mass of each individual puff may be considered unity in discussing the behavior of the center of gravity:

$$\int N(\underset{\sim}{x},t)\,d\underset{\sim}{x} = 1 \tag{5.53}$$

The integration in this and following expressions extends over all available space. The center of gravity of a puff is by definition

$$\underset{\sim}{c}(t) = \int \underset{\sim}{x}\, N(\underset{\sim}{x},t)\,d\underset{\sim}{x} \tag{5.54}$$

The vector $\underset{\sim}{c}(t)$ is a random variable with mean $\bar{\underset{\sim}{c}}(t)$ and standard deviation $\underset{\sim}{\rho}(t)$. All these have two horizontal components, (c_x, c_y) $(\bar{c}_x, \bar{c}_y)$ and (ρ_x, ρ_y), the latter if one supposes the mean

cross product $\overline{c_x' c_y'}$ to be zero.

The time derivative of the vector $\underset{\sim}{c}$ is a puff center velocity

$$\underset{\sim}{w} = \frac{d\underset{\sim}{c}}{dt} \tag{5.55}$$

This velocity is of interest, because the kinematic properties of puff center displacements and velocities can be analyzed in exactly the same way as individual diffusing particle displacements and velocities, which are discussed in standard texts on turbulent diffusion. Arguments relating to puff center velocities lead to results relating to the statistics of puff center displacements, i.e., to the distribution $P(\underset{\sim}{c}, t)$ sought here. For example, the standard deviation along the x-axis, ρ_x, is related to fluctuating velocities $w_x' = w_x - \bar{w}_x$ as follows:

$$\rho_x^2 = \int_0^t \int_0^t \overline{w_x'(t')\,w_x'(t'')}\; dt'dt'' \tag{5.56}$$

At short times after release the correlation in this integral is close to unity and one has

$$\rho_x = u_p t \quad (t \text{ small}) \tag{5.57}$$

where $u_p = (\overline{w_x'^2})^{1/2}$ is the root-mean square fluctuating velocity of the puff center. A similar result holds along the y-axis.

Physically, the meandering of waste plumes generated by relatively large discharges is caused by flow structures of a length scale large compared to initial cloud dimensions. First and foremost, this includes tidal oscillations, but in non-tidal waters the larger shore-bound eddies, due to the irregularities of a coast, play a similar role. In such non-tidal waters one finds that artificially generated tracer plumes have a sinuous outline, although their direction is generally parallel to the coast. The amplitude of the sinusoidal plume-meanders in the cross-shore direction (which will be the y-axis in the calculations below) approaches a finite limit, determined by the principal eddies of the coastal boundary layer. Tidal motions add to these random displacements (and often dominate them) but their principal physical characteristic is also a well-defined limit to cross-shore excursions. Thus the mean cross-shore plume center velocity is zero, $\overline{w}_y = 0$. In addition, the standard deviation ρ_y asymptotically tends to a constant limit. Physically, the constraint imposed by a coast limits and damps cross-shore movements sufficiently to "trap" waste plumes within a coastal boundary layer. From observation, there is a great deal of evidence supporting this point of view with the qualification that, on the occasion of major current reversals, the entire coastal water mass is replaced and tracer or waste plumes are, for all practical purposes, "lost", becoming undetectable by normal instrumentation.

The coastal constraint which results in a trapping of plumes near the coast (except for the influence of catastrophic events) may be simply modelled by assuming puff center velocity along the y-axis to be stationary random process akin to the velocity of a harmonic oscillator subject to a random force. The correlation function in (5.56) is then only a function of the time differential $\tau = t'' - t'$. A simple function satisfying the asymptotic constraints at $\tau = 0$ (Eq. 5.57) and $\tau \to \infty$ is

$$\overline{w_y'(t')w_y'(t'')} = v_p^2 e^{-\tau/T}(\cos \omega\tau - \frac{1}{\omega T} \sin \omega\tau) \tag{5.58}$$

where ω is tidal frequency and T a frictional decay period. A graph of this function against time delay τ shows positive and negative loops alternating with the tidal frequency ω and decaying in amplitude with a time constant of T. The total area of positive loops equals the area of negative loops.

After the double integration indicated in (5.56) the following expression for ρ_y emerges:

$$\rho_y{}^2 = \frac{2\ v_p{}^2}{\omega^2 + 1/T^2} \left\{1 - e^{-t/T} [\cos \omega t + \frac{1}{\omega T} \sin \ \omega t]\right\} \quad (5.59)$$

At short times this satisfies the y-axis analogue of (5.57), while at long times ρ_y tends to a constant:

$$\rho_y = v_p T(1 + \omega^2 T^2)^{-1/2} \quad (5.60)$$

Where tidal excursions are not significant, ω may be interpreted as a characteristic frequency of shore-bound eddies. Although (5.58) is a rather arbitrary statistical model, constructed from simple functions in such a way as to satisfy asymptotic constraints, it does represent the key physical processes acting, a harmonic oscillation and a "damping" by random motions. Experience in turbulent diffusion theory has shown that the exact shape of the correlation function in (5.56) is much less important than its asymptotic properties, on account of the double integration involved.

Puff center movements in the longshore direction behave quite differently. Back and forth motions due to tides and large eddies are still present, but they are superimposed on wind- or pressure gradient-driven flow of not much smaller intensity than typical tidal oscillations. For periods of the order of 10 tidal cycles one usually finds the coastal current, with the tidal oscillation removed, points in the same direction, at a typical velocity of 10 cm sec $^{-1}$ or so. Then follows a current reversal and another moderately long period of non-tidal flow in the opposite longshore direction. Such behavior, at any rate, characterizes open coastal locations over Atlantic-type shelves. The long-term (Lagrangian) average longshore flow along the coast is usually also of significant magnitude (order 3 cm sec^{-1}) but this is not a very important quantity practically because "catastrophic" current reversal events remove waste or tracer fluids bodily from the coastal zone. In the language of theoretical hydrodynamics, Eulerian mean velocities (e.g., monthly means) may be quite unlike Lagrangian mean velocities.

To construct a simple model of such a complex process requires some drastic simplifications. The mean longshore velocity $\overline{w}_x = U$ will be supposed to be equal to the long-term Eulerian mean, subject however, to random catastrophic removal. Tidal and wind-driven longshore motions will be modelled as a random-walk process with a correlation function:

$$\overline{w_x'(t)w_x'\ (t+\tau)} = u_p^2 e^{-\tau/T} \tag{5.61}$$

where u_p is the root mean square longshore velocity due to tidal and wind action, and u_pT a typical longshore excursion associated with these two effects. The bodily removal of waste from the coastal zone through "catastrophic" events will be modelled by a random-death process, similar to radioactive decay, assuming that the probability per unit time of puff center disappearance is constant. This introduces the factor e^{-kt} into the puff center probability distribution, where k is now the reciprocal time constant of decay or k^{-1} is a typical period between catastrophic events.

Integration of (5.56) and (5.61) substituted yields the standard deviation of excursions along the x-axis:

$$\rho_x^2 = 2u_p^2 T[t - T\ (1 - e^{-t/T})] \tag{5.62}$$

At short times this satisfies (5.57), while at long times it becomes

$$\rho_x = u_p T\ (\frac{t}{T} - 1)^{1/2} \tag{5.63}$$

so that the long-term longshore excursion continues to increase with the square root of time. This behavior is significant only for periods of order k^{-1}, the characteristic period between current reversals.

Because random displacements and randomly occurring events play an important role in the aggregate picture of puff center behavior, a Gaussian model of puff center distribution seems a reasonable theoretical tool to employ. With release supposed to take place a distance a from shore, continuity is satisfied by a mirror image term (mirrored about the coast). The space integral of $P(\underline{x}, t)$ is then unity if the decay-term is set equal to zero; otherwise it decays as e^{-kt}. The resultant probability density function of puff center position is

$$P=\frac{e^{-kt}}{2\pi\rho_x\rho_y}\exp[-\frac{(x-Ut)^2}{2\rho_x^2}]\cdot\left\{\exp[-\frac{(y-a)^2}{2\rho_y^2}]+\exp[-\frac{(y+a)^2}{2\rho_y^2}]\right\} \tag{5.64}$$

with ρ_x, ρ_y as specified before in (5.59) and (5.62).

As pointed out above, a meandering plume causes episodic "fumigation" of a given fixed point by whatever waste it carries, the concentration being negligible for much of the time, but relatively high during fumigation episodes. The fraction of time γ (intermittency factor) for which a plume is close enough to affect concentrations at a given fixed point is thus a practically important parameter. Especially at larger distances from the source, where γ is low, the long-term <u>mean</u> concentration one calculates from a classical plume model has little to do with the hazard or nuisance the waste plume may be responsible for. On the other hand, an estimate of γ , and information on what concentration may be observable within a plume, when present, gives one a sound basis of judging the waste discharge's local impact.

The fraction of time γ for which a plume is "present" may be more precisely defined as that fraction of time for which plume center is within vector $\underset{\sim}{b}$ of $\underset{\sim}{x}$, where $|\underset{\sim}{b}|$ is the expected half-width of the plume in this location. This is clearly also the probability of finding the plume within $\pm\, \underset{\sim}{b}$ of $\underset{\sim}{x}$, obtainable by integrating the distribution $\Pi(\underset{\sim}{p},\underset{\sim}{x})$. For <u>slender</u> plumes, for which $\Pi(\underset{\sim}{p},\underset{\sim}{x})$ varies negligibly from one edge of the plume to the other, the intermittency factor is therefore

$$\gamma = 2b\Pi\,(0,\underset{\sim}{x}) \tag{5.65}$$

This may now be calculated using (5.52) and (5.64) assigning a reasonable value to V_p, and estimating $b(\underset{\sim}{x})$.

The velocity V_p is typical instantaneous plume transport velocity, which is mostly determined by tidal- and wind-driven motions, its order of magnitude being thus 30 cm sec^{-1}, similar for an entire coastal zone of interest. A constant value of V_p of this order should realistically reflect the physical effect described by V_p, the stretching out of waste material along the axis of an instantaneously observable (<u>not</u> mean) plume.

It is more difficult to prescribe a rule for calculating $b(\underset{\sim}{x})$, because plume width depends on the typical length of time a puff takes to travel from the source to point $\underset{\sim}{x}$. Close to the source, $b \cong b_o$, the initial half-width, because plume elements only grow slowly after initial mixing. For a large source, $b = b_o$ is a realistic prescription for travel times that are as long as a tidal cycle. Beyond that, it is necessary to estimate how long a typical plume element takes to reach a distant point x.

For travel times long compared to a tidal cycle it is reasonable to represent puff displacements as a random walk process, for which one may write $|\underset{\sim}{x}| = \sqrt{2K_r t}$, where K_r is an effective diffusivity of such random walk, t travel time. Plume half-width at this time is $b = 2\sigma_y$ or $b = 2\sqrt{2K_y t}$ with K_y a lateral plume diffusivity, which is much less than K_r. Hence $b = 2\alpha\,|\underset{\sim}{x}|$, where $\alpha = \sqrt{K_y/K_r}$, a factor small compared to unity. A simple interpolation formula between nearby points (where $b = b_o$) and distant points is then

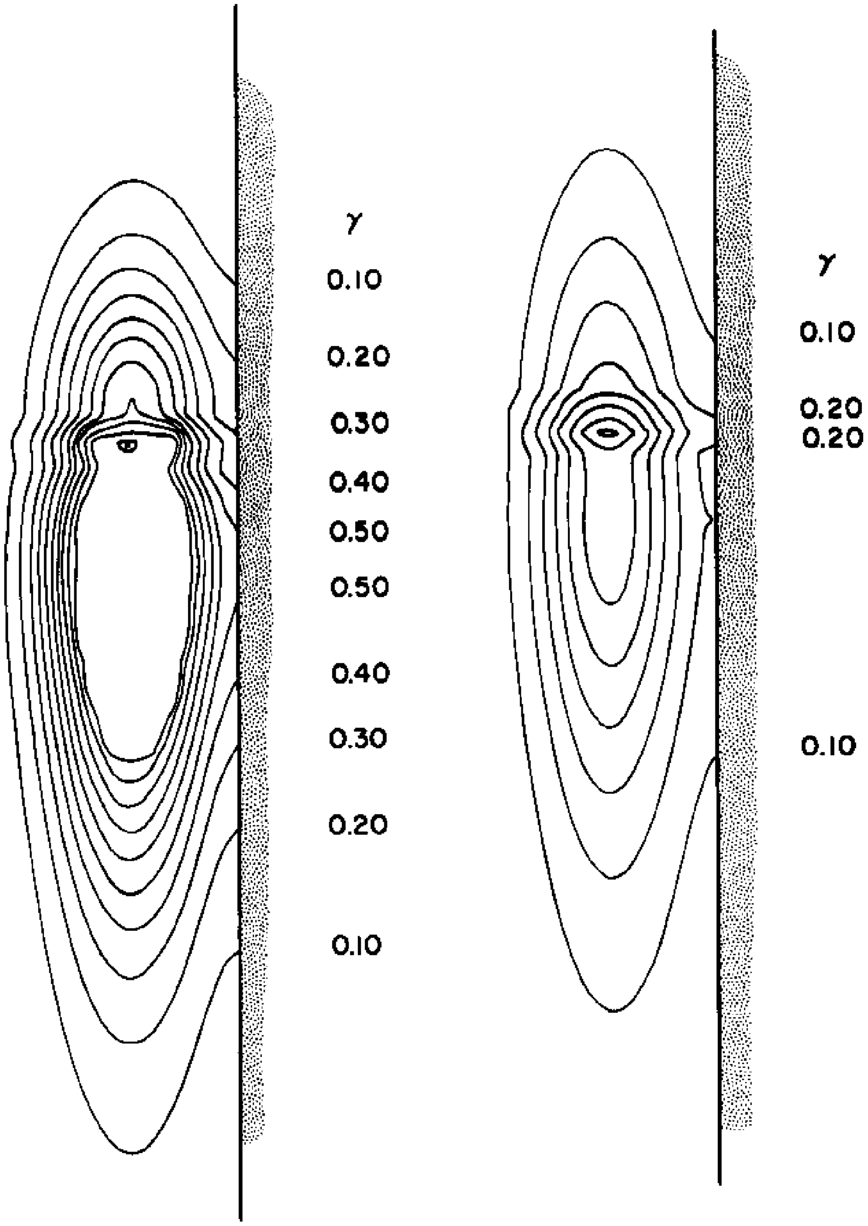
$$b^2 = b_o^2 + 4\,\alpha^2[x^2 + (y-a)^2] \qquad (5.66)$$

In terms of previously introduced quantities one may estimate $K_r = u_p^2 T$, which is typically at least a thousand times greater than K_y. A realistic set of quantitative parameters is, for example

frictional decay time, T	10^5 sec
renewal time, k^{-1}	4.10^5 sec
plume transport velocity, V_p	30 cm sec^{-1}
longshore mean velocity, U	5 cm sec^{-1}
rms longshore velocity, u_p	20 cm sec^{-1}
rms cross shore velocity, v_p	10 cm sec^{-1}
tidal frequency,	$1.4 \times 10^{-4} sec^{-1}$
initial plume width, b_o	5×10^4 cm
lateral eddy mixing coefficient, K_y	10^4 cm^2 sec^{-1}
source distance from shore, a	2×10^5cm

Writing $K_y/u_p^2 T$ for α^2, this quantity becomes 2.5×10^{-4}. The calculated distribution of the intermittency factor γ for these values of the parameters is shown in Figure 5.16. Changing the source

Figure 5.16 Typical appearance of constant intermittency factor contours for a source placed relatively close to the shore. A large piece of coastline is affected by the waste plume for a substantial fraction of the time.



distance to shore to 5 km (from 2 km) results in a γ-distribution displayed in Figure 5.17. The effect on shore fumigation is seen to be considerable.

Although the distribution of the intermittency factor γ by itself is a practically useful guideline regarding the hazard or nuisance that may be experienced with some waste discharge, the full benefit of the statistical approach is realized only if also the probability is estimated that some threshold concentration is exceeded at locations of interest, e.g., along the coastline.

Returning to the conceptual experiment which led to the definition Π (p, x), consider again plume cross sections in planes passing through the fixed point $\underset{\sim}{x}$. If a sufficient number of plume cross sections have been traversed with an instrument recording the instantaneous waste concentration N, a population of these is available at given values of the plume center position $\underset{\sim}{p}$, from which a probability distribution Ω (n, $\underset{\sim}{p}$, y, x) may be determined, such that Ω is the probability of the observed concentration N being greater than n, at a distance y from plume center $\underset{\sim}{p}$. At the fixed point $\underset{\sim}{x}$ itself, the probability of N being greater than some prescribed value n depends on Ω <u>and</u> the probability of finding a plume center at $\underset{\sim}{p}$:

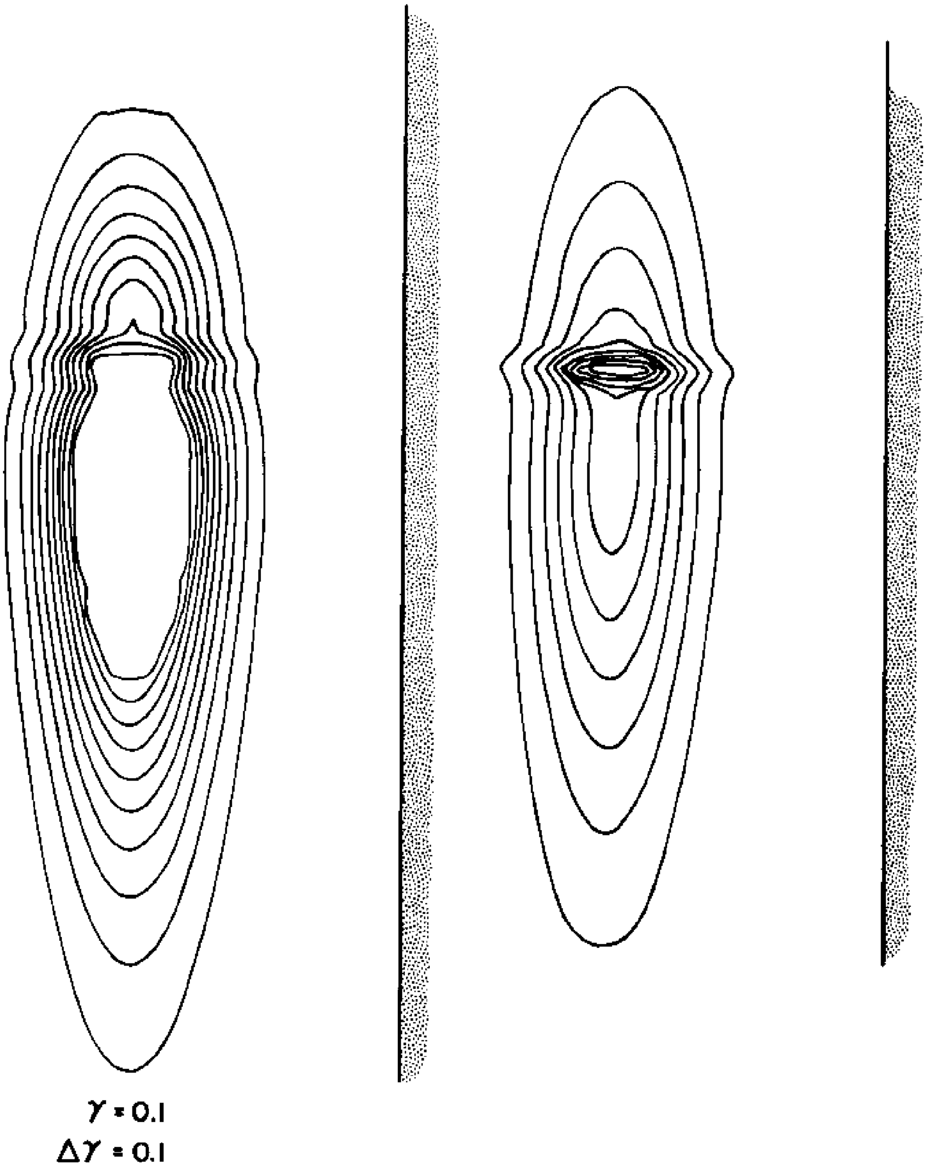
$$W(n,\underset{\sim}{x}) = \int \Omega(n,\underset{\sim}{p},y = -|\underset{\sim}{p}|,x)\ \Pi(\underset{\sim}{p},\underset{\sim}{x})d\underset{\sim}{p} \tag{5.67}$$

This expression is useful to the extent that a reasonably simple idealization of Ω may be found. Diffusion experiments usually show sharp instantaneous boundaries between tracer or waste and ambient fluid. The irregularly occurring peaks in the concentration cross sections are sometimes near the center, sometimes near the fringes of the plume. It is reasonable to idealize these observations into the hypothesis that the probability Ω is constant "within" a plume, zero without, for any finite n (i.e., the probability of finding any tracer outside is zero). Under these circumstances Ω is not a function of y, except insofar that at $|y| > b$ it becomes zero.

Supposing also that plumes are slender, and that neither Ω nor Π change significantly within one plume-width, (5.67) reduces to

$$\begin{aligned} W(n,\underset{\sim}{x}) &= \Omega(n,\underset{\sim}{x}) \int \Pi(o,\ \underset{\sim}{x})d\underset{\sim}{p} = \\ &= 2b\Pi(o,\underset{\sim}{x})\ \Omega(n,\underset{\sim}{x}) = \gamma\Omega(n,\underset{\sim}{x}) \end{aligned} \tag{5.68}$$

Figure 5.17 As the previous figure, but for a source placed sufficiently far offshore not to affect the shoreline very often.



where γ is again the intermittency factor discussed in the previous section. The physical interpretation of this result is that the probability of finding a concentration in excess of a specified threshold n at a fixed point x is the intermittency factor times the (conditional) probability of finding the same concentration, provided that the plume is present.

The concentration distributions "within" a plume are reasonably accurately described by a log-normal function (Csanady, 1973):

$$\Omega = \frac{1}{2} \{1 - \mathrm{erf} (\frac{\ln (n/m)}{\sqrt{2}\ \sigma})\} \tag{5.69}$$

where m is median concentration and σ is the logarithmic standard deviation. This latter is a measure of the patchiness of a plume and its value for large clouds may be expected to be low, $\sigma = 0.1$ or less. The median concentration is related to the mean χ by

$$m = \chi e^{-\sigma^2/2} \tag{5.70}$$

For small values of σ the mean and median are the same for all practical purposes. The mean concentration χ is related to the initial concentration χ_i and plume width by

$$b_o \chi_i V_{pi} = b\chi V_p \tag{5.71}$$

With the aid of such relationships it is possible to calculate contours of constant probability W (say, 0.1) for exceeding some threshold concentration (say 1/10 of the initial concentration). In the neighborhood of the source, with $V_{pi} \cong V_p$ and $b \cong b_o$, χ is not substantially different from χ_i, hence Ω is near unity for $n << \chi_i$. There the contours of W coincide with the contours of the intermittency factor γ. In the far field also the drop in concentration due to mixing and chemical/biological decay affect W = constant contours, although in most practically important situations it appears that λ remains the dominant influence.

CONCLUSIONS

The modelling part of this section could be continued by considering other practical problems such as the time-dependent one of concentration buildup during stagnant periods, or the effects of particulate deposition and resuspension over wider areas. These are, however, classical problems which may be treated with the aid of the diffusion equation so that their discussion can be dispensed with in a chapter which has already exceeded its length limitation. A few general conclusions affecting the choice of strategy in disposing of municipal wastewaters, which arise from the above discussion of models, should on the other hand be emphasized.

From a physical point of view, the "assimilative" capacity of the ocean for municipal wastewaters translates into "dispersive" capacity. To dispose of the wastewaters of a large metropolitan area, one, rather expensive, method of dispersal would be to build many outfalls of small discharge, dispersed along shore and offshore so as to produce "forced" dispersal. If, instead, one builds one or two outfalls of large discharge, one relies on the natural dispersive capacity of the coastal ocean to do an equivalent job. The discussion of models above has shown the limitations of such an approach, which may be summarized as follows.

1. Shallow continental shelves of the Atlantic-type have a limited ability to flush away large quantities of municipal wastewaters. The situation is potentially better on Pacific-type shelves, provided that other problems (e.g., coastal upwelling) do not complicate matters. Where the receiving waters are of order 10 m depth, the limited flushing ability of the coastal ocean effectively limits the size of the outfall that can safely be accommodated.

2. The environmental impact experienced at the coast drops dramatically when the outfall is moved beyond the range of cross-shore motions due to eddies, tidal oscillations and upwelling-downwelling cycles. Along an open coastline of the Atlantic-type, an outfall distance from shore greater than about 5 km typically yields a much reduced probability of encountering significant waste concentration at the shore. On the other hand, increasing the offshore distance of the release point beyond 10 km brings little further improvement. Thus, for example, barging of sewage sludge to 100 km instead of 10 km from shore may not be cost effective. The main difference is between a 1-2 km long outfall and piping or barging of wastes to just 10 km from the coast.

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6

Geochemistry of Municipal Waste in Coastal Waters

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INTRODUCTION

As we mine primary ores at an increasing rate, as we synthesize more exotic compounds in greater quantities, as we produce expanding heaps of waste, as we reroute rivers through our faucets, we are becoming an important and sometimes a dominant agent of the global geochemical cycle. Disposal of municipal wastes is a key process in this anthropic part of the elemental fluxes, for a municipal sewage system is a giant funnel which brings in one place at each instant the end products of much of the dispersed consumptive activities of a whole community. In addition to its net contribution to the flux of natural elements and to the exotic nature of some of its constituents, it is this increasingly prevalent concentration process that gives human waste its unique position in the elemental economy of the planet.

Lest we should be too conceited, even in our ability to pollute, the laws of nature must have their way. Ultimately all elements in the sea must be controlled by the biogeochemical processes that govern their oceanic cycles. The question posed by the practice of municipal waste disposal into the ocean is then principally one of rates: are natural biogeochemical processes in the oceans fast enough to "assimilate" human waste? Are the dispersive and degrading mechanisms suitably rapid to maintain the concentration of all potential toxicants at acceptably low concentrations? Are the ecological processes sufficiently dynamic to buffer the impact of concentrated elemental loads, to adapt to the presence of new chemical constituents? These questions can be asked on various geographical scales, from local to global, and on various time scales from hours to centuries.

On the whole we are still quite ignorant of the functioning of oceanic systems; we do not comprehend sufficiently many of the processes that govern the fate of waste constituents; we cannot answer some of our basic questions. Yet, we are in the process of learning a great deal. This chapter is an attempt to organize some of the key known facts on the biogeochemistry of waste in coastal waters, to develop a conceptual framework for research and decision making. There are on the order of ten thousand chemical constituents in wastewaters, only about a hundred of which we know anything about. It appears that our sole hope is to develop general principles to provide, in the long run, some of the necessary answers.

Municipal wastewaters are a varied lot. Although domestic sewage has a fairly uniform composition throughout the country, the industrial wastes often added to it do not. Metal finishing plants contribute high concentrations of some metallic compounds; chemical manufacturing processes release highly specific sets of organic constituents. In cities with combined sewers, urban storm water runoff, with its own characteristic composition, is included in the municipal sewer system. Also varied are the levels of treatment and the methods of disposal. A few cities still dispose of raw sewage while others have added tertiary treatment to their systems. Efficient outfalls with diffusers are used in some places to carry the effluents far offshore and dilute them effectively; in many others, wastewaters are released close to shore with inefficient mixing. Barge dumping of sludge is prevalent in many areas. Just as diverse are the hydrodynamic and hydrological characteristics of the receiving waters: confined bays, harbors and estuaries in some places, open coastline in others; rapidly increasing water depth offshore on one coast, extended continental margins on the other. Current and tidal regimes which vary with time and location result in widely different waste dilution and transport processes.

All this variability in effluent composition, in initial mixing, and in short- and long-term transport processes affects to a large degree the fate of the waste constituents. At this point, it would be a hopeless task to attempt to cover all combinations of these, to consider the problem of disposal of all types of municipal wastes in all types of receiving waters. By a fortune of sorts, one is quite limited by the available information. We have made no attempt in this chapter to be exhaustive; rather we have concentrated on those systems for which extensive data were available. In this way it is hoped that a self-coherent picture will be obtained from which one may draw information to be applied to other situations. However, major caveats are clearly in order: 1. the available information concerns almost exclusively the major urban centers; in some instances it may be of little relevance to small- or medium-size communities; 2. The Southern California Bight--which is by no means typical--has been the locus of the most intensive and extensive research efforts on the geochemistry of waste. As such it provided the data for much of this chapter. (For convenient reference on names and locations, a map of the major Southern California outfalls is provided in Figure 6.1.) One should keep in mind these demographic and geographical biases.

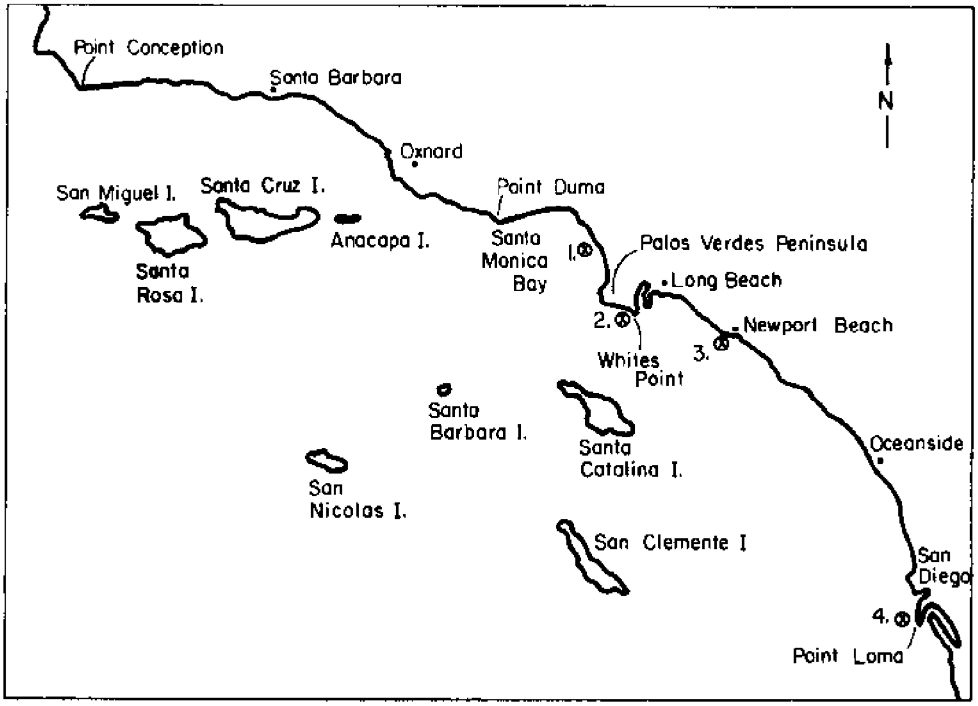
This chapter is organized in five sections. The first one is a review of the basic principles that govern the major chemical variables in waste fields (e.g., pH and redox). This section is mostly didactic and can be skipped by those more interested in results than in basic principles.

In the second section the properties of waste particles and their sedimentation in the water column are discussed. With the notable exception of nutrients, the largest fractions of most types of waste constituents (trace metals and organics) are associated with the particulate phase. Hence, the fate of particles determines to a very large extent that of the waste constituents. Through a reinterpretation of available laboratory data, it is argued that the dominant process controlling the sedimentation rate of particles in seawater is coagulation among particles. A dynamic view of particle suspensions in seawater is projected in which smaller particles continuously aggregate into larger ones and large particles are rapidly eliminated from the water column by settling to the sediments.

The third section deals with nutrients (N, P, Si), principally nitrogen. It is shown how the fate of nitrogen is governed mostly through mixing and biological processes, primarily phytoplankton uptake. Natural biological processes normally keep this "limiting nutrient" at very low concentrations in coastal waters and recycle it rapidly. As a result, even though the massive input of nitrogen from municipal waste sources may be significant compared to the natural soluble pools, its net flux is normally small compared to the natural regeneration flux. The productivity of the water being controlled primarily

Figure 6.1 Major municipal waste outfalls in the Southern California Bight.

1. Los Angeles City Hyperion outfalls
2. Los Angeles County Sanitation District outfalls (LACSD)
3. Orange County outfalls (OCSD)
4. San Diego City outfall at Point Loma



by the turnover rate of nitrogen, not by its concentration, the net impact of the anthropogenic nitrogen flux is usually small.

The fourth section, on trace metals, has a more chemical slant. In addition to transport processes, the major factors in determining the fate of metals are the chemical transformations associated with the change from the reduced waste environment to well-oxidized seawater. In the water column, metal enrichments are quite localized and usually limited to the particulate fraction. Anoxic benthic areas which sometimes develop in the vicinity of waste discharge points are shown to be quasi-conservative sinks for the (usually small) fraction of metals that reach them. On a regional basis, increases in metal concentrations in the water column due to sewage outfalls are so small that they are difficult to detect and separate from natural fluctuations in background concentrations. As a result, dramatic ecological effects are neither seen nor expected (except for particular organometallic complexes -- e.g., methyl-mercury-- that are peculiarly toxic and concentrate up the food chain as some of the other trace organics). Nonetheless, if trace metals naturally play a role in controlling planktonic species assemblage in coastal waters--as has been hypothesized--it may be that small metal enrichments resulting from waste discharges have a subtle but important impact in determining the nature of the local flora and fauna.

The fifth and longest section is devoted to organic constituents. These present the major conceptual difficulty given their great number and diversity. After reviewing briefly the composition of the organic matter in municipal wastewater, this section emphasizes the relative importance of the physical, chemical and biological processes in determining the fate of the various organic constituents in oceanic waters. The relative rates of evaporation, hydrolysis, oxidation, microbial degradation and photochemical transformations control the residence time of waste organics in the oceanic environment. The accumulation of organics by organisms is largely correlated with their partition coefficients between water and organic solvents. To illustrate these general principles, a few families of compounds covering a wide range of properties are chosen as specific case studies. There are, of course, many documented examples of ecological damage caused by the disposal of waste organics in coastal waters.

No matter how purely objective and scientific the intent, value judgments cannot be eliminated from a presentation like that of this chapter. Our personal opinion, that trace organic compounds present the greatest environmental hazard associated with municipal waste disposal in coastal waters, is plainly evident, if only in the relative lengths of the various sections. As we see it, the hypothetical compound we should worry about most is the one which escapes control due to its diffuse sources and low concentration, which is refractory to degradation and accumulates in some part of the biosphere owing to its physicochemical properties, and whose biological effect may only become apparent after years of incubation. Of course there may not be any such compound but certainly we should focus much of our attention on the long-term fate and biological effects of synthetic organics in an environment into which they are introduced for the first time.

MAJOR VARIABLES: GENERAL CHEMICAL PRINCIPLES

Upon entering the ocean, waste constituents are subjected to a number of dramatic changes in their chemical environment: they are diluted; the total salt content of their medium increases; they react with major seawater ions; the ambient pH and redox conditions become dominated by the chemistry of the receiving waters. In this section, the fundamental principles that govern these changes in major chemical variables are briefly reviewed, one by one. (A good general reference providing a detailed presentation of these principles is the book by Stumm and Morgan, 1970 and 1981, and that by Morel, 1983.) As a major illustration, an equilibrium model of sewage is sequentially subjected to these various changes: dilution, increase in ionic strength, introduction of major seawater ions, decrease in pH, and last but not least, oxidation (Table 6.1, Parts 1-6). Obviously, in reality such changes occur more or less simultaneously. The organization of this section is thus didactic, not chronological; its goal is to outline basic concepts, not to describe historical events.

Table 6.1 The Effects of Major Variables on a Model Sewage

Chemical equilibrium calculations for a model sewage system subjected sequentially to 125-fold dilution, increase in ionic strength to 0.5 M, introduction of major seawater ions, increase in pH to 8.2 and oxidation to pE = 12.0. At each step a complete equilibrium calculation is performed with the program MINEQL2 (Westall et al., 1976). Concentrations are given as pX = -log (molar conc. of X). The initial composition of the sewage is

as follows: $pCa_T = 2.75$; $p(CO_3)_T = 2.0$; $p(SO_4)_T = 2.3$; $pCu_T = 5.5$; $pFe_T = 4.90$; $pAg_T = 7.0$; $pCd_T = 6.7$; $pNi_T = 5.5$; $pPb_T = 6.8$; $pZn_T = 5.4$; $pBa_T = 5.0$; $pMg_T = 3.0$; $pCl_T = 1.8$; $p(NH_3)_T = 3.0$; $p(PO_4)_T = 4.2$; $pHg_T = 8.1$; $pMn_T = 6.7$; $pCr_T = 5.4$; $p(CN)_T = 5.3$; pH = 7.7; pE = -3.26.

Table 6.1 The Effects of Major Variables on a Model Sewage

1. UNDILUTED SEWAGE: Ionic Strength 0.01M; No Seawater Ion; pH = 7.7; No Oxidation

			-log(Conc)	Major Species	%
Nutrients:	NH_3	Total	3.00	NH_3	4.8
		Free	4.32	NH_4^+	95.2
		Soluble	3.00		
	PO_4	Total	4.20	$Ca_5(PO_4)_3(OH)(s)$	99.1
		Free	10.58		
		Soluble	6.25		
Trace Metals:	Cd	Total	6.70	CdS(s)	100
		Free	14.58		
		Soluble	14.43		
	Cr	Total	5.40	$Cr(OH)_2^+$	3.2
		Free	12.94	$Cr(OH)_4^-$	12.2
		Soluble	6.21	$Cr(OH)_3(s)$	84.6
	Cu	Total	5.50	CuS(s)	100
		Free	24.92		
		Soluble	9.19	[Cu(I)]	
	Fe	Total	4.90	Fe^{2+}	76.4
		Free	7.11	$FeSO_4$	13.1
		Soluble	4.90	$FeCl^+$	4.1
				$FeOH^+$	6.3
	Hg	Total	8.10	HgS(s)	100
		Free	40.48		
		Soluble	12.14		
	Ni	Total	5.50	$Ni(CN)_4^{2-}$	19.7
		Free	9.68	NiS(s)	80.3
		Soluble	6.21		
	Pb	Total	6.80	PbS(s)	100
		Free	14.68		
		Soluble	12.00		
	Zn	Total	5.40	ZnS(s)	100
		Free	9.78		
		Soluble	10.36		

Table 6.1 The Effects of Major Variables on a Model Sewage

2. EFFECT OF DILUTION: Sewage/Seawater = 1/125

			-log(Conc)	Major Species	%
Nutrients:	NH_3	Total	5.10	NH_3	4.8
		Free	5.32	NH_4^+	95.2
		Soluble	5.10		
	PO_4	Total	6.30	HPO_4^{2-}	82.4
		Free	10.63	$H_2PO_4^-$	17.5
		Soluble	6.30		
Trace Metals:	Cd	Total	8.80	CdS(s)	100
		Free	13.30		
		Soluble	13.29		
	Cr	Total	7.50	$Cr(OH)_2^+$	20.6
		Free	14.23	$Cr(OH)_4^-$	79.2
		Soluble	7.50		
	Cu	Total	7.60	CuS(s)	100
		Free	23.80		
		Soluble	11.30 [Cu(I)]		
	Fe	Total	7.00	Fe^{2+}	92.1
		Free	7.04	$FeOH^+$	7.6
		Soluble	7.00		
	Hg	Total	10.20	HgS(s)	100
		Free	39.20		
		Soluble	13.26		
	Ni	Total	7.60	NI^{2+}	16.0
		Free	8.40	$NiOH^+$	1.0
		Soluble	8.37	NiS(s)	83.0
	Pb	Total	8.90	PbS(s)	100
		Free	13.40		
		Soluble	12.60		
	Zn	Total	7.50	Zn^{2+}	10.1
		Free	8.50	ZnS(s)	89.8
		Soluble	8.50		

Table 6.1 The Effects of Major Variables on a Model Sewage

3. EFFECT OF IONIC STRENGTH: Dilution 1/125, Ionic Strength 0.5 M.

			-log(Conc)	Major Species	%
Nutrients:	NH_3	Total	5.10	NH_3	4.8
		Free	6.42	NH_4^+	95.2
		Soluble	5.10		
	Po_4	Total	6.30	HPO_4^{2-}	89.4
		Free	10.21	$H_2PO_4^-$	10.5
		Soluble	6.30		
Trace Metals:	Cd	Total	8.80	CdS(s)	100
		Free	13.24		
		Soluble	13.24		
	Cr	Total	7.50	$Cr(OH)_2^+$	16.2
		Free	13.95	$Cr(OH)_4^{2-}$	83.6
		Soluble	7.50		
	Cu	Total	7.60	CuS(s)	100
		Free	23.74		
		Soluble	11.30 [Cu(I)]		
	Fe	Total	7.00	Fe^{2+}	94.2
		Free	7.03	$FeOH^+$	5.8
		Soluble	7.00		
	Hg	Total	10.20	HgS(s)	99.7
		Free	39.14		
		Soluble	12.80		
	Ni	Total	7.60	Ni^{2+}	18.1
		Free	8.34	NiS(s)	81.0
		Soluble	8.32		
	Pb	Total	8.90	PbS(s)	100
		Free	13.34		
		Soluble	12.70		
	Zn	Total	7.50	Zn^{2+}	11.4
		Free	8.44	ZnS(s)	88.5
		Soluble	8.44		

Table 6.1 The Effects of Major Variables on a Model Sewage

4. EFFECT OF MAJOR SEAWATER IONS: Dilution 1/125, I = 0.5 M, Major Seawater Ions

			-log(Conc)	Major Species	%
Nutrients:	NH_3	Total	5.10	NH_3	4.8
		Free	6.42	NH_4^+	95.0
		Soluble	5.10		
	Po_4	Total	6.30	$MgHPO_4$	3.2
		Free	11.61	HPO_4^{2-}	3.5
		Soluble	7.48	$Ca_5(PO_4)_3OH(s)$	94.0
Trace Metals:	Cd	Total	8.80	CdS(s)	100
		Free	13.37		
		Soluble	11.84		
	Cr	Total	7.50	$Cr(OH)_2^+$	16.1
		Free	13.95	$Cr(OH)_4^-$	83.6
		Soluble	7.50		
	Cu	Total	7.60	CuS(s)	100
		Free	23.87		
		Soluble	11.30 [Cu(I)]		
	Fe	Total	7.00	Fe^{2+}	42.7
		Free	7.37	$FeSO_4$	10.9
		Soluble	7.00	$FeCl^+$	43.8
				$FeOH^+$	2.6
	Hg	Total	10.20	HgS(s)	100
		Free	39.27		
		Soluble	12.67		
	Ni	Total	7.60	NI^{2+}	13.5
		Free	8.47	$NiSO_4$	3.4
		Soluble	8.24	$NiCl^+$	5.5
				NiS(s)	76.9
	Pb	Total	8.90	PbS(s)	99.5
		Free	13.47		
		Soluble	11.18		
	Zn	Total	7.50	Zn^{2+}	8.5
		Free	8.57	$ZnSO_4$	2.2
		Soluble	3.46	ZnS(s)	88.7

Table 6.1 The Effects of Major Variables on a Model Sewage

5. EFFECT OF pH: Dilution 1/125, I = 0.5 M,
Major Seawater Ions, pH = 8.2

			-log(Conc)	Major Species	%
Nutrients:	NH_3	Total	5.10	NH_3	13.6
		Free	5.97	NH_4^+	85.7
		Soluble	5.10		
	PO_4	Total	6.30	$Ca_5(PO_4)_3OH(s)$	100
		Free	11.71		
		Soluble	8.08		
Trace Metals:	Cd	Total	8.80	CdS(s)	99.9
		Free	13.49		
		Soluble	11.98		
	Cr	Total	7.50	$Cr(OH)_2^+$	1.9
		Free	15.88	$Cr(OH)_4^-$	98.1
		Soluble	7.50		
	Cu	Total	7.60	CuS(s)	100
		Free	23.99		
		Soluble	11.30	[Cu(I)]	
	Fe	Total	7.00	Fe^{2+}	40.4
		Free	7.39	$FeSO_4$	10.3
		Soluble	7.00	$FeCl^+$	41.5
				$FeOH^+$	7.8
	Hg	Total	10.20	HgS(s)	99.7
		Free	39.29		
		Soluble	12.65		
	Ni	Total	7.60	Ni^{2+}	10.0
		Free	8.59	$NiSO_4$	2.5
		Soluble	8.34	$NiCl^+$	4.1
				$NiOH^+$	1.5
				NiS(s)	81.9
	Pb	Total	8.90	PbS(S)	99.6
		Free	13.59		
		Soluble	11.30		
	Zn	Total	7.50	Zn^{2+}	6.5
		Free	8.69	$ZnSO_4$	1.7
		Soluble	8.59	ZnS(s)	91.8

Table 6.1 The Effects of Major Variables on a Model Sewage

6. EFFECT OF OXIDATION: Dilution: 1/125, I = 0.5 M, Major Seawater Ions, pH = 8.2, pE = 12.00

			-log(Conc)	Major Species	%
Nutrients:	NH_3	Total	5.10	NH_3	13.6
		Free	5.97	NH_4^+	85.6
		Soluble	5.10		
	PO_4	Total	6.30		
		Free	11.71	$Ca_5(PO_4)_3OH(s)$	100
		Soluble	8.08		
Trace Metals:	Cd	Total	8.80	Cd^{2+}	2.9
		Free	10.33	$CdCl_x$	96.0
		Soluble	8.80		
	Cr	Total	7.50	CrO_4^{2-}	100
		Free	7.50		
		Soluble	7.50		
	Cu	Total	7.60	Cu^{2+}	12.9
		Free	8.49	$Cu(CO_3)_x$	51.4
		Soluble	7.60	$Cu(Cl)_x$	7.7
				$Cu(NH_3)_x$	12.2
	Fe	Total	7.00	$Fe(OH)_3(s)$	100
		Free	26.66		
		Soluble	9.64		
	Hg	Total	10.20	$Hg(CN)_2$	100
		Free	28.40		
		Soluble	10.20		
	Ni	Total	7.60	NI^{2+}	54.1
		Free	7.87	$NiSO_4$	13.9
		Soluble	7.60	$NiCl^+$	22.1
				$Ni(CN)_4^{2-}$	1.6
				$NiOH^+$	8.3
	Pb	Total	8.90	$PbCO_3$	9.8
		Free	11.20	$PbCl^+$	85.8
		Soluble	8.90	$PbOH^+$	3.1
	Zn	Total	7.50	Zn^{2+}	74.3
		Free	7.63	$ZnSO_4$	19.1
		Soluble	7.50	$ZnCl_x$	4.4

Dilution Effects

Ideally, the equilibrium concentrations of reacting chemical species are related by mass law equations; e.g.,

$$Ni^{2+} + 4\ CN^- \rightleftarrows Ni\ (CN)_4{}^{2-}$$

$$K = \frac{(Ni(CN)_4{}^{2-})}{(Ni^{2+})\ (CN^-)^4}$$

or,

$$CuS(s) \rightleftarrows Cu^{2+} + S^{2-}$$

$$K_s = (Cu^{2+})\ (S^{2-})$$

where the constants K and K_s are the equilibrium constants of the corresponding reactions. Given the appropriate analytical information and a set of equilibrium constants, the equilibrium composition of any complex mixture can then be computed, in principle. Table 6.1 (Part 1) shows the results of such computation for a model sewage system resembling closely the final wastewater effluent at the Los Angeles city treatment plant.

As a result of the multiplicative nature of the governing mass law equations, significant changes in the speciation of sewage components may occur simply due to dilution effects. This is illustrated in Table 6.1 (Parts 1 & 2) which shows the variations in the chemical speciation of the components of the model sewage when it is diluted by a factor of 125, all other parameters being kept constant. Some solids such as $Cr(OH)_3$ and FeS dissolve as their solubility products are no longer satisfied; some complexes such as $Ni(CN)_4{}^{2-}$ dissociate as the reactant concentrations are reduced.

Ionic Strength Effects

While the mass law expressions described above are strictly applicable in very dilute solutions, they need to be considerably modified in aqueous systems of high salt content such as seawater. Long-range electrostatic interactions among ions become important in such systems and this is usually accounted for by replacing concentrations (X) by activities $\{X\}$, which are idealized quantities defined to verify strictly the mass law equations: e.g., :

$$^{a}K = \frac{\{Ni(CN)_4{}^{2-}\}}{\{Ni^{2+}\}\{CN^-\}^4}$$

$$^{a}K_s = \{Cu^{2+}\}\{S^{2-}\}$$

The activity of ions decreases as the total salt content of the solution increases-- the so-called ionic strength or non-ideal effect. (For the purpose of this discussion interactions among ions that depend partly on the chemical nature rather than exclusively on the electrical charge of ions are considered as ion pair formation--and discussed in the next section--whether or not identifiable ion pairs actually exist in solution.)

Besides its effect on the activities of solutes, the increase in background electrolyte concentration to which the sewage constituents are subjected affects the properties of suspended particles by reducing the domain of electrostatic influence of their surface charge. This "compression of the double layer" may be the most significant of the ionic strength effects when sewage or sludge is diluted in seawater. Adsorption properties are affected to some extent, but more importantly, interactions among particles are profoundly modified, resulting in new sedimentation characteristics of the suspended matter.

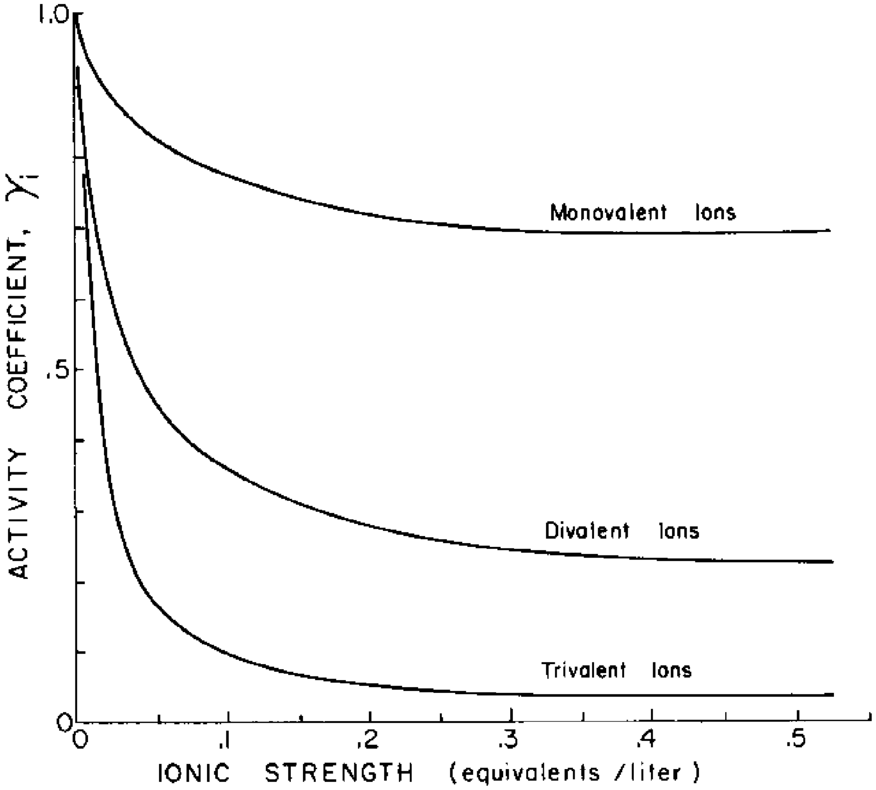
Ionic strength vs. salinity While thermodynamicists describe the concentration of background electrolyte as the ionic strength of the solution, oceanographers talk of salinity and/or chlorinity. Definitions for these quantities and relationships among them are given in Table 6.2.

Activity coefficients Activity coefficients are defined as the ratios of activities $\{X_i\}$ to concentrations (X_i):

$$\gamma_i = \frac{\{X_i\}}{(X_i)}$$

Figure 6.2 presents the variations of activity coefficents as a function of ionic strength for mono-, di- and trivalent ions. Note that, at the ionic strength of seawater, the activity coefficients are in a region of a broad minimum and that changes in ionic strength from 0.2 to 0.7 eq. l^{-1} have no measurable effects on ion activities. The important ionic

Figure 6.2 Activity coefficients as a function of ionic strength (Based on Davies' equation: Stumm and Morgan, 1970).



strength effects are thus fully developed as soon as a 1:1 mixture of wastewater with seawater is obtained; this is normally a matter of seconds. For all practical purposes, sewage plumes can then be considered to have the ionic strength (and the background electrolyte composition) of seawater.

Table 6.2

Ionic Strength:	$I = 1/2\ \Sigma_i\ Z_i^2\ C_i$	$-Z_i$ is the charge of ion i $-C_i$ is the concentration in moles per litre.
Chlorinity:	The mass in grams of silver necessary to precipitate all the chloride in 328.5233 grams of seawater in which bromide and iodide are replaced by chloride, all organic carbon is oxidized and carbonate has been converted to oxide.	
Salinity:	S = 1.80655 Cl	-Cl is the chlorinity in g/kg

Operational Equilibrium Constants To understand quantitatively the effect that the increase in ionic strength has on the chemistry of wastewater constituents, it is most convenient to consider operational equilibrium constants defined as the equilibrium concentration quotient; e.g., :

$$Ni^{2+} + 4\ CN^- \rightleftarrows Ni(CN)_4^{2-} \qquad {}^cK = \frac{(Ni(CN)_4^{2-})}{(Ni^{2+})\ (CN^-)^4}$$

$$CuS(s) \rightleftarrows Cu^{2+} + S^{2-} \qquad {}^cK_S = (Cu^{2+})\ (S^{2-})$$

Given that pH is usually defined and measured on the basis of the proton activity, mixed acidity constants are preferred to describe the acid base reactions, e.g., :

$$H^+ + HS^- \rightleftarrows H_2S \qquad {}^cK' = \frac{(H_2S)}{\{H^+\} \cdot (HS^-)}$$

Expressing concentrations as the ratio of activities and activity coefficients, the relationships between operational constants and the thermodynamic constants (defined as the equilibrium activity quotients) are readily obtained.

For the three examples above:

$$\mathrm{Ni(CN)_4^{2-}}: \qquad \frac{{}^{c}K}{{}^{a}K} = \frac{\gamma_{\mathrm{Ni}^{2+}} \cdot \gamma^{4}_{\mathrm{CN}^-}}{\gamma_{\mathrm{Ni(CN)}_4^{2-}}}$$

$$\mathrm{CuS(s)}: \qquad \frac{{}^{c}K_s}{{}^{a}K_s} = \frac{1}{\gamma_{\mathrm{Cu}^{2+}} \cdot \gamma_{\mathrm{S}^{2-}}}$$

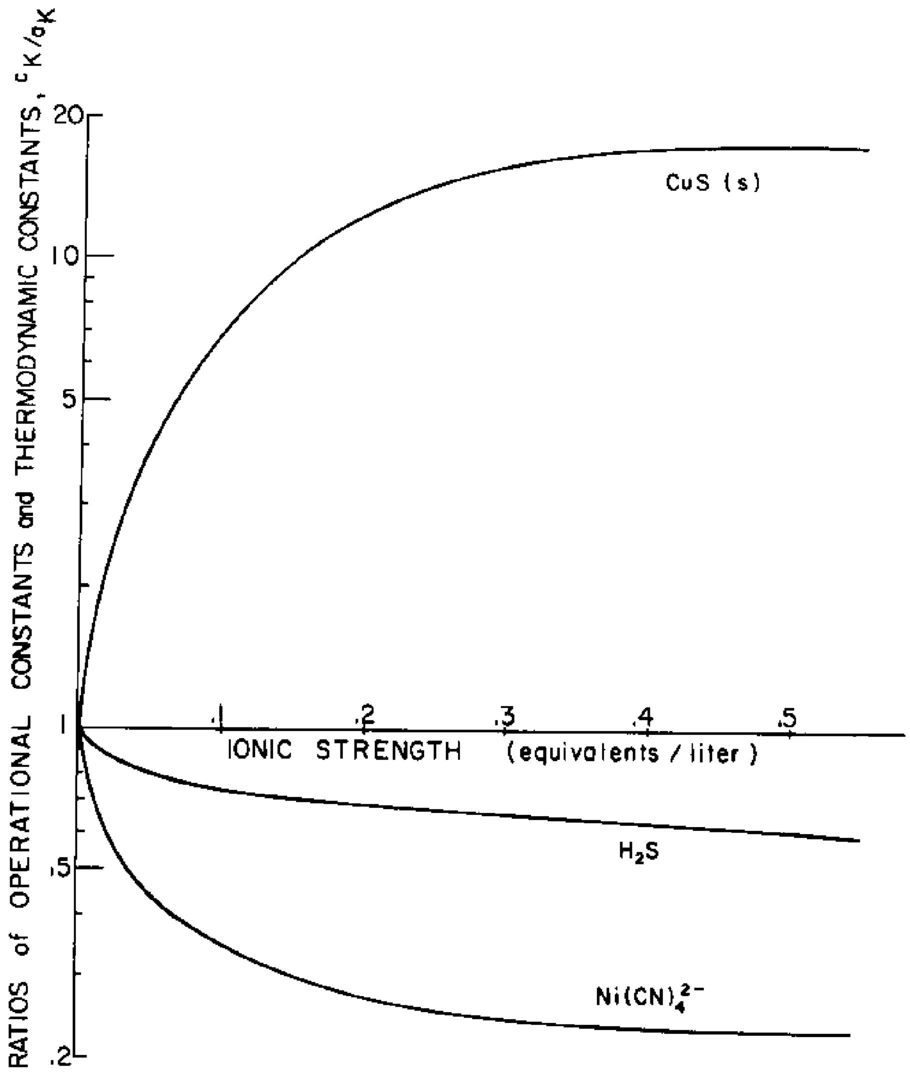
$$\frac{{}^{c}K'}{{}^{a}K} = \frac{\gamma_{\mathrm{HS}^-}}{\gamma_{\mathrm{H_2S}}}$$

Figure 6.3 shows the variations of these three ratios as a function of ionic strength. Note the large effective decrease in the formation constant for the tetracyano nickel complex as the ionic strength increases from the sewage to the seawater value; note also the large increase in the solubility of copper sulfide. It is important to realize, however, that the actual shift in equilibrium speciation cannot be assessed simply by examining changes in individual equilibrium constants since the shifts in all interacting reactions (such as the protonation of the ligand in the examples above) have to be considered simultaneously. Table 6.1 (Parts 2 & 3) shows the variations in metal and nutrient speciation when the ionic strength of the diluted model sewage is increased to that of seawater while maintaining all concentrations and the pH constant. The effects are modest, being mostly evidenced by small decreases in the free ion concentrations.

Particle double layer. The interactions among waste particles (e.g., coagulation) and those among waste particles and solutes (e.g., adsorption) are affected by changes in ionic strength as waste is diluted by seawater. By occupying space adjacent to a charged particle surface, counter ions neutralize to some degree the effect, or rather the extent, of the surface charge in the solution. This "electrical double layer" effect is conveniently measured by a distance that characterizes the decrease of the electrical potential from the solid interface to the bulk solution:

$$\text{(for small potentials):} \quad \Psi = \Psi_0 e^{-\kappa x}$$

Figure 6.3 Ratios of operational constants and thermodynamic constants (Based on Davies' equation: Stumm and Morgan, 1970).



where Ψ is the electrical potential at any distance x from the surface, Ψ_o is the surface potential and $1/\kappa$ is the so called "double layer thickness". Following classical Gouy Chapman theory, $(1/\kappa)$ is a unique function of the ionic strength:

$$\text{(for water at } 20^{o}\text{C)} \qquad 1/\kappa = \frac{2.8 \cdot 10^{-10}}{I}$$

where $(1/\kappa)$ is in meters and I in moles per liter. As sewage particles enter the ocean environment, their double layer thickness decreases from a few nanometers (nm) to about 0.4 nm. The effect that such compression of the double layer may have on decreasing the electrostatic repulsion between particles of like charge and consequently on destablilizing the suspension is rather intuitive and shall be discussed in the next section. Less intuitive is the possible effect on surface adsorption of ions.

Sewage particles are probably best approximated as having constant surface potentials determined by the pH of the solution. The effect of ionic strength on the specific adsorption of ions onto the surface can then be considered null in a first approximation, since the effective adsorption constants remain unchanged:

$$K_{ads} \approx K_{chem} \cdot \exp\left(\frac{ZF}{RT}\Psi_o\right)$$

where K_{chem} is the specific chemical adsorption constant, ZF is the charge change for the adsorption reaction (F is the Faraday constant), R is the gas constant and T is the absolute temperature. The diffuse adsorption in the Gouy layer will increase as the ionic strength and consequently the surface charge σ increases:

$$\sigma \simeq 7 \times 10^{-10}\kappa \cdot \Psi_o$$

(σ is in coulombs m^{-2}, κ in meters^{-1} and Ψ_o in volts). However, adsorption in the diffuse layer is usually unimportant compared to specific surface adsorption, and since it affects ions exclusively on the basis of their charge, the result is only a minute spatial rearrangement of the distribution of seawater electrolytes.

Competition with Major Seawater Ions

While they affect the chemistry of the diluted sewage unspecifically as an ionic strength effect, the major ions of seawater (See Table 6.3) also interact with sewage components through specific chemical interactions. Complexes (including ion pairs and other coordination compounds) are formed between the metals in the sewage and the chloride, sulfate bicarbonate and carbonate ions. At the same time the major cations of seawater, particularly calcium and magnesium, react with the sewage ligands including organics and surface reaction sites, resulting in a competition with the sewage cations. The general result of such interactions with the major seawater ions is a decrease in the degree of coordination among sewage constituents besides that caused by dilution or ionic strength effects. Individual metal ion activities may consequently decrease or increase depending on whether the complexation by seawater anions or the competition by seawater cations is the dominant process.

Table 6.3 Major Seawater Ions (Stumm and Morgan, 1970)

Ion	Seawater Concentration (M)
Na^+	0.47
K^+	1.0×10^{-2}
Mg^{2+}	5.4×10^{-3}
Ca^{2+}	1.0×10^{-2}
F^-	7×10^{-5}
Cl^-	0.55
SO_4^{2-}	3.8×10^{-2}

A good example of the first process is given by the formation of sulfate and chloride complexes of nickel (Table 6.1; Parts 3 & 4). As the chloride and sulfate concentrations increase to their seawater value, the soluble fraction of nickel increases markedly due to the formation of these complexes. This increase in solubility should be compared to that due to the ionic strength effect per se (Table 6.1; Parts 2 & 3).

Competition between the abundant seawater cations and the sewage trace metals for the same complexing ligands is difficult to quantify given the dearth of specific information regarding the nature and concentration of soluble organics in sewage. A qualitative analysis of this effect is obtained by considering model ligands ranging from weak complexing agents such as amino acids to strong chelating agents such as EDTA (ethylenediamine tetraacetic acid). Although computer calculations may be used to study this competition effect, a simple general formula can be obtained if the complexing ligands are assumed to be in excess of the trace metals.

Consider, for example, calcium, copper and a ligand Y as the components of interest. If the formation constant for CaY is sufficiently high to make it the major specie of the ligand in seawater, the mass law for the formation of the copper complex can be written:

$$(\mathrm{CuY}) = \frac{K_{\mathrm{Cu}}}{K_{\mathrm{Ca}}} \cdot \frac{(\mathrm{Y})}{(\mathrm{Ca}^{2+})} \cdot (\mathrm{Cu}^{2+})$$

Since by hypothesis $K_{\mathrm{Ca}}(\mathrm{Ca}^{2+})$ is larger than 1 (CaY is the major Y species in seawater), the result of the competition effect is a simple decrease in the "apparent binding constant" of Y for Cu:

$$K_{\mathrm{Cu}}^{\mathrm{app}} = \frac{1}{K_{\mathrm{Ca}}(\mathrm{Ca}^{2+})} \cdot K_{\mathrm{Cu}}$$

The importance of such decrease in effective binding constant depends on the importance of the metal complex (CuY in our example) for metal speciation or solubility. Since soluble organic complexes are not likely to be dominant metal species in sewage, gross metal speciation is unlikely to be affected. However, organic ligands may well be responsible for maintaining part of the metal in solution and the competition effect from major seawater cations could then result in a sizeable decrease (orders of magnitude) in total metal solubility. Conversely, the preceding analysis can be applied to examine the effect of seawater cations on the adsorption or the coordination of metals on particle surfaces by considering Y to represent surface sites. In this case, surface complexes may well often be the major forms of the trace metals and the competition by seawater cations can result in a major speciation shift and a large increase in the total soluble fraction of the metal.

Variations in pH

Municipal wastewaters reaching treatment plants have a slightly acidic hydrogen ion activity: pH ≃ 6 to 7, the lower part of this range being observed in the summer. Industrial wastewaters have a highly variable pH, some of them being quite alkaline resulting in a somewhat basic pH for the raw wastewater reaching the treatment plant in some combined sewer systems. Typically the pH is then adjusted to the range 6.5 to 7.1, if needed, by addition of acid or base for optimum performance of the digesters. During anaerobic digestion the pH usually increases slightly (less than 8) while in activated sludge the pH remains about constant (and neutral) due to the efficient gas exchange which does not permit supersaturation of the $CO_2(g)$ formed in the aerobic oxidation process.

Coastal and estuarine surface waters are roughly in the same pH range, typically from 7.4 to 8.3 depending on the temperature and biological activity, both of which show a pronounced seasonal and diurnal variability. Temperature and biological activity affect pH mostly through modification of the carbonate system: the solubility of CO_2 and thus the pH decrease with increasing temperature; photosynthesis utilizes CO_2 and increases pH; conversely respiration releases CO_2 and decreases pH. These pH variations which occur because of CO_2 variations at approximately constant alkalinity* are much dependent upon mixing conditions in the water column and most importantly upon gas exchange at the sea surface.

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* The pH of an aquatic system is determined by the constraint of charge balance between its weak acid-weak base and its strong acid-strong base components. The alkalinity of a solution which is defined experimentally as the concentration of strong acid necessary to bring the pH down to the CO_2 end point (ca. pH 4 to 5) can be conceptualized simply as the positive charge due to the excess of strong bases over strong acids. This charge is of course balanced by the negative charge due to the dissolution of weak acids. The extent of this dissociation determines the pH of the solution. In systems such as seawater where carbonate and borate are the dominant weak acid-weak base system, the alkalinity can be written:

$$\begin{aligned}\text{Alk} &= (Na^+) + (K^+) + 2(Ca^{2+}) + 2(Mg^{2+}) - (Cl^-) - 2(SO_4^{2-}) \\ &\simeq (HCO_3^-) + 2(CO_3^{2-}) + B(OH)_4^- + (OH^-) - (H^+) \\ &\simeq 2.3\ 10^{-3}\ \text{eq. liter}^{-1}\end{aligned}$$

Since municipal wastewater and coastal waters have pHs that are typically less than 0.5 units apart, the pH changes associated with dilution of sewage into seawater are relatively small and, given the dilution effect, are in fact much smaller than the natural variability of surface seawater. As a result, despite the fact that pH is the dominant parameter in controlling chemical speciation in aqueous systems, the effects of pH changes in sewage plumes are usually far from dramatic. For example a pH increase from 7.7 to 8.2 in our diluted model sewage results in only a minor redistribution of the major metal and nutrient species (Table 6.1; Parts 4 & 5).

Redox in Oxic Surface Water

Municipal wastewater discharges in coastal waters do not usually result in anoxic conditions in the water column. The decrease in oxygen content in sewage plumes is often hardly measurable. In some estuaries where the flow conditions are restricted, the large ultimate dilutions which give coastal waters their great assimilative capacity for oxygen consuming waste may not be achieved. Anoxic conditions may then sometimes develop. (It should be noted that this discussion focuses on the redox status of the plume [the initial sewage dilution zone], not on the possible regional effects of waste discharges. Through stimulation of plant growth and subsequent decomposition of the plant material, sewage discharges may, in some instances, contribute to oxygen deficits in coastal and estuarine waters.)

While engineers and biologists use the oxygen concentration (O_2) (usually expressed in mg liter^{-1}) to describe the redox status of a body of water, chemists use the electrochemical redox potential (E_H) or (the negative log of) the electron activity (pE) for describing oxidation-reduction states. E_H (expressed in volts) and pE (nondimensional) are related by the formula

$$E_H = \frac{2.3RT}{F} \quad pE$$

where R, T and F are respectively the gas constant, the absolute temperature and the Faraday constant

$$\therefore \; E_H \simeq 0.058 \text{ pE (at } 20^{\circ}\text{C)}$$

(In this discussion, we shall use pE rather than E_H). For any half redox reaction,

$$\mathrm{Ox} + e^- = \mathrm{Red} \quad ; \quad pE^o = \log K$$

The pE gives, then, a measure of the "oxidation potential" of any redox couple:

$$pE = pE^o + \log \frac{(\mathrm{Ox})}{(\mathrm{Red})}$$

Applying this equation to the oxygen-water redox reaction, one obtains a relation between oxygen concentration and pE:

$$\frac{1}{4}\, O_2\ (g) + e^- + H^+ = \frac{1}{2}\, H_2O \quad ; \quad pE^o = 20.75$$

at a pH ca. 8.15:

$$pE \simeq 12.6 + \frac{1}{4} \log (P_{O_2})$$

Where P_{O_2} is the partial pressure of oxygen in units of atmosphere. Note that pE is a relatively insensitive function of the partial pressure (or the concentration) of oxygen and that in any "oxic" environment (say $(O_2) > 0.1\ \mathrm{mg\ l^{-1}}$) the pE of the oxygen-water couple is always in the range 12 to 13. This should be contrasted with the negative pEs obtained in anoxic systems, usually characterized by the presence of the sulfate-sulfide couple.

It should also be noted that although the pE of the oxygen-water couple is well defined, that of the whole system is not, as redox reactions are not fast and many redox couples are not in equilibrium with each other (different pEs) in the system. If one talks of the pE or of the redox potential of a body of water, one really speaks of the dominant redox couple, that which drives other couples to more oxidized or reduced conditions. Attempts to measure redox potentials of natural waters by direct potentiometric techniques usually fail for this very reason. The pE that they measure is that of whatever redox couple react fast and reversibly at the electrode surface, not automatically that of the dominant redox couple. For example, a platinum electrode in oxic waters does not measure the oxygen-water couple but some other reaction such as the hydrolysis of platinum. The reason why the high dilutions typically obtained upon discharges in coastal waters do not permit the development of anoxic conditions can be seen from elementary engineering analysis. The oxygen utilization (Y) due to microbial oxidation of sewage organics is obtained simply as a function of time, from the carbonaceous BOD (the nitrogenous or secondary BOD takes 6 to 10 days to develop and this is beyond the time scale of this analysis):

$$Y = BOD^{o} - BOD^{t}$$

$$Y = BOD^{o} (1-e^{-Kt})$$

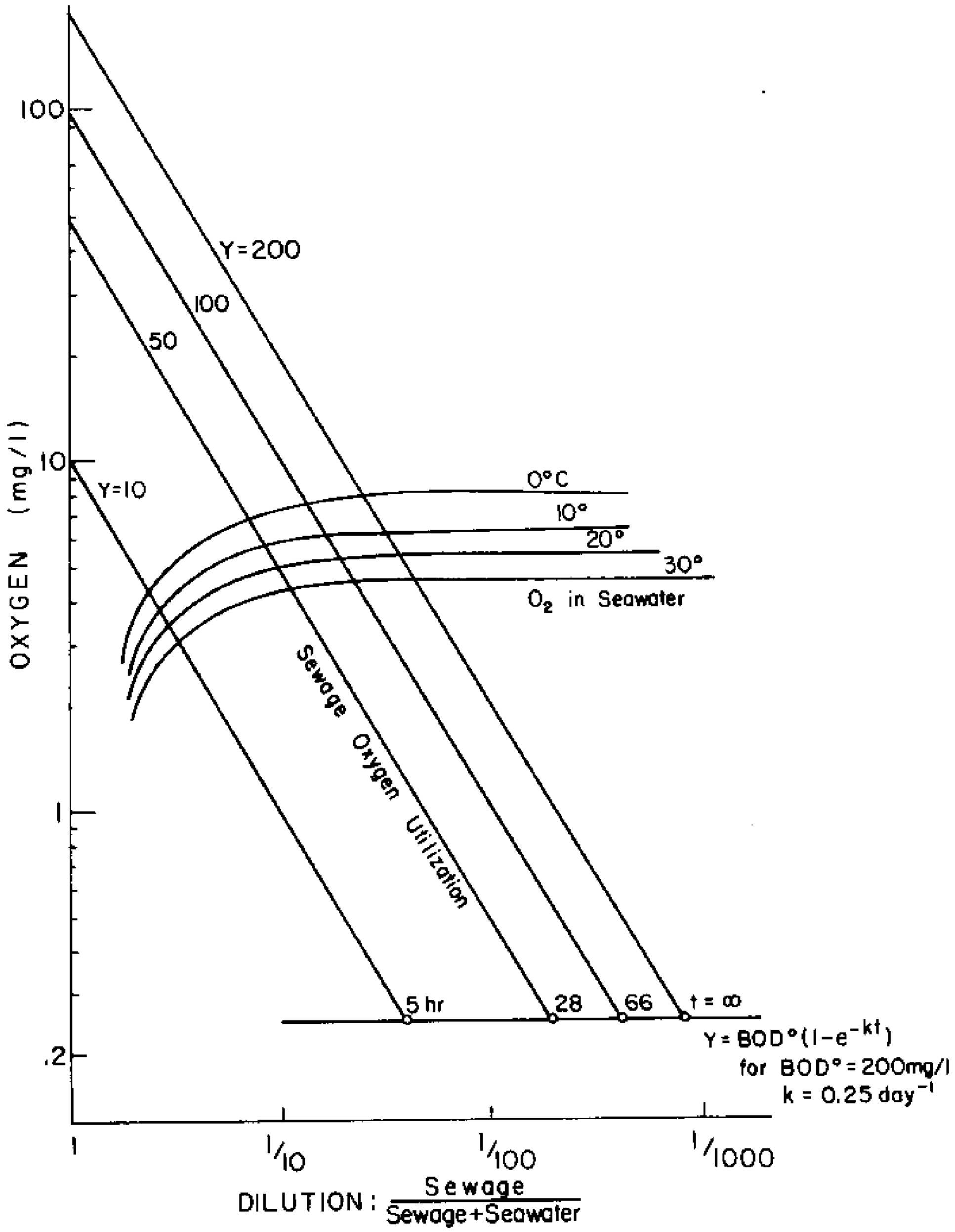
where the decay constant K has a typical value of 0.25 day^{-1} (range 0.1 to 0.7 day^{-1}). The sewage is oxygenated by rapid initial plume mixing with saturated seawater and, in the case of a surface sewage field, additional oxygen is dissolved from the atmosphere. Neglecting this second process, the biological oxygen utilization and the oxygen supply due to mixing are compared in Figure 6.4. Given that dilutions by a factor of 100 are readily obtained within minutes it is evident from the figure that the water can never come close to anoxic. This analysis is not valid for systems with restricted water circulation such as bays, estuaries or deep basins, where the mixing water may reflect previous BOD loading and may not be saturated with oxygen. In the case of sludge disposal, the much higher initial BOD (up to 40,000 mg l^{-1} can result in local oxygen depletion. This effect is mitigated by the relatively small volumes of sludge compared to wastewaters.

As they are diluted in seawater, the constituents of the waste are thus subjected to a rapid change in their redox environment from highly reduced conditions in pure sewage to oxidized conditions in the plume. The effect of complete oxidation of the model diluted sewage is shown in Table 6-1 (Parts 5 & 6). The changes are dramatic for most metals, simply due to the dissolution of sulfide solids as the sulfide is oxidized to sulfate. If one compares the stepwise changes in the speciation of sewage constituents due to dilution, ionic strength, major seawater ions, pH and redox (Table 6.1, Parts 1 to 6), the last effect is by far the most important one and redox chemistry will be a focus of the discussion regarding the fate of metals.

Redox in Anoxic Bottom Waters

One of the most visible impacts of sewage and sludge disposal in coastal waters is the frequent establishment of an area of reduced sediments adjacent to the disposal site and easily characterized by the presence of sulfide. In the case of large outfalls, this area can extend over a few kilometers along the

Figure 6.4 Comparison of oxygen utilization by waste with the oxygen supplied by diluting seawater.



principal current directions as illustrated in Figure 6.5 for the Los Angeles County outfall system at Whites Point in 1974.

Although they are common features of freshwater systems, reduced sediments are rare features in the marine environment: localized lagoons, fjords, estuaries, and salt marshes and such well known systems as the Cariaco Trench, the Gotland Deep and the Black Sea all have anoxic sediments for the same basic reason of restricted water circulation. The formation of anoxic sediments near sewage disposal sites where water movement is usually unrestricted is thus a peculiar and highly dynamic feature of particular scientific interest.

Figure 6.6 depicts diagrammatically the principal gross chemical events that lead to the formation of such anoxic environments. Oxygen depletion is maintained by a steady input of waste particles with high BOD such that the rate of oxidation of organic matter is greater than the rate of oxygen supply from the water column through advection and diffusion. Sulfate then becomes the principal oxidant (electron acceptor) resulting in the formation of sulfide, some of which diffuses through the water column and is oxidized by oxygen to various forms: elemental sulfur, polysulfides, thiosulfate and sulfate. The rest of the sulfide remains associated with the sediments as elemental sulfur or various solid metal sulfides.

To assign a representative pE to the reduced sediment and the associated water is a difficult task, perhaps even a meaningless one conceptually. Although the driving redox couple is obviously the organic matter/CO_2 couple, it is hardly representative of the chemistry of the system. Both it, and the other dominant couple $SO_4{}^{2-}/S^{2-}$, involve many intermediary reactions, several of which are microbially mediated and far from reversible. Yet, despite these difficulties, it is still worthwhile to define a characteristic pE for the reduced sediments in order to examine thermodynamically the redox chemistry of metals. For this purpose, it seems appropriate to choose the pE of the sulfate/sulfide couple for several reasons: 1. the abundance of the sulfate as a major seawater anion precludes its disappearance from solution due to the slow reduction by organic matter; 2. oxidation-reduction reactions for metals are relatively fast (they often catalyze redox reactions for ligands) and even if, through reactions with organic matter, metals are reduced to

Figure 6.5 Anoxic area near the Whites Point outfall off Los Angeles (Hendricks, 1974).

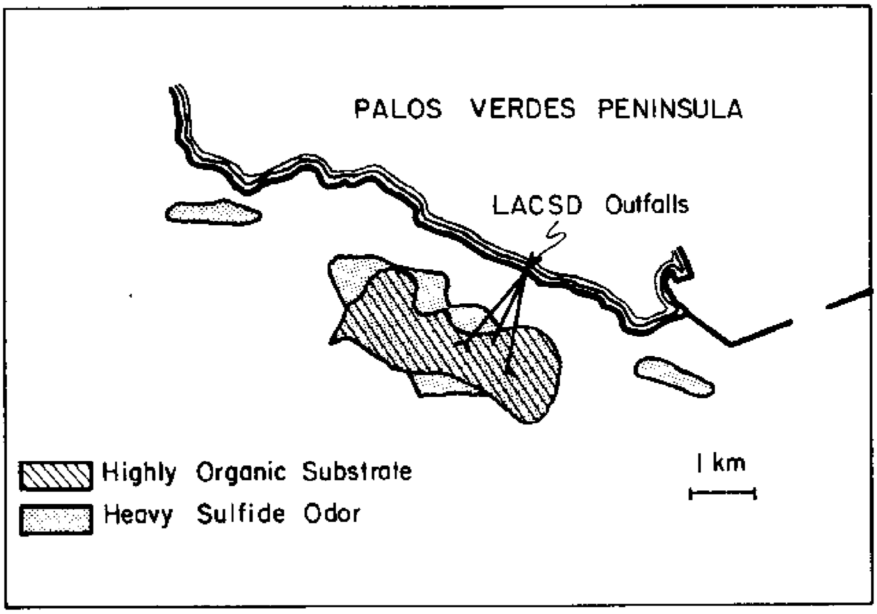
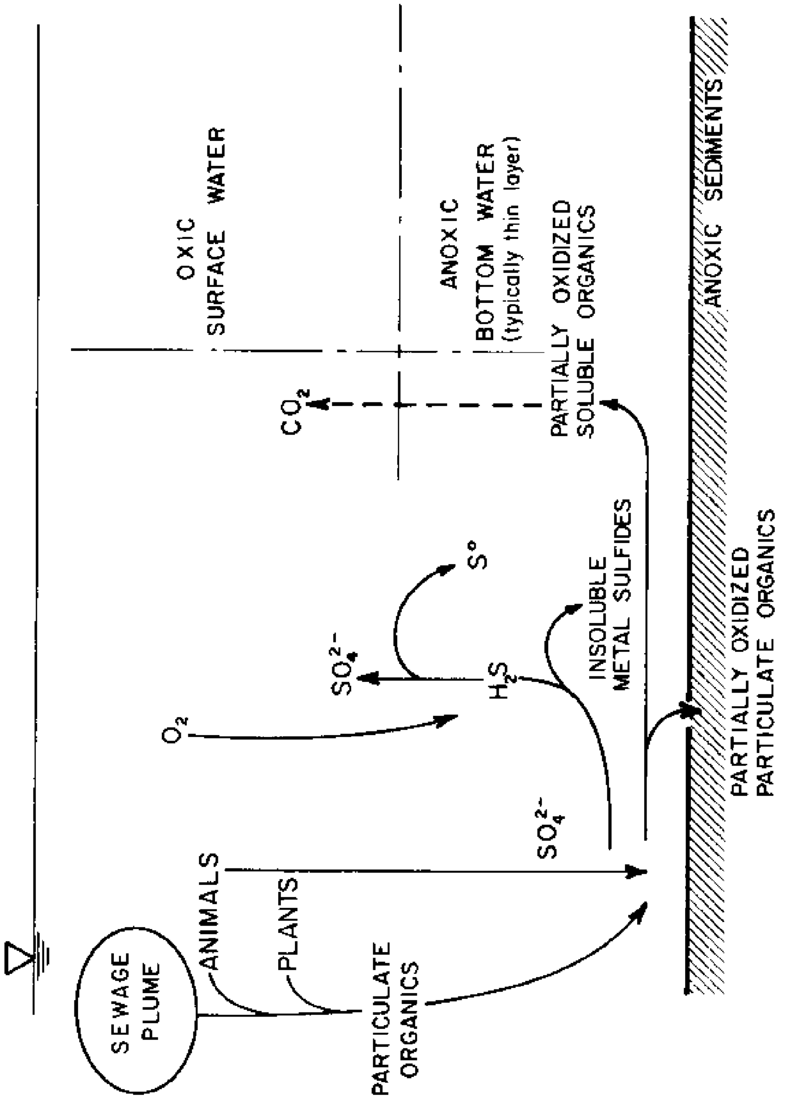


Figure 6.6 Development of anoxic conditions in bottom sediments and overlying water.



higher electron activities than that of sulfide, reoxidation by sulfate is likely to take place; 3. through direct measurements of sulfide species or through consideration of solubility products, the sulfide ion activity can be determined leading to a straightforward estimation of the pE:

$$\frac{1}{8}\,SO_4^{2-} + e^- + \frac{9}{8}\,H^+ = \frac{1}{8}\,HS^- + \frac{1}{2}\,H_2O$$

$$pE = pE^{o} - \frac{1}{8}\log\frac{(HS^-)}{(SO_4^{2-})} - \frac{9}{8}\,pH$$

Given $pE^{o} \simeq 4.1$ and $pH \simeq 8$, the pE of sulfide containing systems is in the range -5, -4.

Although sulfate is typically the principal oxidant in anoxic waters, there are some aquatic systems in which nitrate may be sufficiently abundant to play a major role in the oxidation of waste organics. For example, it has been calculated that disposal of sludge in the deep coastal basins off Los Angeles would not result in sulfate reduction despite low ambient oxygen concentrations (Jackson et al., 1979). Nitrate reduction (denitrification and ammonification) is thermodynamically more favorable than sulfate reduction after exhaustion of the available oxygen, and microorganisms utilize nitrate before sulfate as an electron acceptor. Such systems for which the redox chemistry is controlled by nitrate reduction have characteristic pEs intermediate between those of oxic waters and anoxic sediments (ca. pE ≃ 0-5).

PARTICLES

Typically some seventy-five to ninety percent of the organic and trace metal load of waste effluents are contained in the particulate fraction. Even when the suspended solids are removed from the wastewater by advanced separation techniques (e.g., flocculation or centrifugation), the remaining small particles still contain a large fraction of the metallic and organic pollutants. Although in the following sections we shall emphasize the transformation processes to which the various waste constituents are subjected, it remains that their transport, and hence their fate, is primarily dominated by their partitioning between the soluble and the solid fractions. In a first, rough approximation, we may consider that this partitioning does not change drastically upon disposal in the marine environment. The spatial and temporal distribution of much of the waste constituents (the major exception being the nutrients; see next section) is thus controlled primarily by the transport of particles.

There is a fundamental difficulty regarding the definition of what constitutes a particle vs. what constitutes a solute. From the point of view of the hydrodynamicist, a particle is any constituent whose motion is different from that of the fluid; i.e., a solid whose net settling velocity contributes non-negligibly to its transport. Such a criterion translates into a characteristic diameter of the order of 10 μm (depending on density and flow conditions), which excludes the colloidal fraction of the suspended load. By and large the colloidal fraction is also excluded from the analyst's definition of the suspended solids, which is given operationally by the fraction retained on a given size filter, usually 0.45 μm (although such a nominal size is only loosely related to the diameter of the particles that are actually filtered). These definitions are very different from that of the physical chemist for whom the distinction between soluble constituents and solids is based on thermodynamic properties. The transition from macromolecular solutes to suspended colloids occurs around diameters of 0.01 μm. A sizeable fraction of the trace metals and organics is contained in the smaller, colloidal particles.

In this section which focuses on the fate of waste solids, it is ostensibly the hydrodynamicist's definition of particles that is most pertinent. However, we shall argue that particle sizes are determined dynamically by coagulation processes, that larger particles are formed continuously by aggregation of the smaller ones. The colloidal fraction of the waste, including that which passes the analyst's filters, must then also be included in our definition of particles.

For the purpose of this discussion, we shall ignore the chemical transformations considered earlier, particularly precipitation and dissolution, and examine the fate of the suspended waste fraction by considering it as a conservative entity. In addition to advective and diffusive transport, the fundamental processes that govern the fate of such a fraction are: settling, coagulation, and ingestion by pelagic and benthic organisms (which may be considered as a peculiar sort of coagulation).

Fundamental Sedimentation Processes

Settling. In the range of particle diameters and densities of interest in wastewater disposal (low Reynolds number for particle motion), the settling velocity of particles is usually assumed to be given by the familiar Stokes' law.*

$$v_s = \frac{g}{18\mu} (\rho_s - \rho)\ d^2$$

(where v_s is the settling velocity; g, the acceleration of gravity; μ, the dynamic viscosity; ρ_s the density of the particle; ρ, the density of the water; d, the particle sedimentation diameter). With regard to settling processes, the major physical characteristics of interest are thus the density and the size of waste particles. (As we shall see, little is known about either.)

Coagulation. The most common misconception regarding suspended solids is to consider the individual particles themselves as conservative (non-reactive) entities as if they were rocks, pebbles, or sand grains. In the size range below diameters of 10 µm, the reality is drastically different; particles continuously coagulate with each other to form larger particles. From a thermodynamic point of view, suspensions of small particles are unstable since the surface energies are greater in the dispersed state than they are in the aggregated state. The classical treatment of the energetics of interactions among particles in suspension, known as the DLVO theory (Derjaguin, Landau, Verwey and Overbeek; Stumm and Morgan, 1970), considers short range Van der Waals attraction energies and long range electrostatic (usually repulsive) energies. Typical plots of these energies as a function of distance between particles is shown in Figure 6.7. When the particles are very close together (<0.001 µm), the Van der Waals attraction forces are much greater than the electrostatic repulsion and the particles are coagulated. When the particles are farther apart, the electrostatic repulsion between them creates an energy barrier that prevents coagulation. Because of the decrease of the extent of this electrostatic repulsion with increasing ionic strength of the solution (compression of the double layer; See first section) the "stability" of a suspension of waste solids

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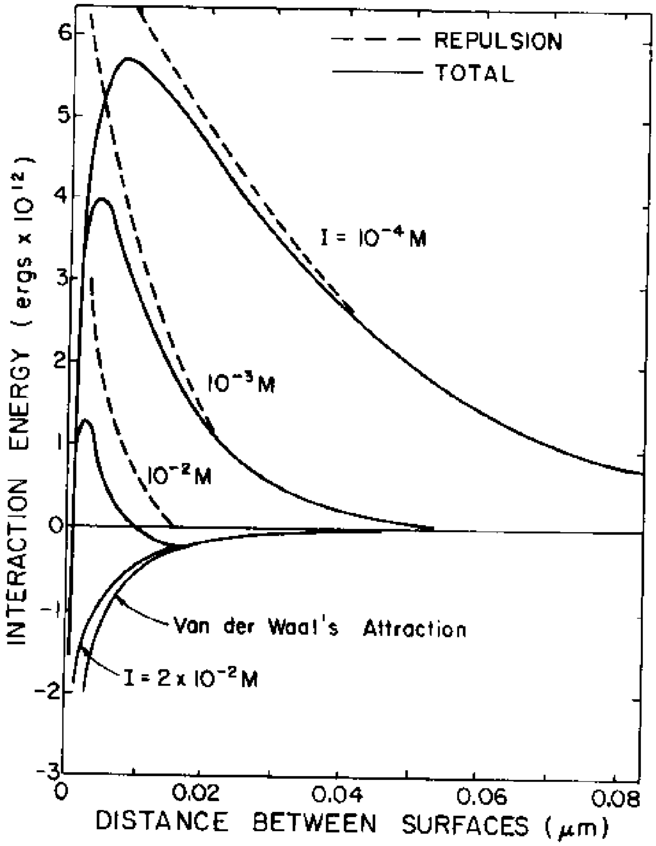
* See contrary evidence in Chase, 1979.

Figure 6.7 Variations of interaction energies with separation distance. Particle diameter = 0.2 μm, Ψ_o = 50 mv, and Hamaker constant = 10^{-12} ergs. I is the ionic strength of the medium (Kasper, 1971).



decreases dramatically as the waste plume is diluted by seawater; i.e., the electrostatic energy barrier becomes relatively small.

There are three ways particles can overcome the electrostatic repulsion and effectively collide: Brownian motion (perikinetic coagulation), laminar or turbulent fluid shear (orthokinetic coagulation) and differential sedimentation (Hunt, 1980). Under typical conditions prevailing in wastewater plumes, it is the second of these processes--collisions due to the relative motions of the particles imparted by the turbulence of the water--that controls the coagulation of particles between ca. 1 μm and 100 μm. Brownian motion and differential sedimentation cause most of the collisions among smaller and larger particles, respectively (Hunt, 1980).

Given that the collision rate among particles is proportional to the square of the particle concentration (number per unit volume) and, in the case of orthokinetic coagulation, to some mean shear rate characteristic of the water*, the two dominant parameters controlling coagulation in waste plumes are: i) the particle concentration (controlled mostly by initial dilution) and ii) the turbulence of the receiving water. The chemical factors controlling particle interactions are of relatively little importance in seawater (see Figure 6.7); the suspension is effectively destablized, and to a first approximation, its coagulation is controlled entirely by the stochastic process of particle collision.

Ingestion by organisms. Although this section will deal minimally with the question of ingestion of waste particles by marine animals, a few general principles are worth mentioning. It is generally agreed that zooplankton play an important role in the sedimentaton of natural particles (Mullin, 1980). By ingesting and assimilating smaller particles, by often packaging their feces and by shedding various outer layers in molting processes, they can modify considerably the settling characteristics of the suspended solids. As such processes vary among

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* At very high shear rates as might be encountered near the ports of a waste diffuser, particle aggregates can be broken up. However, after the initial dilution of the waste one would not expect the fluid motion in receiving waters to be sufficiently energetic for such "reverse coagulation."

zooplankton species, it is difficult to obtain a general, quantitative assessment of their importance. Usually a given zooplankter feeds on a particular fraction of the available food, selecting particles on the basis of size, and perhaps of chemical composition and of algal species. Ingestion rates (μg carbon per organism per hour) typically increase with the concentration of the food source, up to some saturating value (Frost, 1972; Mullin et al., 1975). For the micro-zooplankton (<200 μm), which are presumably responsible for most of the grazing activity on the waste particles, maximum ingestion rates in excess of 10 percent of their body weight per hour (for ambient food concentrations > 50 μg C/l) have been reported (Heinbokel, 1978a, b). Under such conditions the assimilation efficiency (C assimilated/ C ingested) can be in excess of 50 percent resulting in growth rates of more than a doubling per day. Considering total zooplankton crops of a few grams C per m^2, the grazing effect on bacteria and bacterial debris from wastewater discharges could be significant.

Composition and Properties

Nature of waste particles. The suspended matter in domestic waste is a mixture of inorganic and organic solids, some of which originates from the influent, and some of which is formed during waste treatment by precipitation or growth of organisms.

The visible matter is made up of refractory solids from the influent and is predictably heteroclite: plastic bits, seeds, hair, metal foil, sand grains, pieces of egg shell, etc. are all characteristically found in domestic wastes (Faisst, 1980). In terms of elemental composition, 30 percent to 40 percent of the waste solid is carbon with typically less than 1 percent of this carbon in inorganic form (Myers, 1974). By far the largest fraction of the particles is thus made up of organic solids, principally bacterial cells and cell fragments. Electron micrographs of the colloidal fraction (0.01 to 1 μm) show bacterial cell walls as the dominant material with much lower concentrations of other organisms such as viruses (Dean et al., 1967). The degree of aggregation of the various organic debris is difficult to assess in such micrographs owing to disruptive preparation techniques. As will be discussed later, the trace elements are almost entirely found in the solid fraction of the waste, partitioned between its organic and inorganic constituents. Major inorganic solids are siliceous and carbonaceous materials (largely calcium carbonate).

Density. Owing to its mostly biological nature, the density of the suspended waste material is not easily defined. The density of a bacterial suspension is hardly an intrinsic property as osmotic processes effectively tend to adjust the density of the cells to values close to that of the surrounding water regardless of its salt content. Also, depending on the extent of the coagulation, the quantity of water associated with the particles varies widely. Given that they do settle when sufficiently coagulated or flocculated, it is a fair estimate that sewage particles are "slightly" denser than their surrounding water.

Separation between the inorganic and organic fractions of the solids by sedimentation in an upflow clarifier has been reported (Hayes and Theis, 1978). This may reflect a difference in effective density between inorganic and organic particles; it may also reflect a difference in ability to coagulate under the particular conditions of the experiment.

Size. Size distribution of particle suspensions can be obtained by a variety of techniques including sieving, centrifugation, light scattering and resistive pulse electronic counting (Coulter Counter). Some of these techniques have their own inherent difficulties (e.g., reduction of effective pore size by clogging, dependence of centifugation velocity on particle density, effect of particle shapes on light scattering, etc.), but all of them provide results that are obviously dependent on the degree of particle aggregation. As we shall argue later, coagulation is the single most important process in determining the size distribution (and hence the fate) of particles in wastewaters. Available size distribution data have been gathered without sufficient awareness of this fact and, in most instances, particle aggregates have been broken up to an unknown degree during the measurement process. Be this as it may, Table 6.4 gives size distributions of primary and digested sludges obtained with a Coulter Counter. Here the largest particles (>6 μm) account for about 80 percent of the total particulate volume but only 2 percent of the total particle number. Although these data provide some rough estimation of particle size distributions in wastewaters, what they

Table 6.4 Particle Size Distributions by Coulter Counter (From Faisst, 1979)

LACSD Digested Primary Sludge

Diameter Interval	Aperture(1,2)	Number	Volume	Area
0.89 to 2.72	30	1.06×10^{12}	2.34×10^{-3}	7.17
2.75 to 6.04	70	1.48×10^{11}	4.35×10^{-3}	6.47
5.99 to 12.72	70	2.08×10^{10}	6.69×10^{-3}	4.50
12.43 to 20.55	140	3.96×10^{9}	8.53×10^{-3}	3.05
20.10 to 32.62	140	1.44×10^{9}	10.65×10^{-3}	2.77
33.22 to 60.35	280	3.30×10^{8}	12.58×10^{-3}	1.76
Totals		1.24×10^{12}	4.51×10^{-2}	

City of Los Angeles Digested Mesophilic Sludge

Diameter Interval	Aperture(1,2)	Number	Volume	Area
0.89 to 2.72	30	1.17×10^{12}	2.20×10^{-3}	7.73
2.75 to 6.04	70	1.78×10^{11}	5.65×10^{-3}	8.13
5.99 to 12.72	70	2.06×10^{10}	6.61×10^{-3}	4.44
12.43 to 20.55	140	2.85×10^{9}	5.92×10^{-3}	2.20
20.11 to 32.63	140	1.04×10^{9}	8.48×10^{-3}	2.01
32.22 to 62.99	280	2.55×10^{8}	9.88×10^{-3}	1.36
Totals		1.37×10^{12}	3.88×10^{-2}	25.33

(1) Units: Diameter Intervals - μm
Apertures - μm (10^{-6} meters)
Number - Number of particles/liter
Volume - cm^3/ml
Area - $meters^2/liter$

(2) Aperture used to measure a given diameter interval.

represent quantitatively (with some questions of calibration) is the size distribution in the counting apparatus as the particles are entrained by flow through a small aperture. The sample concentration (and hence the degree of initial coagulation), the fluid shear (and thus the break up of aggregates in the aperture) may be quite different from the conditions prevailing upon disposal of municipal wastes in marine waters.

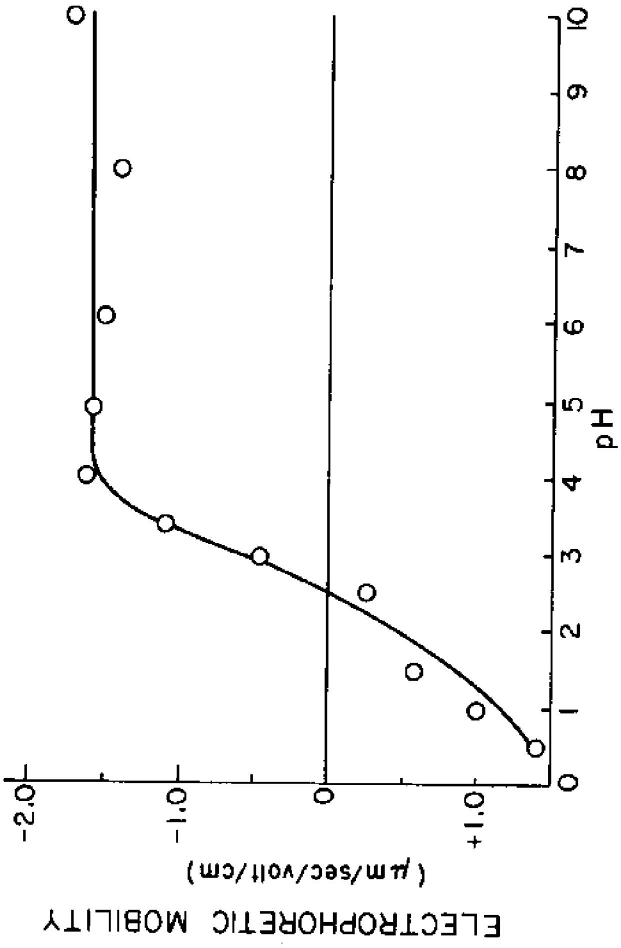
Surface charge. With the exception of clays, which form a minute fraction of the suspended solids, waste particles develop a surface charge mostly by acid-base reactions of surface groups. The surface charge of waste solids is thus controlled, in principle, both by the nature of the solid and the chemistry--mostly the pH--of the ambient water. Bacterial cells, which are characterized by weak organic acid surface groups, are negatively charged in the pH range encountered in waste and receiving waters (Figure 6.8). (The zero point of charge and the charge density have been reported to depend on the stage of growth of the organisms; Tenney, 1965). As bacteria and bacterial cell fragments are the dominant constituents of waste solids, the surface charge of waste particles is characteristically negative and changes little upon disposal in marine waters. The charge on oxides and sulfides depends on the acidity of the surface oxygen and sulfur atoms, respectively (Stumm and Morgan, 1970).

The presence of polyelectrolytes, either added in the treatment process or produced by the bacteria themselves during late stages of growth, can drastically affect the stability of the waste suspension (Tenney, 1965). However, this effect is only partly attributable to a simple reduction of the repulsive surface charge. Bridging mechanisms as well as the importance of the patchy distribution of charges have been invoked to explain the experimental data (Kasper, 1971; O'Melia and Stumm, 1967).

Fate of Waste Particles

Ideally, to understand the fate of particles upon disposal in marine waters, one would want to obtain estimates of deposition rates as a function of location and relate those to the mass emission rates, the sedimentation characteristics of the particles and the hydrodynamic regime of the receiving waters. A number of complicating factors makes it difficult to

Figure 6.8 Effect of pH on the electrophoretic mobility of bacteria (Tenney, 1965).



infer such deposition rates directly from concentration profiles of pollutants in sediment cores: 1. the relatively short history of the disposal practices restricts the measurable enrichments of the upper sediment layer that is often homogenized by the benthos and by water currents; 2. the sedimentation rates of natural particles--often poorly known themselves--may be grossly affected by the presence of domestic waste through coagulation or stimulation of organism growth; 3. the relative contributions of the natural sediments and of multiple pollution sources (there is always, at least, an eolian transport contribution that has to be accounted for) are difficult to estimate; 4. even in the simplest case--stable sediments close to a single disposal site such as will be discussed later in the case of trace metals near the Los Angeles outfalls--the mobilization or degradation rates are not known; thus a given pollutant concentration may be due either to recent inputs not yet mobilized or to a long-term accumulation of conservative material. In short, it is relatively easy to demonstrate the presence of waste contaminants in sediments and to infer that sedimentation of waste particles is important; it is quite difficult to quantitate such sedimentation.

To obviate these difficulties, attempts have been made to model the fate of waste particles by describing their transport as they settle and are advected in the receiving waters. A particular settling velocity is simply ascribed to each particle and included in the transport equations. As mentioned earlier there is an inherent difficulty in such an approach since it ignores the dynamics of particle-to-particle interactions; it does not account for the continuous formation of large aggregates as smaller particles coagulate. With this concept in mind we shall examine some laboratory and field data that have hitherto been analyzed by assuming a fixed distribution of particle settling velocities rather than a time dependent coagulation process. Note that in this discussion we shall distinguish settling rates (downward velocities of particles) from sedimentation rates (rates of particle deposition in sediments) that depend not only on settling rates but also on the rate of supply and formation of particles.

<u>Sedimentation column experiments.</u> The simplest approach to studying the sedimentation characteristic of waste particles is to perform sedimentation column experiments. By choosing various dilution factors of

waste material with seawater one can effectively mimic the situation encountered in waste plumes. A typical experimental setup consists of a cylinder with a sampler at a depth h at which the suspended solid concentration in the water column C (mg l^{-1}) is measured as a function of time, t, starting from a well mixed condition ($C=C_0$; t=0). The results are usually plotted as C/C_0 vs. log(h/t) where h/t (cm sec^{-1}) is interpreted as a settling velocity and C/C_0 as the percent of solids with settling velocities less than h/t.

Typical data are presented in this form in Figure 6.9. Considering that they should represent settling velocity distributions for suspensions made up of particles of the same nature, these data show an extraordinary degree of variability. In fact, even when the same waste material is measured, the presumed "settling velocity distributions" are highly dependent upon the particulars of the sedimentation experiments. As seen in Figure 6.10, increasing dilutions of the waste result in slower apparent settling velocities. The position of the sampler has also been reported to affect the experimental data: sampling at greater depths results in somewhat larger apparent settling velocities (Faisst, 1980). Other factors that can be expected to affect the results--e.g., temperature or nature of the diluting water (NaCl solution vs. filtered seawater vs. unfiltered seawater)--have not been studied systematically. The importance of the waste particle concentration and of the position of the sampler in determining the results of sedimentation column experiments has been naturally attributed to particle-to-particle interactions processes. Here we propose to reinterpret these data not just by considering that they represent settling velocity distributions that are in some minor way affected by coagulation processes, but by suggesting that they reflect predominantly the kinetics of the coagulation itself.

Let us consider a situation where small particles have effectively zero net settling velocity, but where coagulation takes place and larger particles are formed continuously. Even for densities that are hardly greater than that of the suspending medium, above some critical diameter the particles must settle relatively fast (the Stokes velocity is proportional to d^2). In this situation we may argue that the sedimentation rate is controlled not by the settling rate but by the rate of formation of large particles. The sedimentation column data must then be

Figure 6.9 Sedimentation column data for waste particles. Curves are given by the equation $C/C^{o} = 1/1+C^{o}\beta t$ with a value of β chosen to fit the data.

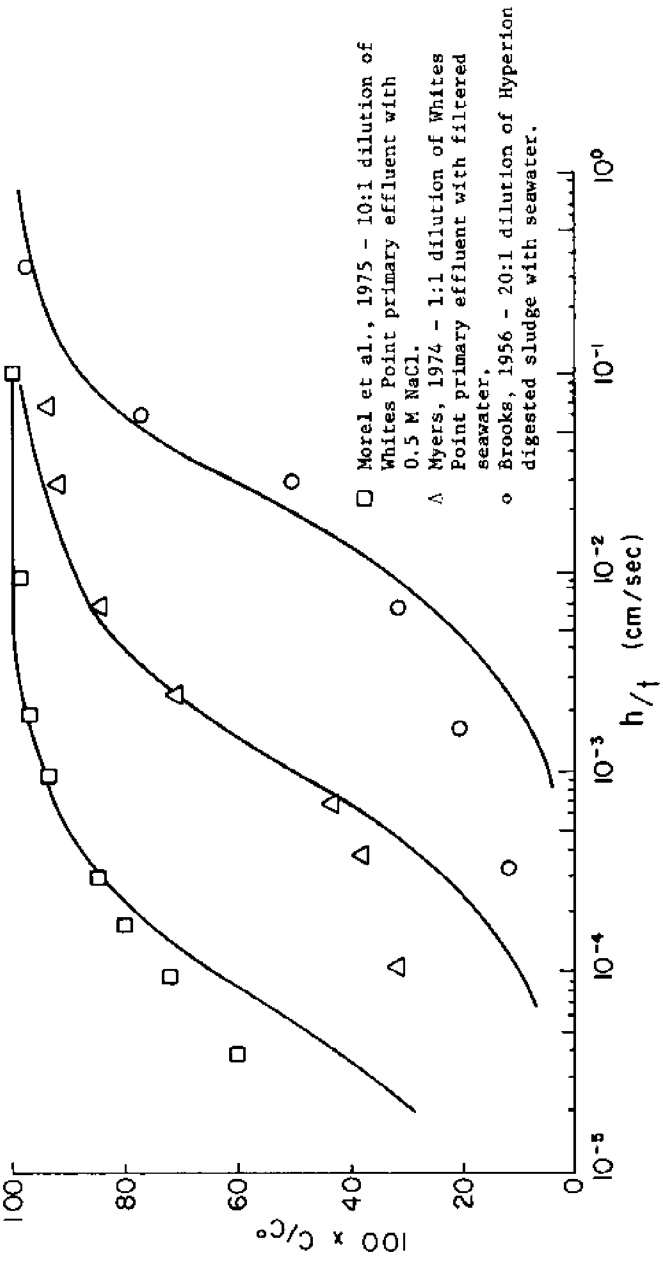
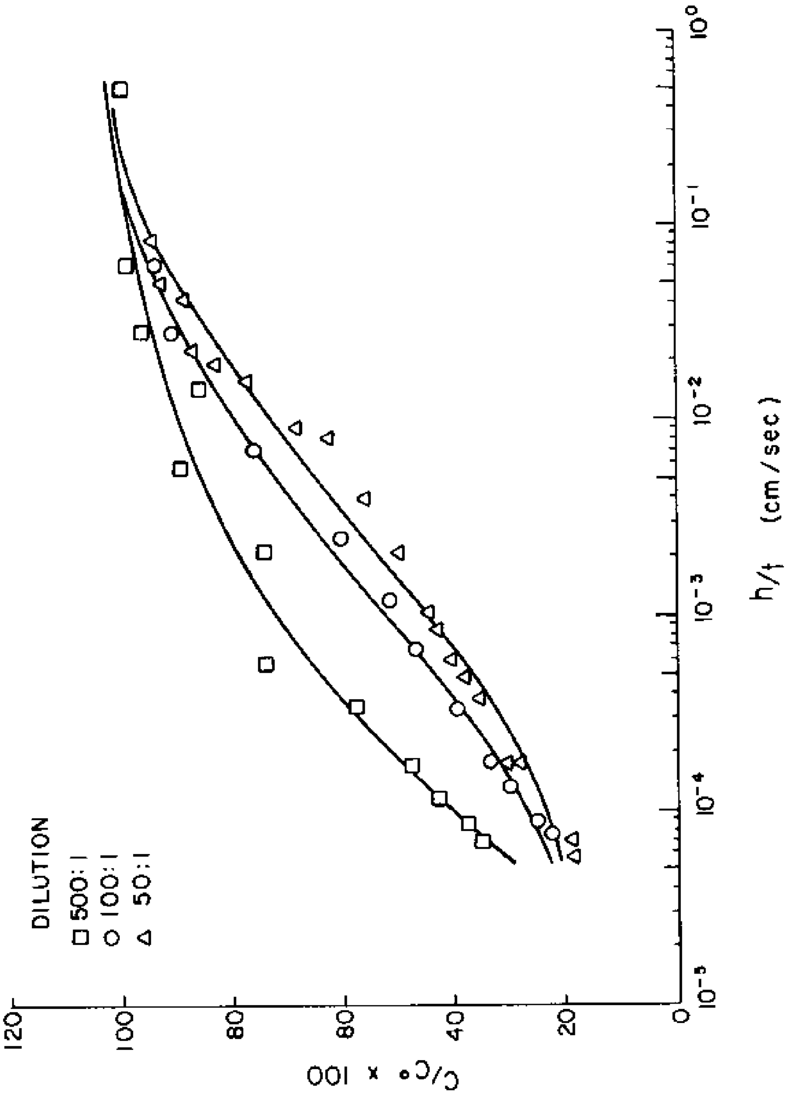


Figure 6.10 Effect of dilution on apparent settling velocities (LACSD Sludge). Curves are third order polynomial fit of the data (Faisst, 1979).



reinterpreted as representing coagulation kinetics, not a distribution of settling velocities.

For this simple extreme case, the relevant equation can be written:

$$dC/dt = -\beta C^2 \quad *$$

which integrates to: $\frac{1}{C} - \frac{1}{C^0} = \beta t$. ($\beta$ is a constant characterizing the frequency of particle collisions). This equation is expected to be valid as long as the particle concentration in the water column is not too depleted, i.e., in the early stages of the experiments. When plotted in the form of Figure 6.9, and assuming h to be constant (which is a poor assumption only when the water level becomes close to the sampler, late in the experiment), this equation gives a curve of characteristic shape that translates along the log (h/t) axis proportionally to log (C^0), to log h and to log β. There are then three predictions from the equation that can be verified with the available data: 1. the data should be fitted by a curve of the characteristic shape. This is seen in Figure 6.9. The discrepancy for the lower points (late data) is expected, due both to lowering of h and to the depeletion of the particles from the water column; 2. a dilution by a factor of α should result in a displacement of the "settling" curve by log α to the left. By considering only the initial data from those experiments that included multiple dilutions, this simple prediction is reasonably well verified in Figure 6.11a and b; 3. data obtained by sampling at different depths, h_1 and h_2 should be translated by log (h_1/h_2). Again this prediction is verified credibly by the available data (Figure 6.12). Note that this last prediction is simply a reflection of

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* The fundamental differential equation $\frac{dC}{dt} = -\beta C^2$ is formally identical to that describing the change in particle numbers in a mass conservative system subjected to perikinetic coagulation (Friedlander, 1977). Note however, that C refers here to particle concentration (in mg l^{-1}), not particle numbers, that mass is effectively being eliminated from the control volume, and that the equation is valid regardless of the coagulation process. (In contrast, in a mass conservative system subjected to orthokinetic coagulation the rate of decrease of the particle number is proportional to the particle number, not its square). The assumptions on which the two equations are based are quite different, and so are their respective implications.

Figure 6.11a Effect of dilution on sedimentation rates (LACSD Primary Effluent). Data from Morel et al., 1975. Curves are drawn 1 log unit apart, following the theory.

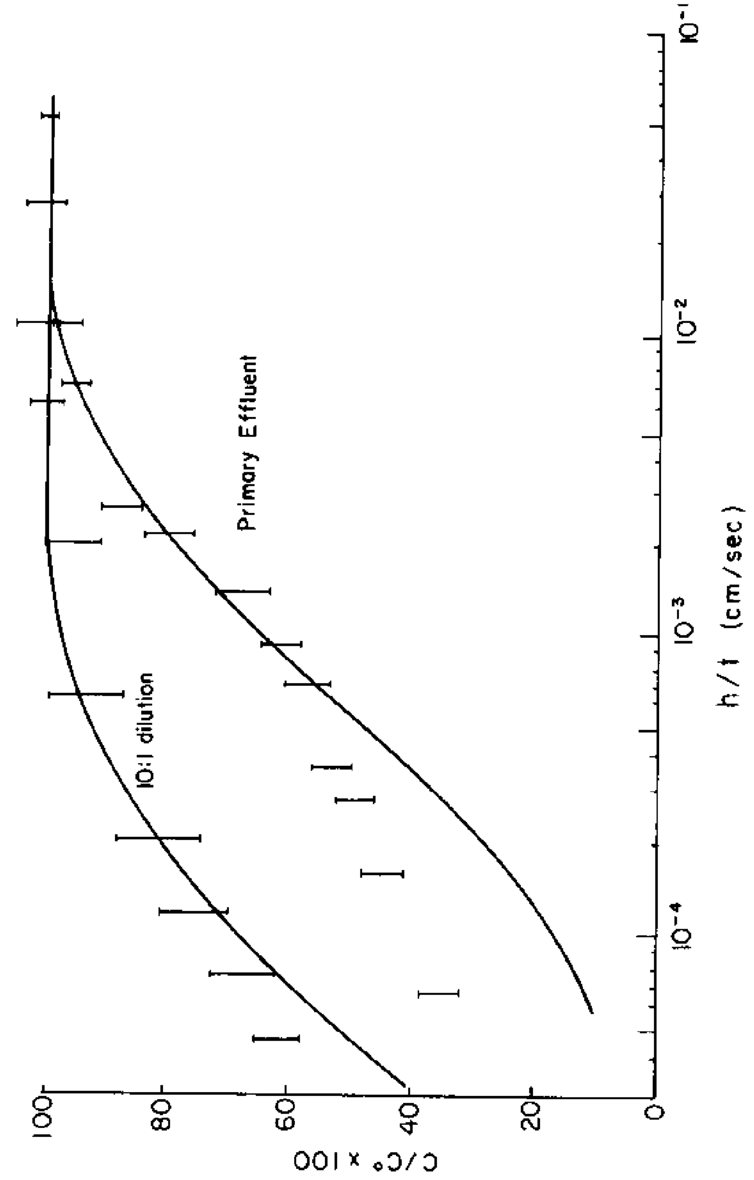


Figure 6.11b Effect of dilution on sedimentation rates (LACSD Sludge). Data from Faisst, 1976. Curves are drawn 0.3 and 0.7 log unit apart, following the theory.

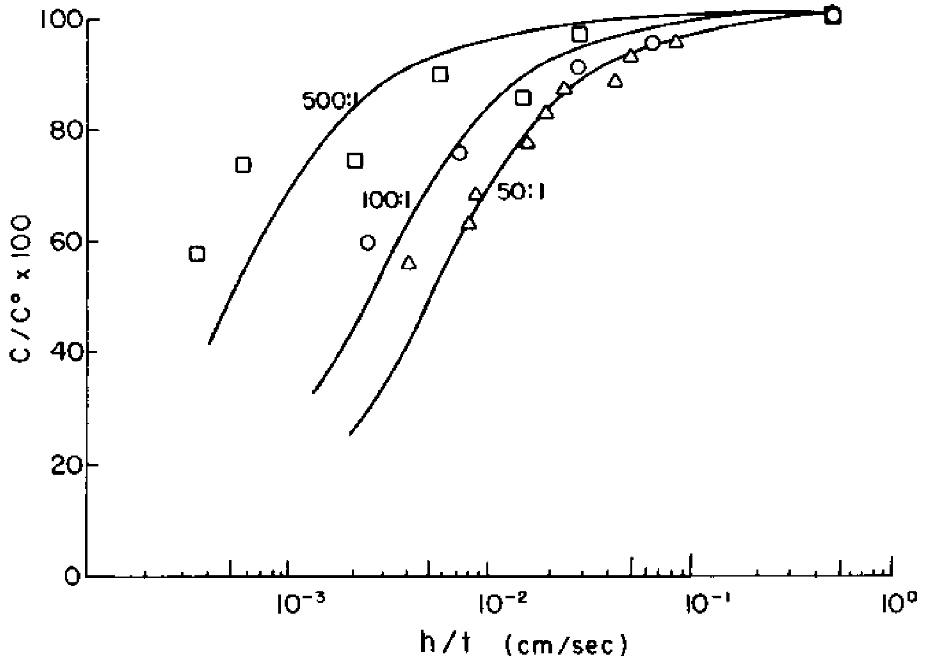
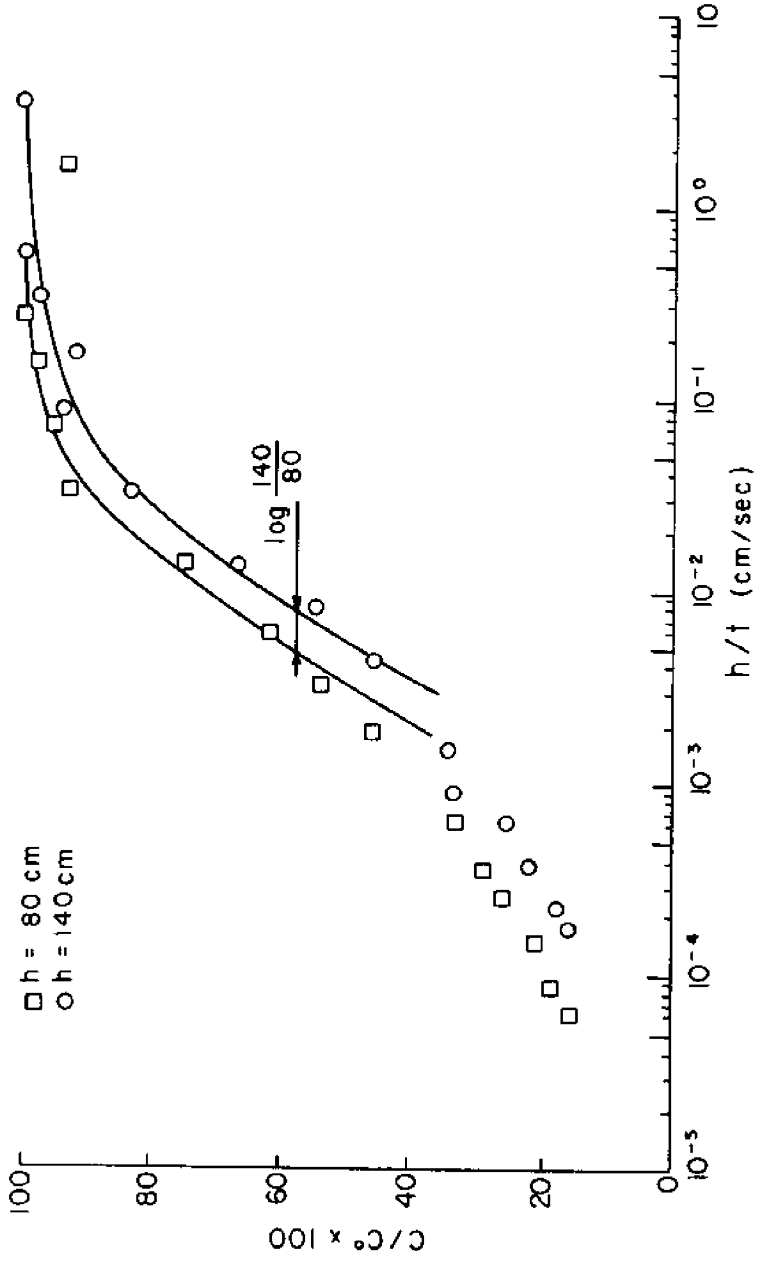


Figure 6.12 Effect of sampler depth on apparent settling velocities (OCSD Sludge). Data from Faisst, 1979. Curves are drawn 0.24 log unit apart, following the theory.



the assumption that coagulation, and hence sedimentation rates, are independent of depth--h appears nowhere in the equation. The time t, which can be calculated back from the log h/t axis, is the time it takes for a certain percentage of the suspended solid--at any depth--to grow to a critical size and settle out.

Although experiments designed specifically to test this new interpretation are necessary, it seems reasonable at this point to consider coagulation as the controlling kinetic process in sedimentation column experiments: sedimentation columns containing destabilized particle suspensions are primarily coagulation tanks, not settling chambers.

Sedimentation in receiving waters. In examining the fate of waste particles in receiving marine waters, we shall retain the major concept derived from the sedimentation column experiments; i.e., coagulation rates, not settling rates, effectively determine the kinetics of particle removal from the water column.

When extrapolating from a sedimentation column to a waste plume, two major factors influencing the coagulation process have to be considered: 1. the particle concentration is usually much lower, thus decreasing the rates of particle collisions and coagulation; 2. the hydrodynamic characteristics of the ambient water are quite different. The turbulence of receiving waters, which depends on a variety of hydrographic and meteorological conditions, always results in a much higher degree of mixing than that usually encountered in sedimentation columns. This greater mixing begets a greater rate of particle collisions and hence a faster coagulation and sedimentation rate. Although a detailed quantitative analysis of these two opposite effects is beyond the scope of this chapter, orders of magnitude estimates can be obtained.

Orders of magnitude of the times necessary for sedimentation of 5 percent, 50 percent and 95 percent of the solids in sedimentation columns is given in Table 6.5 for various solid concentrations. These times are estimated from the available data by simple proportionality to $1/C^o$. (Within half an order of magnitude, all sedimentation column data give: $\beta \simeq 2\ 10^{-7}\ s^{-1}\ mg^{-1}\ l.$) The water in sedimentation columns is very quiescent and the corresponding sedimentation times are, of course, large overestimates of the actual times necessary for sedimentation in waste plumes. Turbulence in receiving marine waters is characterized by shear rates that vary by orders of magnitude depending on the time and the location. Although the absence of systematic study makes it very difficult to estimate the increased collision frequency in natural waters compared to sedimentation columns, a factor of ten for a calm receiving water with a well-developed thermocline is probably reasonable. Greater increases in would be expected for more turbulent waters. As seen in Table 6.5, one would then expect most of the solids from a municipal sludge outfall (solid concentration ca. 10,000 mg l^{-1}; initial dilution ca. 200) to sediment out within two days of disposal in marine waters and to be effectively accumulated near the disposal site. Vice versa only a very small fraction of the suspended solids from a wastewater diffuser (solid concentration ca. 200 mg l^{-1}; initial dilution ca. 200) would be expected to sediment out, nearby, within a day. In the two cases where mass balances have been attempted, these expectations correspond reasonably well to the available data: about 5 percent of the solids from the Los Angeles County wastewater are estimated to accumulate in the nearby sediments off Palos Verdes (Galloway, 1977; Hendricks, 1975); in contrast 70 percent of the sludge solid released in the Santa Monica Canyon by the city of Los Angeles is accounted for within 10 km of the outfall (Mitchell and Schafer, 1975). According to our interpretation, it is the large difference of solid concentration in these wastes (300 mg l^{-1} vs. 8,400 mg l^{-1}) which is responsible for such differences in effective sedimentation rates. (Other major contributing factors must be the differences in the nature of the waste and in the size, depth and mixing of the receiving basins.)

Of necessity the analysis presented here is very sketchy, reflecting our ignorance of the processes governing the fate of waste solids in receiving waters. For example, it is rather evident that the degree of initial dilution is very much coupled to the hydrodynamic regime of receiving waters. With increased currents and turbulence, the initial solid concentration in the plume should decrease while the specific rate of particle collision and the transport kinetics should increase. The net effect on particle sedimentation will be understood only when these various (and opposite) effects are each described quantitatively. Also, in wastewater plumes the initial dilution reduces the suspended solid concentration of the waste to values close to that of

Table 6.5 Time Necessary for Sedimentation of a Given Percentage of the Solid. All Times are Given as Log t ± 0.5, t is in seconds.

Initial solid concentration c^o, mg l^{-1}	% solid sedimenting	Log t (time in seconds)		
		Sedimentation column	Receiving waters	
		$\beta = 2\ 10^{-7}$ $s^{-1}\ mg^{-1}\ l$	$\beta = 2\ 10^{-6}$ $s^{-1}\ mg^{-1}\ l$	$\beta = 2\ 10^{-5}$ $s^{-1}\ mg^{-1}\ l$
500	5%	2.7	1.7	0.7
	50%	4.0	3.0	2.0
	95%	5.3	4.3 (5 hrs.)	3.3
50	5%	3.7	2.7	1.7
	50%	5.0	4.0	3.0
	95%	6.3	5.3 (2 days)	4.3
5	5%	4.7	3.7	2.7
	50%	6.0	5.0 (1 day)	4.0
	95%	7.3	6.3	4.3
0.5	5%	5.7	4.7 (14 hrs.)	3.7
	50%	7.0	6.0	5.0
	95%	8.3	7.3	6.3

typical receiving waters (ca. a few mg l^{-1}). Interactions among natural and waste particles then become quite important and very little is known of the coagulation characteristics of natural suspended solids. It may well be that in such a situation the role of zooplankton in sedimenting waste particles is dominant. Given the dearth of relevant studies this is a matter of pure speculation.

NUTRIENTS

Aside from the matter of public health, the question of overfertilization of receiving water bodies has been the major concern regarding the disposal of municipal waste over the past few decades. The widespread problem of cultural eutrophication of lakes due to anthropogenic phosphorus inputs has been studied extensively. Partly by analogy with the freshwater situation, there has been concern that coastal waters receiving municipal waste may be similarly subjected to higher nutrient loadings than the operative biological and geochemical processes can assimilate while maintaining a healthy ecological balance.

In this section we shall examine the fate of silicon, phosphorus and nitrogen upon disposal of municipal wastes into coastal waters. Unlike most other waste constituents which are mostly bound to suspended solids, these elements are largely present in the soluble fraction of the waste. Their most important common character is to be essential plant macronutrients and their fate is governed more by biotic activity than by chemical phenomena. The biological transformations of these elements--uptake and degradation--take place over the same time scale that the integrity of the initial sewage field is being lost through advection and diffusion. The simultaneity of these biological and physical processes, which all result in a decrease of measurable concentrations with time, render the interpretation of available field data particularly difficult.

It is generally agreed that nitrogen is the limiting nutrient in coastal waters and that the major fertilization effect due to domestic waste inputs is the result of nitrogen enrichment. By far the largest part of this section will thus be devoted to nitrogen.

Concentrations and Chemical Species

Table 6.6 presents typical nutrient concentrations for municipal wastewaters and sludges of major metropolitan areas and for adjacent unpolluted waters. It can be readily seen that ammonia is the most enriched nutrient in wastewaters and that in all cases even an initial dilution of 100 to 500 of sewage by seawater would result in a sizeable increase of concentrations over the background. Phosphate from wastewaters can also result in a sizeable enrichment when it is depleted in the surface waters, while silicate inputs are rarely very significant. In sludge the nutrients are more concentrated by some one to two orders of magnitude than in wastewater (it should be remembered that the sludge flows are only some 0.5 percent of the waste flow) and large enrichments occur for all nutrients in the immediate sludge dilution zone.

There are few analyses regarding the nature of the dissolved organic nitrogen (DON) in wastewaters. The results of a rare complete nitrogen balance for the effluent of a primary treated sewage is shown in Table 6.7. Urea from human waste, which is the major nitrogen input to municipal sewage, is not completely hydrolyzed during treatment and represents some 20-25 percent of the organic nitrogen of the effluent. Free amino acids from the incomplete hydrolysis of proteins represent nearly half of the DON while proteins themselves account for some 15 percent of it. The balance is made up of other complex nitrogenous compounds, mostly uric acid, creatinine and various nucleic acids. It should be noted that, as the level of treatment increases (from raw, to primary, to secondary), there is a slight increase in the NH_3 fraction of the total nitrogen and a drastic decrease in the urea fraction, while the total nitrogen concentration remains roughly constant.

The chemical speciation of the inorganic nutrients is affected by the changes in pH, temperature, ionic strength and complexation with major cations, as the waste is discharged into seawater. Estimates of the effective equilibrium constants applicable to warm surface seawater ($I=0.5$; $T=25^{o}$ C) are presented in Table 6.8 along with the soluble species distribution at an assumed pH of 8.0. H_2SiO_3 and NH_4^+ are the dominant species for Si and N respectively, while P is present as a variety of HPO_4^{2-} complexes. Note that NH_3 represents only 5 percent of the total ammonia and that ammonia gas is extremely soluble (the Henry's law constant of

Table 6.6 Typical Average Concentrations of Nutrients in Wastewater, Sludge, and Coastal Waters. (Concentration in µg-at l^{-1}) Values were obtained from a perusal of references listed herein.

	Wastewater	Sludge	Coastal Waters	
			top	bottom
NH_3	1,000 - 3,000	20,000 - 100,000	<1	2
$NO_3^- + NO_2^-$	5 - 20	50 - 300	0.2	10
DON*	500 - 1,000	20,000 - 60,000	10	10
Total P†	100 - 300	5,000 - 15,000	0.3	1
Total Si	ca 500	ca 7,000	3	10

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* DON = Dissolved Organic Nitrogen

† Roughly 70% of the total P is analysed as orthophosphate.

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Table 6.7 Nitrogen Speciation in Albany Municipal Wastewater Effluent After Primary Treatment (units in mg l^{-1})(Hanson and Flynn, 1964).

Free NH_3 - N	15.0
Urea - N	2.0
Amino Acid as Glycine - N	4.1
Protein - N	1.5
Kjeldahl - N	23.8

Table 6.8 Equilibrium Constants and Speciation of Phosphate, Ammonia and Silicate in Seawater (After Smith and Martell, 1977)

		logK	Distribution of Soluble Species at pH = 8.0		
PO_4^{3-}	$HL^{2-}/H^{+}\cdot L^{3-}$	11.7	(HPO_4^{2-})	≈	16.0%
	$H_2L^{-}/H^{+}\cdot HL^{2-}$	6.5	$(H_2PO_4^{-})$	≈	0.5%
	$H_3L/H^{+}\cdot H_2L^{-}$	1.7	$(NaHPO_4^{-})$	≈	29.0%
	$NaHL^{-}/Na^{+}\cdot HL^{2-}$	0.6	$(KHPO_4^{-})$	≈	0.5%
	$KHL^{-}/K^{+}\cdot HL^{2-}$	0.5	$(MgHPO_4)$	≈	47.0%
	$MgHL/Mg^{2+}\cdot HL^{2-}$	1.8	$(CaHPO_4)$	≈	7.0%
	$CaHL/Ca^{2+}\cdot HL^{2-}$	1.7			
NH_3	$HL^{+}/H^{+}\cdot L$	9.3	(NH_3)	≈	5.0%
	$MgL^{2+}/Mg^{2+}\cdot L$	0.2	(NH_4^{+})	≈	95.0%
	$CaL^{2+}/Ca^{2+}\cdot L$	0.2			
SiO_3^{2-}	$HL^{-}/H^{+}\cdot L^{2-}$	12.6	(H_2SiO_3)	≈	97.0%
	$H_2L/H^{+}\cdot HL^{-}$	9.5	$(HSiO_3^{-})$	≈	3.0%
	$MgL/Mg^{2+}\cdot L^{2-}$	4.2			
	$MgHL^{+}/Mg^{2+}\cdot HL^{-}$	0.6			
	$CaL/Ca^{2+}\cdot L^{2-}$	3.1			
	$CaHL^{+}/Ca^{2+}\cdot HL^{-}$	0.4			

NH_3 is about one thousand times greater than that of CO_2). This explains in part why little ammonia seems to be volatilized during waste discharge and why it is such a good--quasi conservative--tracer for the initial fate of sewage plumes.

Fate of Silicon and Phosphorus

Before focusing on the intricacies of nitrogen transformations, let us examine very briefly the possible fate of silicon (Si) and phosphorus (P) upon discharge into the ocean. For both of these elements biological processes, mostly uptake by algae, compete with chemical processes for removing them from the soluble phase and incorporating them into particles. (In all this discussion, it should be remembered that dilution processes are superimposed on chemical and biological processes.) The rate of biological uptake for P and Si is not determined by the phytoplankton uptake kinetics *per se*--these are effectively saturated--but by the growth kinetics of the plankton. These in turn are controlled by physical factors (light, temperature) or by the availability of nitrogen, the limiting nutrient in most coastal waters. An upper estimate of the rate of phosphorus and silicon removal from coastal waters is obtained by considering a productive coastal diatom population fixing carbon at a rate of 0.2 mg C per liter, per day. Using average elemental ratios of Si/C - 0.5-1.0 (g/g) and P/C - 0.03-0.05 (g/g) for the phytoplankton (Parsons and Takahashi, 1973), roughly 0.1-0.2 mg l^{-1} of silicon and 6-10 g l^{-1} of phosphorus may be removed daily by the plants. Although these estimates are very approximate and depend on the particular conditions of the receiving waters they show that it would take on the order of 1 day and 10 days, respectively, for the phytoplankton to eliminate the waste silicon and phosphorus from a typical sewage plume (initial dilution 1/100).

The chemical processes competing with phytoplakton uptake for the removal of P and Si are adsorption and precipitation. The formation of the more stable solid phases (e.g., quartz and apatite) is completely hindered kinetically while adsorption on metal oxides, is fast (minutes to hours; Stumm and Morgan, 1970). The affinity and the capacity of oxides (particularly fresh hydrous ferric oxide, as may be formed upon waste disposal) for adsorption of phosphate are very high (Benjamin, 1978; Swallow, 1978). If sufficient adsorbing surfaces are not available (e.g., phosphorus is present in excess of iron in wastewater but not in sludge) the precipitation of dicalcium phosphate may be an effective removal process for phosphate.

Fate of Nitrogen

Not only is nitrogen widely recognized as the limiting nutrient in most coastal waters but it has also been shown to be specifically limiting in areas receiving major wastewater discharges and in mixtures of sewage and seawater (Goldman et al., 1973; Thomas et al., 1974). In addition, the growth enhancement obtained by addition of sewage to coastal waters has been demonstrated to be due mostly to nitrogen enrichment (Goldman et al., 1973). These are compelling reasons to make nitrogen a particular focus of interest with respect to municipal wastewater discharges into marine waters.

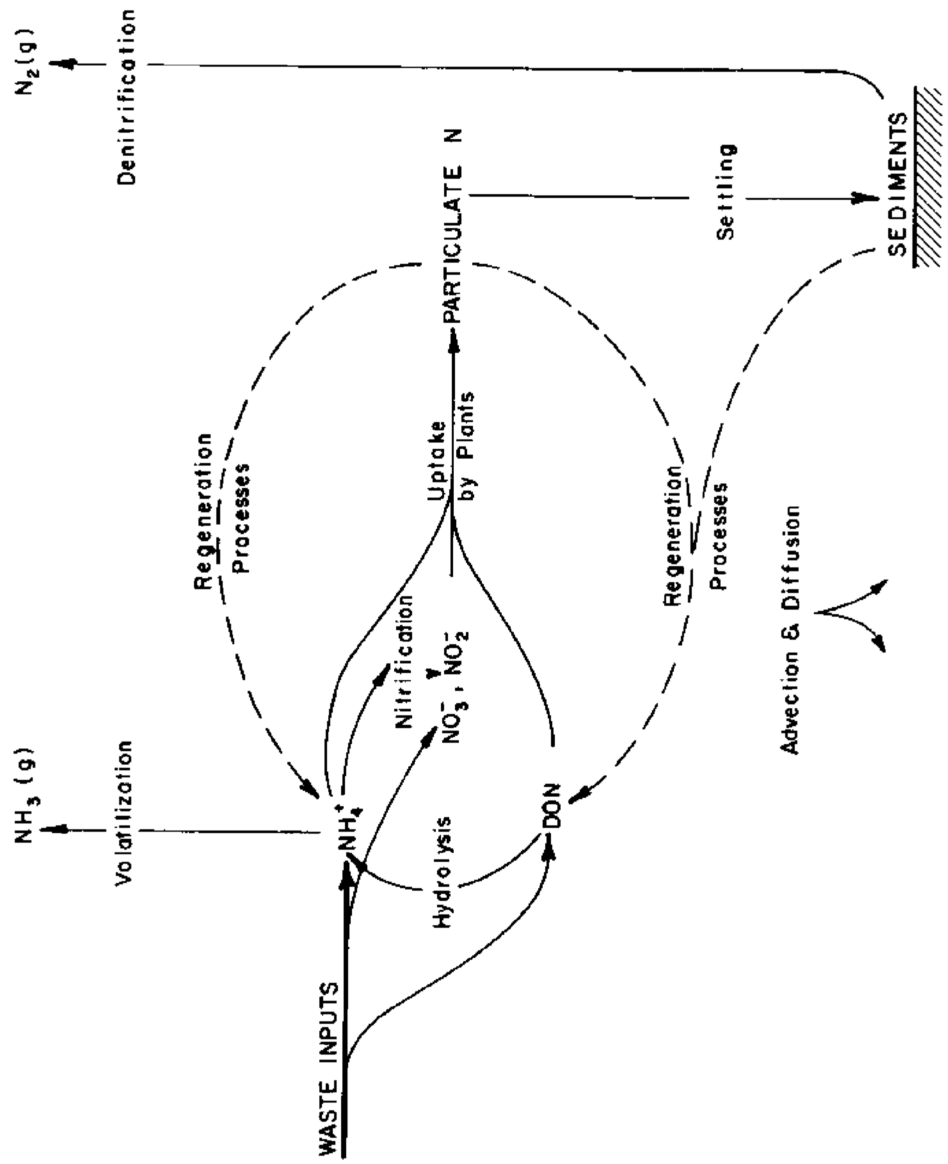
A diagrammatic representation of the major processes responsible for the initial nitrogen transformations in wastewater fields is given in Figure 6.13: transport and volatilization reduce the total nitrogen concentration; nitrification of ammonia and hydrolysis of organic nitrogen transfer nitrogen among its various soluble pools; phytoplankton uptake is responsible for the major part of the incorporation of nitrogen into the suspended phase as the plants take up ammonia and some organic nitrogen (urea and amino acids). Nitrifying bacteria utilize the dissolved organic nitrogen, resulting in part in the formation of more ammonia through hydrolysis of urea and amino acids.

Dilution and volatilization.

Although the general topic of initial dilution of the waste is treated extensively in other chapters, it merits special attention here as field measurements of ammonia concentrations have been used specifically to assess the actual dilutions obtained under a variety of conditions.

Submerged ocean outfalls off southern California have been designed hydraulically to obtain large initial sewage dilutions, typically of the order of 200. Field studies at four major outfalls have shown that, based on measurement of ammonia in the range of a few μM (validated by some simultaneous measurements with Rhodamine WT dye), the actual dilutions are indeed of the order of 100 to 300 depending on the velocity and the direction of the currents (Hendricks,

Figure 6.13 Fate of waste nitrogen in coastal waters.

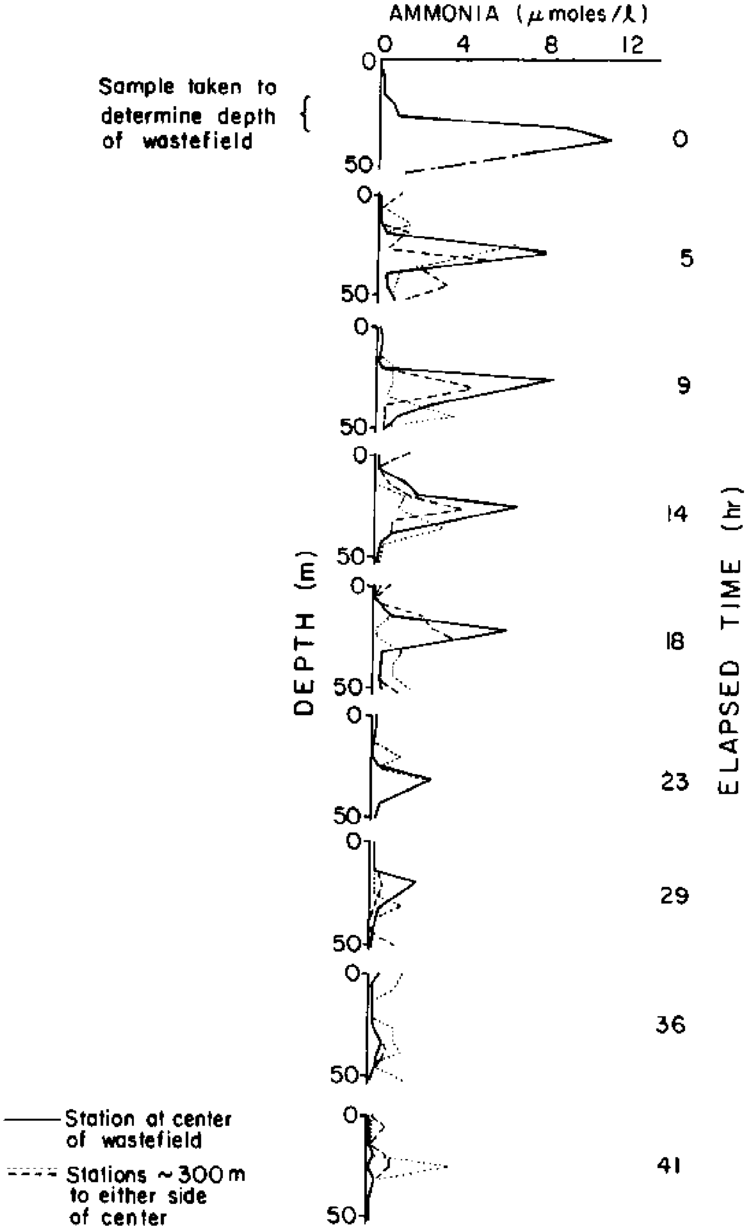


1977). These results are in agreement with most other measurements of ammonia concentrations in sewage plumes, and studies which have resulted in much lower ammonia concentrations must be presumed to have simply missed sampling the plume. Figure 6.14 presents the time history of an ammonia profile in the waste field off Point Loma, California. It has been argued that the rate of disappearance of ammonia is inconsistent with simple diffusion and the apparent drop in ammonia concentrations after 18 hours has been attributed to uptake by vertically migrating phytoplankton (Hendricks and Harding, 1974).

Dilutions obtained during barge dumping of sludge have been estimated by light transmission technique to be on the order of 500 to 1000 within minutes (Callaway et al., 1976). These may be overestimates owing to rapid coagulation and settling of sludge particles. Ammonia measurements have yielded more modest dilution factors: 20 at 110 minutes after a stationary dump (Duedall et al., 1975); 140 about 30 minutes after a moving dump (Duedall et al., 1977). (Probably because of differences between surfaces and subsurface currents, the plume is often hard to locate [e.g., in one instance the ammonia concentrations at 1 m depth went from 1000 μM to <1 μM in 47 minutes (Duedall et al., 1977]; and measurements of ammonia in sludge dumping areas typically yield low concentrations (0.5 to 5μM).)

A very important difference between the behavior of ammonia during waste disposal by barge dumping or through ocean outfalls has to be emphasized here: while barge dumping may result in a surface slick of low salinity wastewater, plumes from ocean outfalls remain normally submerged by design. This difference results in a unique opportunity for volatilization of ammonia gas during dumping operations not found in outfall disposal, and this is much enhanced by the extremely high concentrations of ammonia in sludge. Existing studies of ammonia volatilization (Stratton, 1968; 1969) provide little information to quantitate such effect, but it appears that a sizeable fraction (10 to 90 percent) of the ammonia can be volatilized during barge dumping. The rate of volatilization is proportional to ammonia concentration (and is thus highly pH dependent) and to the area of exchange, making it inversely proportional to the average mixing depth. The kinetics of the process increase with temperature and turbulence. A sizeable fraction of the ammonia lost to the air from the initial waste field may be resolubilized in adjacent waters

Figure 6.14 Ammonia with depth, Pt. Loma, May 1972 (Hendricks and Harding, 1974).



resulting in a very wide areal distribution of the nutrient in the surface waters of the dump area.

Bacterial processes. From the point of view of bacterial processes, waste fields represent a unique system. Little relevant information, especially with respect to rates, can be transferred from the study of normal oceanographic or sanitary processes. Of the extremely high concentrations of bacteria present in the waste, most are not able to survive the transition to the high salinity, oxic environment of the plume. Not all die instantly, however, and a subpopulation of aerobic euryhaline species provides the inoculum for subsequent growth. A critical factor in the kinetics of bacterial processes is then the "memory" given to the system through mixing characteristics: the system may resemble closely a continuous culture with a permanent large population of adapted bacteria (e.g., an estuarine discharge), or it may be better approximated by a batch culture in which the viable bacterial population has to grow from a relatively small inoculum (e.g., a barge dump or a sewage plume advected away from an outfall). In this second situation, an initial high rate of bacterial activity is possible as many bacteria are viable, and metabolically active, for a limited period of time after immersion into the marine environment (Carlucci, 1978). This period may be followed by a period of low bacteria concentration and activity as many organisms die or are eaten by zooplankton before the adaptable species subpopulations grow to significant levels.

If we consider sewage plumes in open waters, it then appears likely that oxidation by nitrifying bacteria will generally be only a minor process in the fate of ammonia. This is especially true given the great efficiency of indigenous phytoplankton in taking up NH_4^+ (as will be discussed later) and the well documented sluggishness in the initial development of populations of nitrifying bacteria (Kott and Ingerman, 1966).

The situation for the competition between phytoplankton and bacteria for DON utilization is less clear. As will be seen later, the high concentrations of ammonia in the waste may inhibit the uptake of urea and amino acids by phytoplankton until the NH_4^+ concentration is reduced below 0.5 to 1 g-at l^{-1}. If the bacterial population is sufficiently active, a significant fraction of urea and amino acids from the waste may then be hydrolyzed (as is the rest of the DON) before it is taken up by phytoplankton. However there appears to be no literature report of direct field measurements of nitrification or DON hydrolysis rate in sewage plumes.

Kinetics of nutrient uptake by phytoplankton. The kinetics of nutrient uptake by phytoplankton are usually described as hyperbolic functions of nutrient concentrations, often referred to as Michaelis-Menten or Monod expressions. Three different rates can be defined. (Note that the nomenclature and the notation are poorly standardized in the literature and that units of g-at l^{-1} instead of molar are used in order to normalize rates per atom of nutrient element; for $NH_4{}^+$, 1 g-at l^{-1} = 1M):

1. The uptake rate

$$\rho_s = \rho_s^{max} \frac{(S)}{K_S + (S)} \quad \text{in } \mu\text{g-at S day}^{-1}\ \text{cell}^{-1},$$

where ρ_{max} is the maximum value of ρ obtained asymptotically for large concentrations (S) of the nutrient S, and K_S is the so-called "half saturation constant" (in μg-at S l^{-1}). ρ is defined for, and obtained experimentally from, pure laboratory cultures.

2. The specific uptake rate

$$v_S = v_S^{max} \frac{(S)}{K_S + (S)} \quad \text{in day}^{-1}.$$

v_S is obtained from ρ_S by dividing by the cellular concentrations (the cell quota) Q_S (μg-at S cell^{-1}) of the nutrient S: $v_S = \rho_S/Q_S$; v_S is also the quantity obtained directly in measurement of uptake by isotope ratios (e.g., $^{15}N/^{14}N$) (Dugdale and Goering, 1967).

3. The bulk uptake rate

$$r_S = r_S^{max} \frac{(S)}{K_S + (S)} \text{ in } \mu\text{g-at S } l^{-1}\text{day}^{-1}.$$

In pure laboratory cultures r_S is related to ρ_S by multiplying by the cell density X (cells l^{-1}):

$$r_S = \rho_S \cdot X.$$

In field studies r_S can be obtained from v_S by multiplying by the total concentration of nutrient in the particles [(PS) in μg-at S l^{-1}]:

$$r_S = (PS) \cdot v_S$$

This multiplication cancels out the systematic underestimation of v_S due to the dilution of phytoplankton nitrogen by detrital nitrogen (Dugdale and Goering, 1967).

The rates ρ_S, v_S and r_S are determined by experiments conducted over a given time (typically an incubation period). The physiological meaning of these quantities is very much dependent on this experimental time which may be of the order of minutes or of the order of days. For short time periods, nutrient uptake (except perhaps for carbon) is unrelated to growth and corresponds to the ability of the organisms that are present to transport and accumulate the nutrient. Over long periods of time, nutrient uptake is dominated by the growth and multiplication processes of the organisms. At the limit if one considers an invariant elemental composition of the biomass, the specific uptake rates for all nutrients, v_S must be equal to the specific growth rate $\tilde{\mu}$ (which is virtually impossible to measure directly in nature).

e.g., for nitrogen and carbon:

$$v_N = \frac{r_N}{(PN)} = v_C = \frac{r_C}{(PC)} = \tilde{\mu}$$

This equation is not applicable to specific uptake rates obtained for short incubation times. Those can be much larger than the specific growth rate, say by a factor of 10 or so for nitrogen.

<u>Phytoplankton uptake of various N species.</u> Nitrate (NO_3^-), nitrite (NO_2^-), nitrogen gas (N_2), ammonium (NH_4^+) and dissolved organic nitrogen (DON) are all potential sources of nitrogen for phytoplankton in the sea. The concentrations of all dissolved forms of nitrogen that have been quantified are naturally very low and it cannot be overemphasized that their relative concentrations bear no relation to their relative importance as nitrogen sources for phytoplankton. For example, ammonium, which is usually near or below the limits of detection in surface waters (<1 μg-at l^{-1}), is now estimated to be the principal N source in most areas. It accounts for about 50 percent of the total nitrogen taken up in eutrophic areas and nearly 100 percent in oligotrophic areas (Dugdale and Goering, 1967; MacIsaac and Dugdale, 1972; McCarthy et al., 1977; Eppley et al., 1979).

The uptake and utilization of dissolved organic nitrogen by marine plants has been the subject of much recent research activity. It used to be commonly believed that bacteria played the major role in taking up and metabolizing DON. There is now increasing evidence that many phytoplankton species effectively compete with bacteria for some of the available DON in coastal surface waters that are normally depleted in nitrogen (McCarthy et al., 1977; McCarthy, 1972; North and Stephens, 1971; Carpenter et al., 1972; Wheeler et al., 1974). Urea and amino acids which compose but a small fraction of the natural DON are probably a significant source of nitrogen for nearshore phytoplankton. In effect this "shunt" permits a faster turnover of the limiting nutrient and the uptake may be more efficient since it can take place at high concentrations, in the immediate vicinity of the point of DON release.

One of the major difficulties in estimating the relative importance of the various N sources is that few extensive studies have included measurements of either urea or amino acids uptake and none has included measurements of both. If the total bulk uptake rate for nitrogen cannot be obtained from the sum of the bulk uptake rates of the various species

$$r_N = r_{NO_3} + r_{NO_2} + r_{NH_4} + r_{urea} + r_{AA} \quad ,$$

it must then be estimated from measurements of plankton composition and carbon uptake rate.

$$r_N \simeq \frac{PN}{PC} \cdot r_C$$

This is of course not very precise as the implied hypothesis of steady composition of the biomass may not be valid for the typical incubation time of 1 day.

Laboratory results. Laboratory studies with pure phytoplankton cultures have shown that ammonia, urea and amino acid uptake (as well as nitrate uptake which is of little interest here) all follow Michaelis-Menten kinetics with low half saturation constants: less than 1 μg-at N l^{-1} for NH_4^+; as low as 0.5 to 2 μg-at N l^{-1} for amino acids and urea. Maximum specific uptake rates measured in short-term experiments vary from more than 10 day $^{-1}$ for NH_4^+ to 1-0.3 day $^{-1}$ for urea and 1-0.1 day^{-1} for amino acids (Carpenter et al., 1972; Eppley et al., 1969; McCarthy, 1972). All such specific uptake rates can theoretically support the specific growth rates observed in nature (<1 day^{-1})

for relatively modest ambient dissolved nitrogen concentrations (ca. 1 μg-at N l^{-1}). Note, however, that not all phytoplankton seem to take up urea or amino acids and not all that do are actually capable of sustained growth with DON as the only nitrogen source.

It is generally well known that the presence of ammonium depresses considerably the uptake of nitrate by phytoplankton (Conway, 1977; Eppley et al., 1969). Similar antagonistic interactions appear to exist for other nitrogenous nutrients (McCarthy and Eppley, 1972; Wheeler, 1977; North and Stephens, 1972). These interactions are a complicated function of the relative concentrations of the various N species, of the previous nutritional status of the cells, and, thus, of the duration of the experiments. Although the available data are incomplete, the situation relevant to sewage plumes may be sketched in the following manner: local phytoplankters, conditioned by the normally nitrogen-poor environment of coastal waters, are capable of very rapid short-term nitrogen uptake. Upon encountering the bonanza of a sewage plume, they accumulate nitrogen at a very high rate initially. If several dissolved nitrogenous compounds are present, say as mixture of NH_4^+ , urea, and AAs, they probably take all of them up simultaneously, at first. Over a period of a few hours, as the nitrogen requirements of the cells become satisfied, ammonium becomes practically the only nitrogen source and other uptake mechanisms are suppressed. The rate of NH_4^+ uptake is then much lower than the initial one and is effectively controlled by the phytoplankton growth rate. Over a period of days as the ammonium concentration decreases (through uptake and/or diffusion) to less than 1-0.5 μg-at N l^{-1}, the cells may start again to use the other nitrogen sources. DON from wastewaters may thus be a significant source of nitrogen for phytoplankton in two instances: 1. initially if the waste is discharged into the euphotic zone containing a population of severely N limited phytoplankton; 2. on a regional basis, after the ammonium concentration has been reduced to near background levels.

Field studies. Although laboratory experiments provide the basic information from which one may develop a hypothetical scenario for the fate of nitrogen following wastewater disposal into the ocean, they cannot be simply extrapolated to field situations. Field data are necessary to assess directly how fast the various nitrogenous compounds are effectively taken up by the phytoplankton; one of the major complications that may arise being the possible inhibitory effects of other sewage components.

In the many bioassays which have compared phytoplankton growth in media enriched with municipal sewage and with inorganic nutrients, relative growth or carbon uptake inhibition by sewage have been observed on several occasions. In some instances, short-term inhibitory effects (lag periods) have preceded growth stimulation by sewage enrichment (Thomas et al., 1974).

A recent study of $^{15}NH_4^+$ uptake by shipboard cultures of natural phytoplankton populations off southern California compared the effect of enrichments with inorganic nutrients and with municipal sewage (MacIsaac et al., 1979). Nitrogen uptake was found to be more sensitive to "sewage inhibition" than was carbon uptake. As seen in Figure 6.15a,b, a relative impairment of NH_4 uptake was observed for sewage enrichment corresponding to NH_4^+ concentrations of 15 μM while the carbon uptake ($^{14}C\text{-}HCO_3^-$) was impaired only at the highest sewage enrichment ($NH_4^+ \approx 150$ μM). Note that in this experiment the kinetics of ammonium uptake exhibited a relatively high half saturation constant (2-5 μM).

In order to evaluate the significance of this relative inhibition of ammonium uptake [observed for dilutions of sewage into seawater that are in the range of the initial dilutions near outfalls (100 to 200)], it would be helpful to understand the cause. Unfortunately, we are left to speculate on this matter, and various toxic agents (trace metals, trace organics) from sewage provide a likely and simple explanation. An alternative explanation worth mentioning in the absence of contrary evidence, is that uptake of organic nitrogen (which was not measured in the experiments) may be taking place in this concentration range and could partially inhibit ammonium uptake in an effect symmetrical to the inhibition of DON uptake by NH_4^+. Regardless of the underlying mechanism, two simple facts tend to minimize the importance of this inhibition: 1. it was only observed at relatively high concentrations of sewage and would be reversed as further dilution of the plume was obtained; 2. it was only a relative inhibition; the actual uptake rate was still much higher than that obtained at lower (natural) ammonium

Figure 6.15a Inhibition of NH_4^+ bulk uptake rate due to sewage enrichment (MacIsaac et al., 1979).

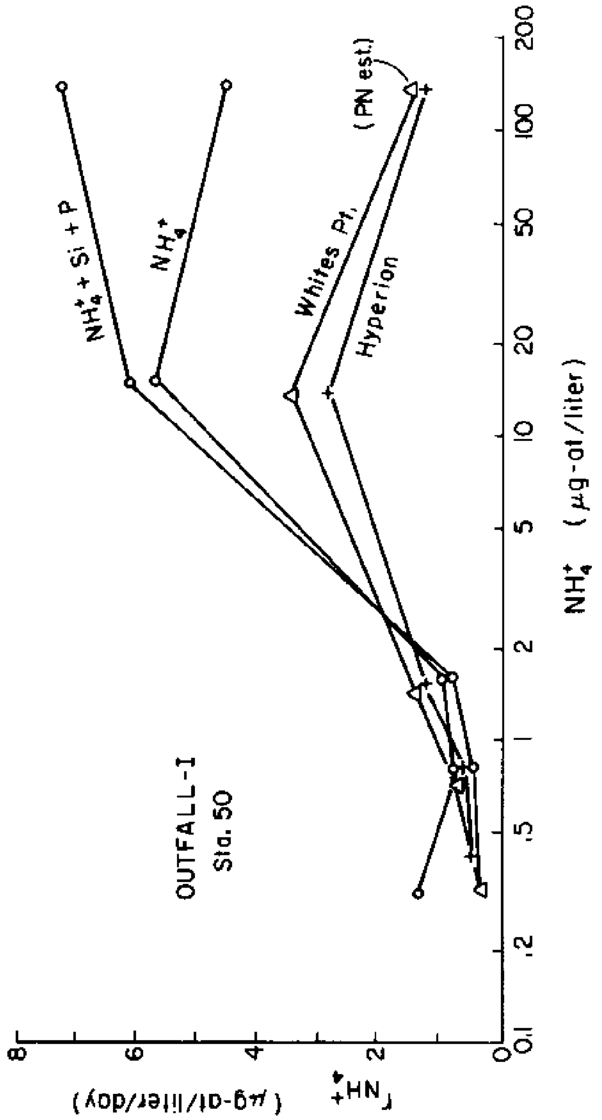
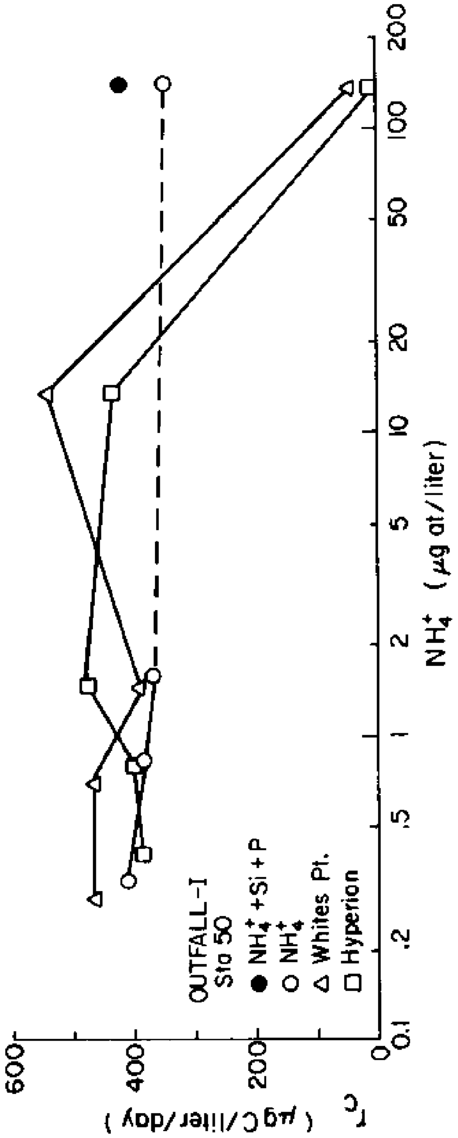


Figure 6.15b Inhibition of carbon bulk uptake rate due to sewage enrichment (MacIsaac et al., 1979).



concentrations and was reduced only compared to a potential uptake rate measured with inorganic nutrient enrichment. If this uptake rate (ca. 3 μg-at N l^{-1} day^{-1}) could be maintained, phytoplankton uptake per se would eliminate the ambient ammonium in the initial plume in 5 days.

Another ^{15}N study near the Los Angeles Whites Point outfall has documented the uptake of urea by phytoplankton (McCarthy, 1972). This study is particularly intriguing because, although the primary productivity and the standing crop were markedly elevated in the vicinity of the outfalls, the nutrient concentrations were not (Eppley et al., 1972). Table 6.9 presents some of the data for three stations. The total bulk uptake rates were significantly enhanced near the outfall while the specific uptake rates were roughly the same at all stations. This is consistent with the fact that the outfall station supported a higher standing phytoplankton crop growing at about the same rate as that at other stations. The relatively low uptake rates for nitrate and urea at station 4 may well reflect an inhibition due to the unusually high ammonium concentration at that station. Turnover rates of all nutrients were rapid at most stations (1-3 days, see column 6). (Evidence that the significant urea uptake was not the result of bacterial hydrolysis was obtained through a number of ancillary observations.) The relatively high ratio of carbon uptake rate to the sum of the measured N uptake rates (column 7), particularly at the station near the outfall, could be evidence that other organic N sources may also have contributed significantly to the total nitrogen uptake.

The absence of measurable N enrichment in waters near waste disposal sites is not typical. For example, Figure 6.16 shows two regions of NH_4^+ enrichment in the Santa Monica Bay: the 9 g-at l^{-1} value is due to a petroleum refinery outfall, while the broad maximum at 30 m is attributed to sewage (Eppley et al., 1979). In this study more than 50 percent of the stations in Santa Monica bay and less than 4 percent of the stations outside of it, had NH_4^+ concentrations in excess of 1 μg-at l^{-1}. However, the same dynamic situation with very high turnover rates of the nitrogenous nutrient pools was observed. As a result the massive waste input in Santa Monica Bay has been estimated to contribute only some 10 percent of the total ammonium flux. The rest is made available to phytoplankton by various regeneration processes.

Figure 6.16 Ammonium concentration, μg-at liter^{-1}, in a section through Santa Monica Bay, December 1975. Note log scale for distance offshore (Eppley et al., 1979).

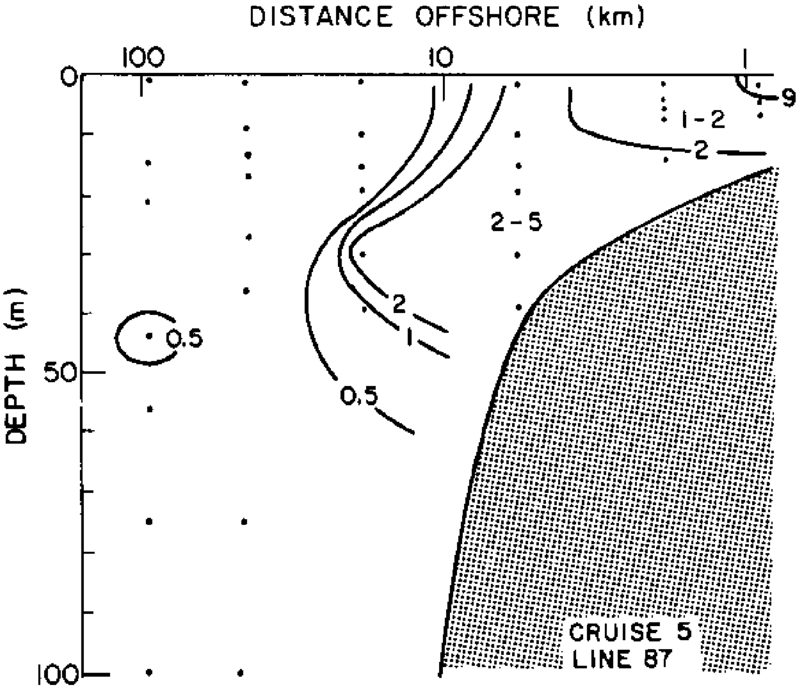


Table 6.9 Observed Soluble Nitrogen Concentrations and Fluxes During a Cruise Off Southern California (June - July 1970) (Adapted from McCarthy, 1972)

Station	Depth (m)*	Concentrations (μg-at N l^{-1})			Specific uptake rates v, hr^{-1}			Bulk uptake rates r, μg-at N $l^{-1}day^{-1}$			% Available N† uptake/day			Relative uptake rates $r_C/(r_{NO_3^-} + r_{NH_4^+} + r_{urea})$ $
		NO_3^-	NH_4^+	Urea	NO_3^-	NH_4^+	Urea	NO_3^-	NH_4^+	Urea	NO_3^-	NH_4^+	Urea	
#1 Off La Jolla near shore	1	0.26	0.00	0.39	3.79	1.11	2.73	0.288	0.065	0.163	64.1	70.1	37.3	11.0
	12	1.57	0.23	0.54	2.79	1.98	1.31	0.278	0.185	0.120	5.0	57.8	18.8	
#4 La Jolla	1	0.00	0.63	0.07	0.23	7.77	0.13	0.005	0.163	0.002	50.2	21.3	1.4	8.8
	16	1.56	0.19	0.25	0.91	4.40	0.54	0.036	0.168	0.022	1.4	59.2	6.1	
#19 Off Whites Point Outfall	1	0.10	0.14	0.40	3.09	0.86	2.35	0.444	0.125	0.338	42.0	53.9	68.0	14.7
	6	0.10	0.15	0.15	2.59	0.98	0.92	0.422	0.166	0.154	40.0	68.6	62.3	

*1 m 87% incident light
12, 16, 6 m 20% incident light

†initial concentration plus isotope addition

$ to be compared with a typical C/N ratio PC/PN 8

Regional Impact of Nitrogen Discharges

The oceanographic studies in the Whites Point area discussed above provide quantitative evidence of what is intuitively expected: the regional enrichment due to municipal discharge results in a high rate of primary productivity (i.e., phytoplankton growth) and this in turn insures fast utilization of the waste nitrogen. This situation may be described as a case of eutrophication. However, one should not be misled by the negative connotations that this word evokes, mostly in the context of freshwater lakes. Not all eutrophic waters need be distrophic, and one of the important questions to be answered with respect to municipal waste discharge in coastal waters is whether or not nitrogen fertilization can ultimately result in oxygen depletion due to algal decomposition. The concept of PDOD (phytoplankton dissolved oxygen deficit) has been proposed to deal with this question in an engineering approach (Officer and Ryther, 1977). If N is limiting, PDOD is related to nitrogen concentration through a direct stoichiometric relationship. According to simple models, PDOD can be more important than BOD in causing oxygen depletion near sewage outfalls. Relationships between water flushing time and waste loading rates have been defined to predict roughly the worst possible oxygen depletion. It should be noted that PDOD, unlike BOD, is merely a potential oxygen demand that is exercised only if the normal trophic relationships--through which photosynthesis is roughly balanced by grazing and respiration--are grossly deteriorated. No anoxic event in coastal waters has yet been unambiguously related to wastewater discharges. It is unclear to what degree waste discharges were significant in the infamous anoxic event in the New York Bight in 1976. If they were significant it may have been through their indirect influence on the nature of the ecosystem (mostly the planktonic species), not through a simple fertilization mechanism.

A word of caution is also warranted in the other direction: nitrogen enrichment may have an effect on the primary production quite in excess of that predicted through stoichiometric arguments. Owing to the rapid turnover of the nitrogenous nutrients, which has been discussed earlier, nitrogen fertilization could, in principle, be magnified several times over. It remains that the naturally fast turnover rate of dissolved nitrogen in oceanic surface waters seems to confer a high degree of homeostasis to the cycle of this element. When studied quantitatively, the impact of municipal waste on the N-cycle has been found to be small, even in waters with restricted circulation such as the Chesapeake Bay (McCarthy et al., 1977).

TRACE METALS

Due to improved analytical and sampling methods over the past few years, it has become apparent that unpolluted coastal waters contain very low concentrations of most metals with molecular weights higher than that of calcium. For example, the concentrations of metals such as lead, cadmium, copper and zinc are now known to be some one to three orders of magnitude lower than previously thought (Bruland et al., 1978). This fact raises new concern that anthropogenic inputs of trace elements to coastal waters may contribute significantly to the geochemical cycle of such elements and result in elevated concentrations.

Municipal wastewaters are one of the major anthropic sources of trace metals, particularly in areas such as Los Angeles where industrial wastes are mixed with domestic wastes (Table 6.10). In places with intensive dredging operations, such as New York City, sewage and sludge, though not a dominant fraction of the total metal load to the bight, still represent a sizeable input (Table 6.11). Note that the percentages shown in Tables 6.10 and 6.11 should be taken with some circumspection, as not all metal fluxes to New York and southern California bights have been precisely quantified.

A rough estimate of the impact of waste metal loads in the vicinity of disposal sites can be obtained by comparing metal concentrations in wastewater to those in unpolluted coastal waters (Table 6.12). Although the source and the treatment of the waste are quite different in New York and in Los Angeles, the total trace metal concentrations are comparable and all in excess of one thousand times the natural concentrations. Concentrations in sludge are even higher. As a result significant increases in total metal concentrations are expected, and observed, in the vicinity of ocean discharges of municipal wastes.

Speciation of Trace Metals

There have been very few studies of the chemical speciation of trace metals in municipal waste. Even

Table 6.10 Contribution by Source to Trace Metal Loads in the Southern California Bight (SCCWRP, 1973)

	Percent of Total Input					Total Mass Emission Rates (tons/year)
	Wastewater Discharge	Surface Runoff	Vessel Coating*	Ocean Dumping	Rainfall & Dry Fallout	
Ag	83.3	5.6	---	8.3	---	18
Cd	78.3	1.4	0.14	20.3	---	69
Co	13.6	22.7	---	63.6	---	22
Cr	92.3	3.6	0.14	4.0	---	700
Cu	40.5	1.3	27.6	2.0	28.6	1,400
Fe	18.6	80.4	---	0.87	0.12	32,000
Hg	17.6	0.59	23.5	8.8	47.1	17
Mn	12.9	23.1	---	3.5	60.5	790
Ni	78.6	4.3	---	7.0	10.1	400
Pb	15.8	6.7	---	2.1	74.7	1,300
Zn	40.0	2.4	3.9	1.3	52.4	4,200

*Including vessel antifouling paints, primers, and spent fuel residues.

Table 6.11 Contributions by Source to Trace Metal Loads in the New York Bight (1972-1974) (Mueller et al., 1976)

Percent of Total Input

	Barging			Atmospheric	Wastewater		Runoff			Total Mass Emission Rates
	Dredged Material	Sewage Sludge	Acid + Chemical Wastes		Municipal	Industrial	Gage	Urban	Ground-water	(tons/year)
Cd	80.4	1.6	0.13	2	5	0.6	5	5	0.001	880
Cr	46.5	1.5	2.1	1	22	0.8	10	16	0	1,800
Cu	45.4	5.1	0.39	3	11	9	10	16	0.006	5,000
Fe	-----------79--------------------			3	5	0.5	6	6	0.01	84,000
Hg	4.5	4.5	0.07	-	71	2	13	5	---	110
Pb	37.4	5.7	1.3	9	19	3	6	19	0.004	4,700
Zn	22.6	5.5	0.78	18	8	2	21	22	0.009	12,000

Table 6.12 Average Total Trace Metal Concentrations for Sewage in Some Major Urban Areas

	New York Average Wastewater[1] (mg/l)	Southern California Average Wastewater[2] (mg/l)	Effluent with Large Industrial Input[2,3] (mg/l)	Effluent with Low Industrial Input[2,4] (mg/l)	Coastal Oceanic Surface Water[5] (μg/l)
Ag	---	0.011	0.013	0.015	0.01
As	---	0.007	0.007	0.014	---
Cd	0.012	0.026	0.026	0.017	0.004
Cr	0.057	0.376	0.750	0.028	0.1
Cu	0.105	0.293	0.41	0.086	0.08
Fe	0.70	---	---	---	---
Hg	0.025	0.0017	0.0014	0.00092	0.001
Mn	---	---	---	---	0.1
Ni	---	0.227	0.320	0.276	0.2
Pb	0.190	0.129	0.220	0.054	0.005
Se	---	0.016	0.011	ND	---
Zn	0.185	0.672	1.32	0.16	0.01

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[1] Mueller et al., 1976
[2] Schafer, 1977
[3] LACSD
[4] Oxnard
[5] Bruland et al., 1978

simple data on partitioning between filterable and "soluble" fractions are not widely available. Notable exceptions for which extensive studies have been performed are the two major municipal waste treatment plants of the Los Angeles area. Much of the discussion that follows is undoubtedly biased by this geographical imbalance of available information and caveats are in order.

Figure 6.17 (a-c) presents data on the filterable fractions of some nine metals in the Los Angeles City plant (Hyperion). These metals have been studied because of their high concentrations, possible biological impacts and the availability of analytical techniques. The striking general feature of the data is the very high degree of association of the trace elements with the particulate (filterable) fraction. A similar result is observed in the primary effluent of Los Angeles County where better than 90 percent of Ag, Cd, Cr, Cu, Fe, Pb, Zn and Hg are retained by 0.45 μM filters and only Ni, Co and Mn are present in the soluble fraction in large proportions (Galloway, 1972; Morel et al., 1975). In digested primary sludge all metals studied are almost totally found in the filterable fraction (Figure 6.17c).

Secondary treatment which is extremely efficient in removing the suspended solids from the waste (90 to 95 percent at Hyperion's secondary treatment facility*) removes, de facto, a large fraction of the metals. However, the efficiency of removal is better for some metals than for others (Fe>Cr>Cu>Hg>Zn>Pb>Cd>Ni>Mn), the less soluble metals being in general more efficiently removed as expected (Chen et al., 1974). In terms of speciation, secondary treatment results in a much higher fraction of soluble to particulate metals (Figure 6.17b), in some instances the absolute soluble metal concentration being in fact increased by the treatment.

In all cases nickel and manganese are observed to be highly soluble (30 to 80 percent) in sewage effluent and sludge. On the basis of limited data, a similar result appears applicable to cobalt. Spurious measurements of high solubility have been obtained in various instances for various other metals; e.g., lead in Figure 6.17a.

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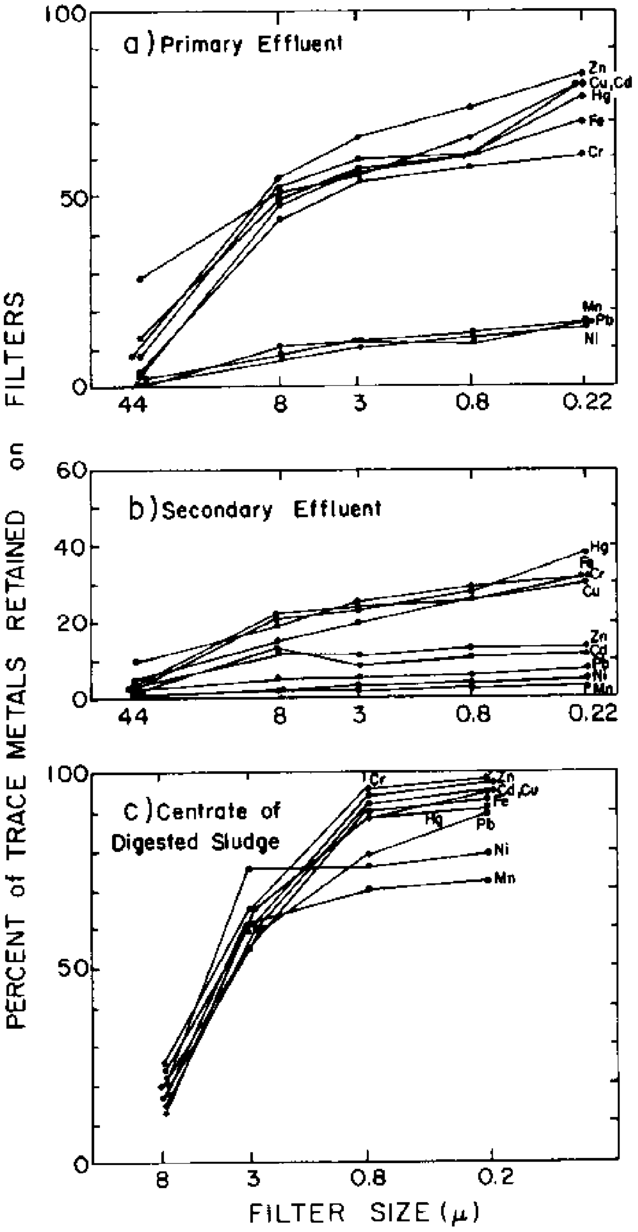
* Only a minor part of Hyperion flow gets secondary treatment.

Figure 6.17 Percentage of trace metals in waste effluent retained by indicated size of membrane filter (Chen et al., 1974).



In the absence of more detailed analytical data on metal speciation in municipal waste, equilibrium models provide some information on the likely important metallic forms--the thermodynamically stable species. A few such models, similar to that of Table 6.1, have been calculated by choosing a redox potential to match the experimental partitioning of nickel between the solid and aqueous phases (Morel et al., 1975; Faisst, 1976). The resulting electron activities are lower (more oxidized) for the final Hyperion effluent that receives partial secondary treatment (ca. pE = -3.0) than they are for the Whites Point effluent which receives only primary treatment (ca. pE = -3.5). Digested sludges are calculated to have even more reduced redox potentials (ca. pE = -4.5).

According to these calculations, metals such as Cu, Cd, Pb, Zn and Hg which form very insoluble sulfides should be present exclusively as solid sulfides in all cases. Nickel is kept partly in solution by formation of a cyanide complex while the rest precipitates as nickel sulfide. Chromium is precipitated as the hydroxide of Cr(III) and, depending on the pH, a sizeable fraction may remain soluble as hydroxo complexes. Manganese is calculated to be soluble as Mn^{2+}. (By including adsorptive surfaces in the model one can account for some fraction of the manganese in the solid form.)

The speciation of iron is a critical factor in these models. Depending on pH, pE and the Fe/S(-II) ratio, the iron may be present as a ferric hydroxide, as a mixture of ferrous sulfide and various ferrous complexes (as in Table 6.1), or as a combination of ferric and ferrous species. When the total iron is in excess of the total sulfide, the equilibrium between $Fe(OH)_3(s)$ and FeS(s) effectively buffers the redox potential of the system.

There is a modest amount of analytical data supporting the results of these model calculations. For example, it has been verified experimentally that chromium is indeed in the +III state in wastewaters (Jan and Young, 1978). Experimental results on metal partitioning between the soluble and solid phases (e.g., Figure 6.17) are roughly in agreement with the calculations. The worst discrepancy concerns the soluble fraction of the metals precipitated as sulfide solids: up to 20 percent of Hg, Cd, Pb, Cu, Zn are measured in the filterable fractions while less than 1 percent are predicted to be soluble. In addition to inaccuracies in equilibrium constants and model inputs, two principal explanations appear likely: 1. filtration through a 0.45 μm filter is hardly an absolute separation technique, and the relatively high "soluble" concentrations measured actually correspond to a colloidal fraction that passes the filter. This is evidenced in Figure 6.17. As the filter size is decreased to 0.2 μm, the fraction of filtered metals is still increasing and it could be extrapolated to virtually 100 percent, for some metals, for filter sizes ca. 0.02 μm.

2. The model does not consider some important soluble species. Calculations with unspecific model organic ligands with representative functionalities fail to incease sufficiently the calculated soluble concentrations. Rather strong complexing agents would thus have to be present in the waste if organic complexes were to account for the soluble metals. Alternatively it now appears that metal polysulfide complexes may be much more important than previously thought. Revision of thermodynamic data to include these possible complexes may increase sensibly the predicted soluble fractions of metals in sulfide dominated systems such as sewage sludge and wastewater.

Another major drawback of thermodynamic models is their completely abiotic nature. In a study of bench-scale anaerobic digesters, it has been estimated that 20 to 50 percent of various trace metals (Hayes and Theis, 1978) was associated with the bacterial mass while the remainder was in the inorganic solid fraction. Since the precipitation of metal sulfides increases sharply with higher pH and lower temperature, it can be expected that the metal partitioning between cells and inorganic solids would be highly dependent on the pH and temperature of the digesters. This could account for large differences in the behavior of metals contained in the sludge of various treatment plants and for temporal variations at a given plant.

Fate of Metals in the Water Column

Thermodynamic and kinetic considerations. As the waste is dispersed into seawater, the trace elements are diluted and concomitantly subjected to changes in all principal chemical variables (I, pH, pE) as discussed in the first section. From the point of view of thermodynamics--not necessarily of kinetics--the dominant effect among these is the change in redox potential from that of a highly reduced environment to the oxic conditions of seawater. As shown in Table 6.1, few major changes in metal speciation occur when sewage comes to equilibrium with 125 times its seawater volume, assuming that no redox reaction is taking place. Dissolution of $Cr(OH)_3$, FeS and of some of the ZnS are the only major changes due to the dilution of the model sewage.

In contrast, the effect of oxidation on metal speciation is dramatic (Table 6.1, Part 6). Oxidation of sulfide results in dissolution of all sulfide solids which are replaced by various soluble metallic species. In the model system with dilution of 125 and a completely oxic redox potential (pE = 12), iron and manganese oxides are the only insoluble metallic forms. This result would undoubtedly be markedly modified by considering adsorption processes: the affinity of most metals for hydrous ferric and manganese oxides is such that they are expected to be found at least partly as adsorbates instead of soluble forms.

To understand the chemical changes to which trace metals are subjected in the water column, it is then critical to understand the kinetics of oxidation. For example it is known that the oxidation of Cr(III) to Cr(VI) is very slow (Jan and Young, 1978). The predicted solubilization of chromium as CrO_4^{2-} is thus not expected to take place fast enough to keep Cr from sedimenting with the rest of the waste particulate fraction.

The kinetics of sulfide oxidation are particularly important to the fate of trace metals since sulfide is thought to control the solubility of most metals. Laboratory studies of dissolved sulfide oxidation demonstrate approximately first order kinetic dependence on dissolved oxygen and sulfide concentration (O'Brien and Birkner, 1977). Transition metals, particularly nickel, act as catalysts, while nitrogenous compounds (CN^-, NH_4^+ , organics) are inhibitors. As the sulfide in waste seems to be controlled by precipitation with iron, a critical question is that of the relative rates of FeS dissolution compared to that of direct FeS oxidation (oxidative dissolution). Under conditions prevalent in seawater, it appears that direct oxidation of the solid is much faster than non-oxidative dissolution (Pankow and Morgan, 1980). The mechanism of FeS oxidation appears to be oxidation of the surface sulfide by molecular oxygen (Nelson et al., 1977).

First order kinetic dependence on O_2 (for $O_2 < 10$ mg l^{-1}) and on surface area is noted as well as a slight decrease with increasing pH. A temperature increase of 10°C doubles the rate of oxidation. Nickel at concentrations $>10^{-5}$M has a dramatic catalytic effect on the reaction. Concentrations of chloride in excess of 0.1M severely limit the oxidation of sulfide past S^0 but have no effect on the rate of initial oxidation. The oxidation of Fe(II) and the formation of hydrous ferric oxide (or γFeOOH) is fast. The dominant reaction in seawater can thus be written:

$$FeS(s) + \frac{3}{4} O_2 + \frac{1}{2} H_2O \rightarrow S^0 + FeOOH(s)$$

Experiments with natural sediments and with synthetic FeS have shown complete oxidation of FeS in seawater in about 3 hours. There seems to be little doubt that sulfide oxidation takes place in the plume following the initial dilution, although it appears that no direct verification of this fact has been obtained. The important question here is what is the effect of such oxidation on the speciation of sewage trace metals? A few experimental studies with sewage and sludge in the Los Angeles area provide relevant and somewhat contradictory information.

Laboratory results. Experiments with Hyperion digested sludge diluted with aerated seawater showed that a sizeable fraction (>20 percent) of all sulfide-forming metals, except copper, were released to the water within 5 days (Figure 6.18a). Chromium and iron showed little release even over 5 weeks. Similar results were obtained with mixtures of wastewater and seawater: sulfide-forming metals (Cd, Cu, Ni, Pb and Zn) were released to a large degree from the solid phase while oxide-forming metals (Fe, Mn, Cr) remained precipitated (Rohatgi and Chen, 1975).

By contrast, similar experiments with Los Angeles County digested sludge and primary waste effluent showed no measurable release of any metal except nickel after mixing with seawater and aerating for up to 1 month (Faisst, 1976). (A rapid--presumably short-term--release of Mn has been reported upon mixing wastewater with seawater). In contrast, nickel release was relatively rapid, reaching equilibrium within 3 days (Figure 6.18b).

Since there appears to be no difference in experimental procedures that would explain these differences in waste metal release to aerobic seawater, the difference is presumably in the nature

Figure 6.18a Release of trace metals upon dilution of Hyperion sludge with seawater (Data from Rohatgi and Chen, 1975).

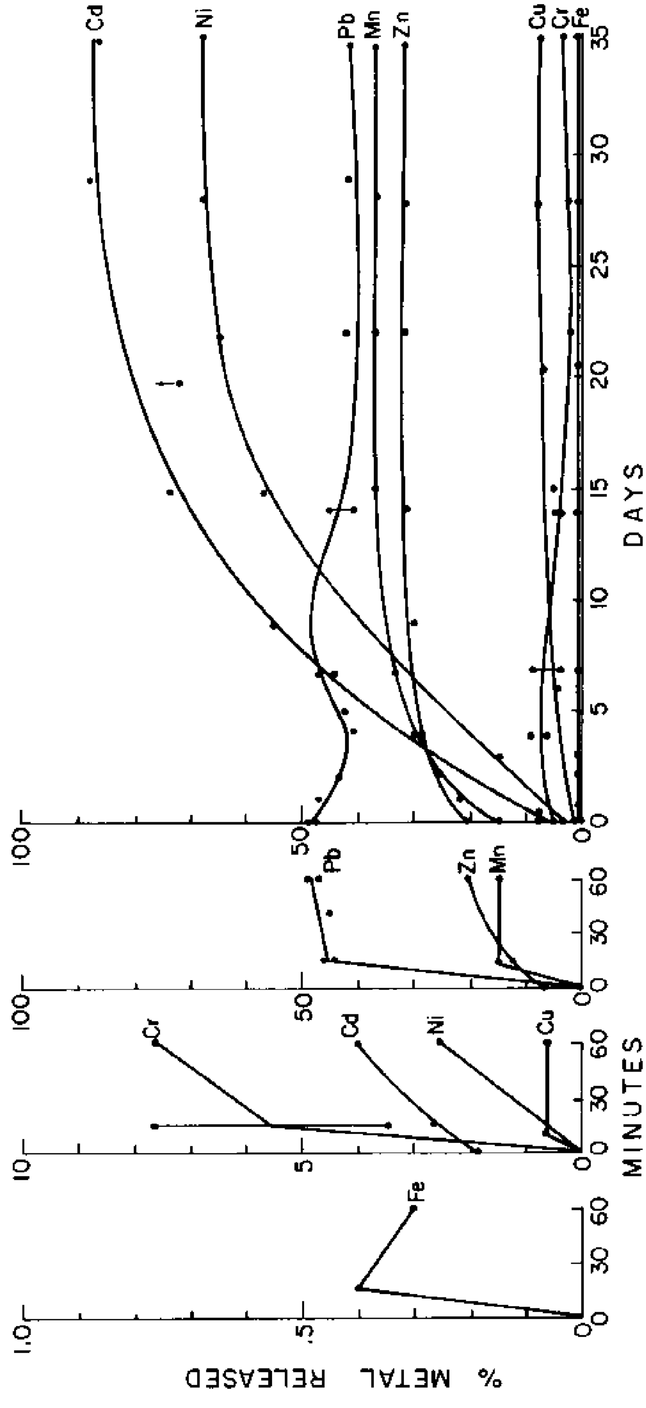
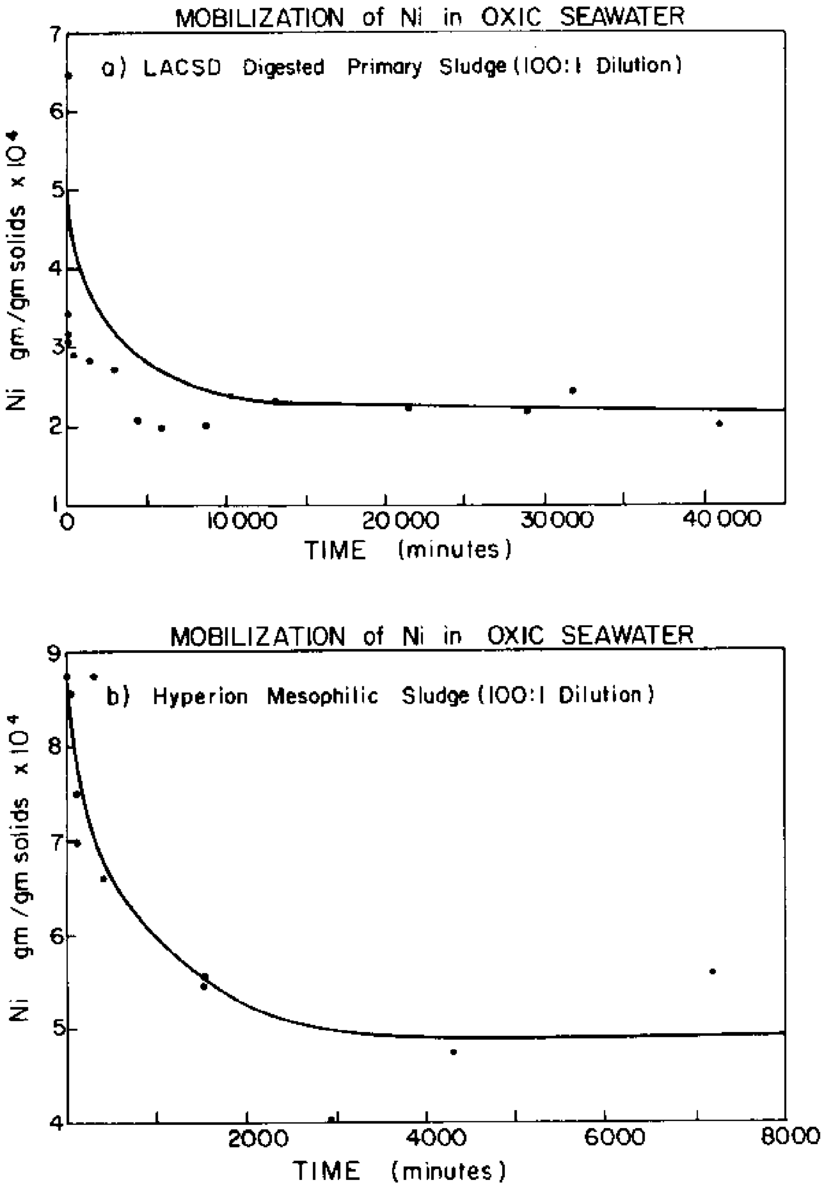


Figure 6.18b Mobilization of Ni away from the sludge particles during mixing in oxic seawater (Faisst, 1976).



of the waste itself. The explanation probably lies in part in the kinetics of sulfide oxidation. Ferrous sulfide oxidation takes place relatively fast, and this is demonstrated by the changing color of the solid fraction and the increase in soluble iron during the first 1/2 hour. While iron is precipitated as a hydrous oxide, nickel, which catalyzes the oxidation reaction (and is probably present partly as a solid solution with FeS) is released into solution as observed in all experiments. For all other metals, the dissolution of the sulfides is presumably very slow under such conditions and apparently does not take place in the time of the experiments. The large metal fractions that are released from the particles of the Hyperion plant may correspond to the fractions contained in the bacterial mass: as the cells die off, there is no sulfide left in solution to precipitate the metals, and these remain soluble. Differences in digestion procedures (particularly temperature and pH) could well account for differences from 0 to 100 percent of some metals in the biomass. Many other explanations are of course possible, including the presence or formation of complexing agents in solution or the presence of particular inhibitors of oxidation reactions.

Field data. In any case, it appears that release of trace metals to the water column upon disposal of the waste occurs in a matter of days for most metals (nickel being the notable exception) and the kinetics vary from treatment plant to treatment plant as well as from metal to metal. A rare direct measurement of metals in the sewage plume off Whites Point supports this general assertion (Table 6.13). While the concentrations of Cd, Cr, Cu and Ni are markedly enriched in the particulate fraction, the dissolved concentrations are only slightly above those of the control seawater (Young and Jan, 1975). Nickel and copper are the most enriched in the filterable fraction. On the basis of the preceding discussion, this is expected for Ni, but not for Cu. This may be due to the formation of organic complexes of copper. Taken at their face value, these results are truly remarkable: in the midst of the sewage plume from a major municipal outfall receiving large industrial inputs and after no more than a primary treatment, the soluble metal concentrations are only marginally above the seawater background.

Table 6.13 Median Concentrations of Dissolved (<0.4 micron) and Particulate (>0.4) micron) Metals in LACSD Municipal Wastewater and in Seawater collected 24 February 1975 around the Whites Point Submarine Outfalls (Young and Jan, 1975).

	LACSD Effluent*	Outfall Plume			Control Seawater
Station		120	121	122	123
Depth (m)	-	16	26	44	25
Temperature (^{o}C)	24.4	10.60	10.72	10.65	11.70
Attenuation (% per m)	99	67	61	70	5
Suspended solids (mg l^{-1})	290	2	1.5	2	0.05
NH_3 mg l^{-1}	39	0.21	0.33	0.21	0.015
Cadmium µg l^{-1}					
Dissolved	2	0.06	0.08	-	0.05
Particulate	36	0.17	0.09	0.18	0.02
Chromium µg l^{-1}					
Dissolved	35	0.50	0.18	0.24	0.23
Particulate	640	2.0	1.3	1.9	0.03
Copper µg l^{-1}					
Dissolved	25	0.61	0.49	0.26	0.10
Particulate	480	1.2	0.89	1.4	0.02
Nickel µg l^{-1}					
Dissolved	180	1.2	0.72	1.0	0.29
Particulate	150	0.23	0.18	0.26	0.02

*Primary, plus centrate from centrifugation of digested sludge.

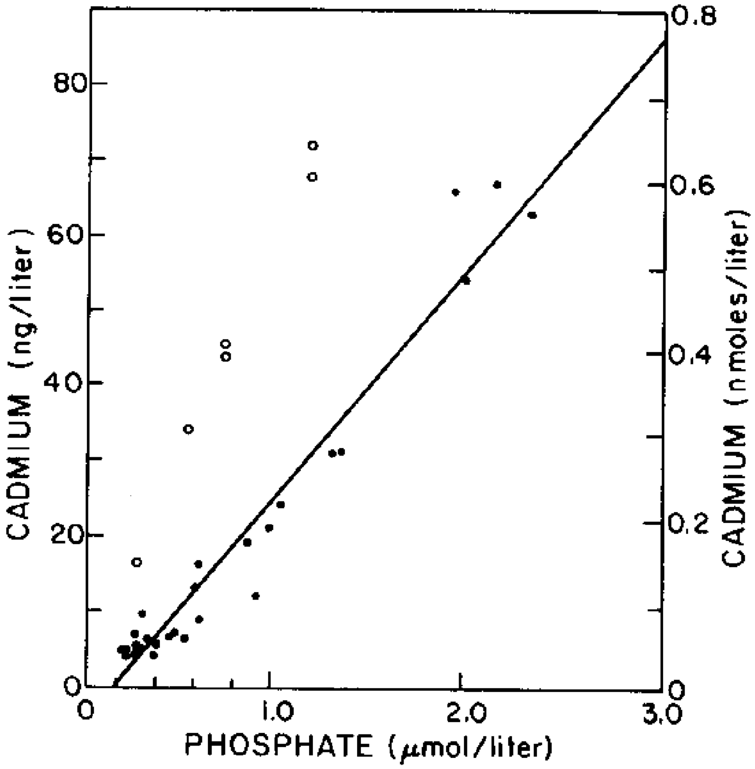
Given the experimental difficulties associated with trace element analysis in seawater, it is then not surprising that there is practically no experimental evidence for regional trace metal enrichment in the water column near waste disposal sites. There exists, nonetheless, one set of data demonstrating regional cadmium enrichment in the waters off Whites Point (Martin et al., 1976). Figure 6.19 shows how the ratio of Cd to PO_4 concentrations for samples collected off Palos Verdes deviate markedly and systematically from the Cd/PO_4 ratio in unpolluted seawater. Note that the cadmium concentrations _per se_ (presumably largely in the particulate fraction) are within the natural variability for seawater. The enrichment due to waste sources becomes evident only when Cd and PO_4 concentrations in the same samples are compared (and the analytical and sampling techniques are pushed to their limits). This serves to illustrate both that the enormous dilutions of waste in coastal waters result in concentrations of trace metals that are within the natural concentration ranges, and that we need to understand better the geochemistry of these elements (what causes the correlation between P and Cd) before we can evaluate cogently the long-term potential impact of their disposal.

Uptake by the plankton. As demonstrated in a number of recent studies, the uptake of trace metals by planktonic organisms is largely controlled by the free metal ion concentrations. For example, the incorporation of copper, cadmium and zinc by various algae has been shown to depend on the free concentrations of Cu^{2+}, Cd^{2+} and Zn^{2+} in the surrounding medium (Sunda and Guillard, 1976; Anderson and Morel, 1978; Anderson et al., 1978). For zooplankton the situation is of course more complicated, as ingestion of particles could, in principle, contribute largely to metal uptake. Although our knowledge in this matter is limited, the available evidence indicates that ingestion is not normally a major route for metal uptake by zooplankton (Wright, 1978; Renfro et al., 1975; Andrew et al., 1976; Hall, 1978). Intracellular concentrations in some species appear in fact to be determined, as they are in phytoplankton, by free metal ion concentrations in the water.

From the data presented above, it appears that the total _soluble_ concentrations of metals, let alone their free ion concentrations, are not markedly

Figure 6.19 Correlation between cadmium and phosphate concentrations in seawater (Martin et al., 1976).

(•) Surface samples off Baja California
(∘) Stations in the southern California Bight



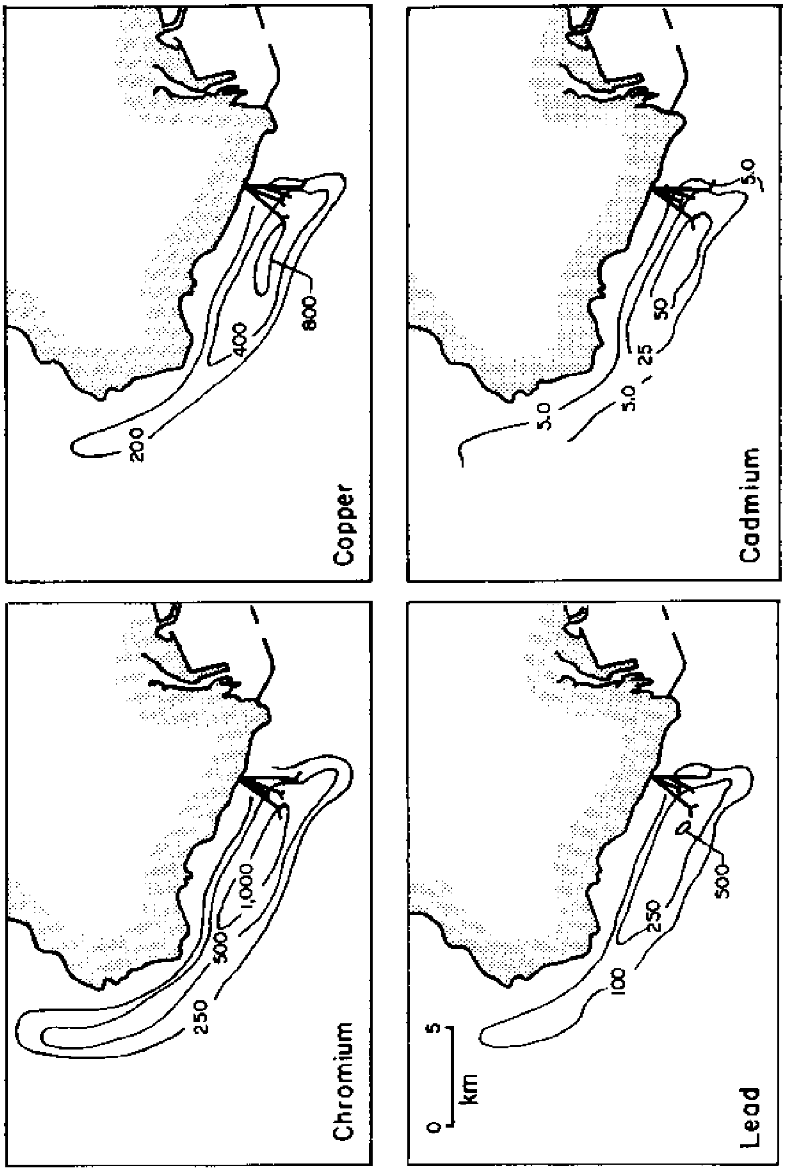
enriched in the vicinity of municipal waste discharges. One then does not expect uptake by planktonic organisms to be a major process in the fate of waste trace metals. Since the natural free metal concentrations are only marginally, if at all increased by the presence of the waste (in some cases, they may in fact be decreased through complexation, adsorption or precipitation), they should not be enriched in the organisms. No more than a few percent of the total metals are normally associated with the biota in unpolluted coastal waters (Martin and Knauer, 1973).

One cannot overemphasize that, except in the case of specific organo-metallic complexes (e.g., methylmercury), trace metals are not subject to "biomagnification"; i.e., they are not found at higher concentrations in organisms at higher trophic levels in the food web.

Fate of Metals in Proximal Sediments

Trace metal enrichment is commonly observed in coastal sediments adjacent to the sites of disposal of municipal waste. Such enrichment is one of the most obvious and dramatic manifestations of waste disposal activities and it may well be also the reason for their major biological impact even if only a small percentage of the waste constituents are actually retained in proximal sediments. Studies of trace metal concentrations in the sediments of the New York and California bights demonstrate marked areas of enrichment in both. The situation in New York is complicated by the multiplicity of sources: sewage of various origins enters the Bight from New York Bay, the New Jersey and the Long Island coast, and a variety of other waste material (municipal sludge, dredge spoil, industrial waste, etc.) is dumped in designated areas of the Bight by barging operations (Segar and Cantillo, 1976). In southern California the picture is relatively clear, demonstrating point sources at the major municipal outfalls (Galloway, 1972). This is illustrated in Figure 6.20 which shows contour maps of metal concentrations in the sediments off Palos Verdes. This simplicity makes the major California outfalls particularly good examples for the study of metals in proximal sediments.

Figure 6.20 Concentration of isopleths (mg/dry kg) of trace metals in the top 5 cm of sediments off the Palos Verdes Peninsula, 1975 (Hershelman et al., 1977).



Sedimentation. The waste material that composes the polluted sediments in the vicinity of disposal sites is obviously the material that sediments fastest--due to either coagulation or settling characteristics--since the slower sedimenting fractions are advected away. On this basis, it would be interesting to elucidate the composition of the various fractions of the waste as a function of their sedimentation kinetics. There have been a few sedimentation column experiments for trace metals in sewage and sludge, and the results shown in Figure 6.21 and 6.22 are somewhat inconclusive. To a first approximation, there is no difference in metal concentrations among the various fractions (i.e., the metals all sediment at approximately the same rate as the total suspended solids). However, the data are quite noisy and contain suggestions that some metals in some wastes may be enriched in the fast sedimenting fractions (e.g., Pb in L.A. County sludge) while in other cases they may be enriched in the slower sedimenting fractions (e.g., Cr in L.A. County sludge). As will be discussed later, even very small differences in sedimentation kinetics among metals could result in marked relative enrichment in the local sediments. (Such enrichments of one metal over another compared to the waste source have been observed, and we shall attempt to offer an adequate explanation for this observation.) It remains, however, that the sedimentation characteristics of trace metals are, on the average, similar to those of the largely organic waste particles with which they are associated, and this should be reflected in the distribution of metal concentrations in the sediments near disposal sites. Note that, given average displacement current velocities in excess of 1 cm s^{-1} (over several tidal cycles), the waste material deposited within a few kilometers of the outfalls must have settled out of the water column within a few days of disposal.

Dissolution of sedimented metals: Laboratory data. According to our discussion of the fate of metals in the water column, the waste metals that reach the nearby sediments within a day or so after disposal are probably in the same chemical forms--mostly solid sulfides--as those in the waste itself. The most notable exception is Fe which should be oxidized, at least partly. In the region near the disposal sites where the influx of organic matter maintains anoxic conditions, the sulfide-forming metals are not expected to be oxidized or dissolved

Figure 6.21 Settling velocity distribution of 24 hr LACSD sewage composite (Morel et al., 1975).

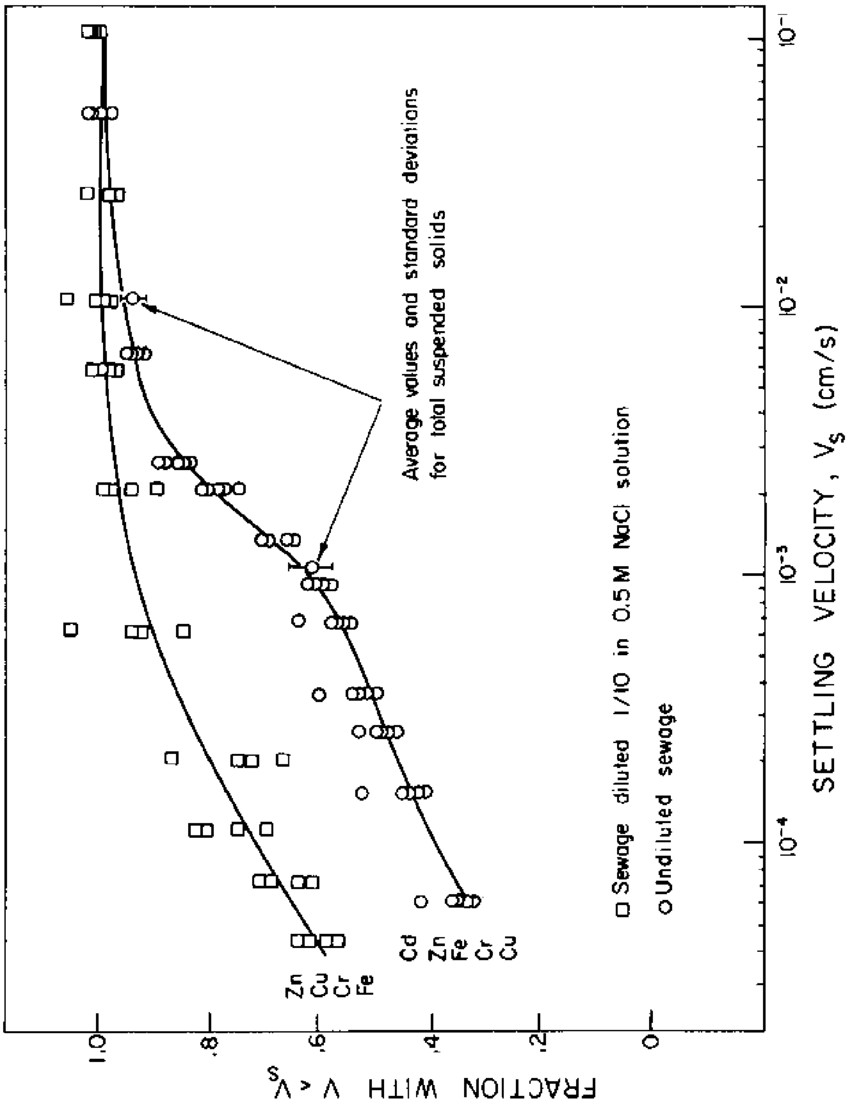
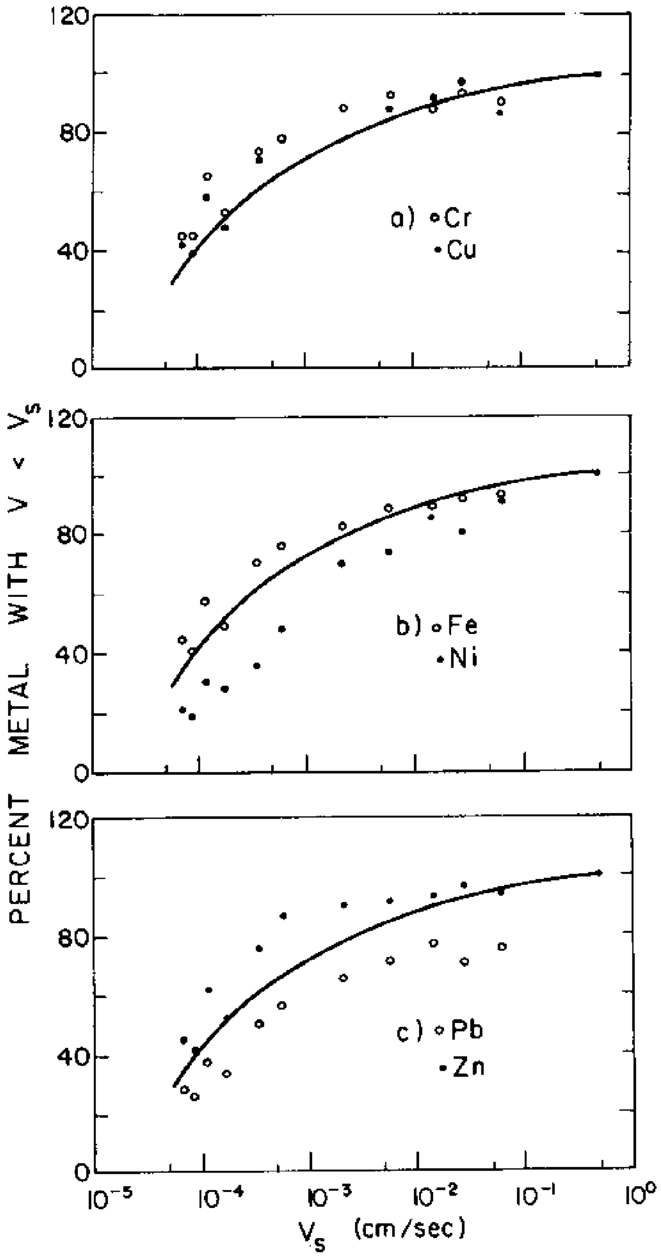


Figure 6.22 Behavior of filterable metals during sedimentation of a 500:1 dilution of LACSD sludge in seawater. Solid curve is fitted from total solids data (Faisst, 1976).



and iron should be reduced again and transformed in part into FeS. Both Fe and Mn should be solubilized, at least partly, into their +II states.

Laboratory experiments with sewage polluted natural sediments and carefully controlled redox conditions have verified these thermodynamic expectations (Lu and Chen, 1977). As seen in Figure 6.23, under reducing conditions, Fe and Mn were released to the aqueous phase while the concentrations of Cd, Cu, Ni, Pb and Zn remained low. Much like in the waste itself, the soluble concentrations of these metals were in excess of those expected on the basis of solid sulfide solubilities only. In this case, complexation with organic ligands has been calculated to be a possible explanation for the relatively large apparent solubilities. Nonetheless, the other explanations offered earlier are also plausible: 1. incomplete separation of small solids by filtration; 2. formation of poorly documented polysulfide complexes.

In regions further from the outfalls where the rate of organic deposition is not sufficient to maintain anoxic conditions, the release of sulfide-forming metals is expected as the sulfide is oxidized. With the exception of mercury this is what is observed in the laboratory experiments (Figure 6.23, oxidizing conditions). Note, however, that the kinetics of this mobilization are quite slow, often taking months before a steady soluble concentration is reached. The slow kinetics of oxidation of metal sulfides undoubtedly account for much of the sluggishness of the system. Adsorption on iron and manganese hydrous oxides probably largely accounts for the final retention in the sediment phase. It may also account, perhaps, for some of the slow kinetics: initially high adsorption by the freshly precipitated oxides could result in minimal release of metals from oxidizing sulfides; slow aging of the hydrous oxides could later result in desorption and release of the metals into the solution phase.

Mixing of waste particles with natural sediments: Sediment trap data. Sediments near disposal sites are a mixture of natural sediments and waste particulate matter. Such "mixing" is the major "dilution" effect which accounts for the lower

Figure 6.23 Release of metals from sewage polluted natural sediments (Lu and Chen, 1977).

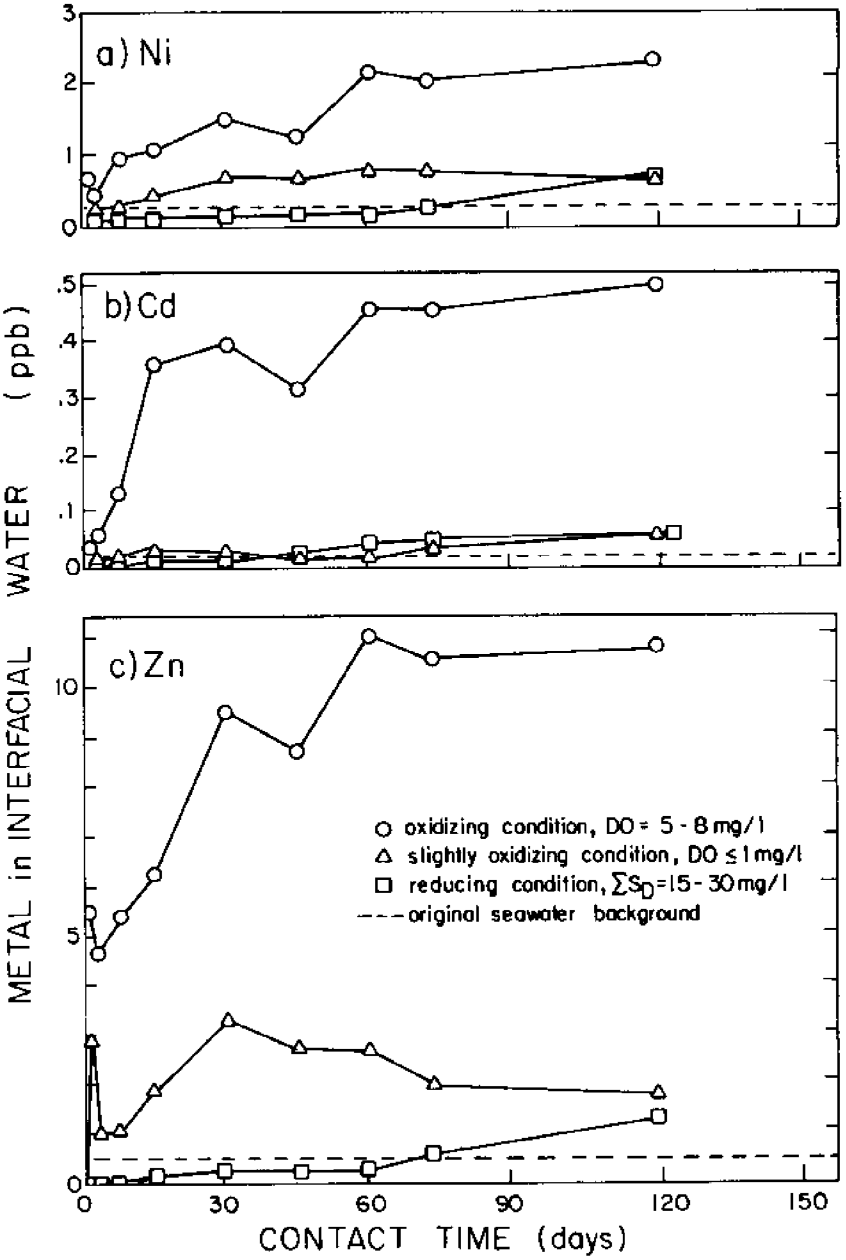
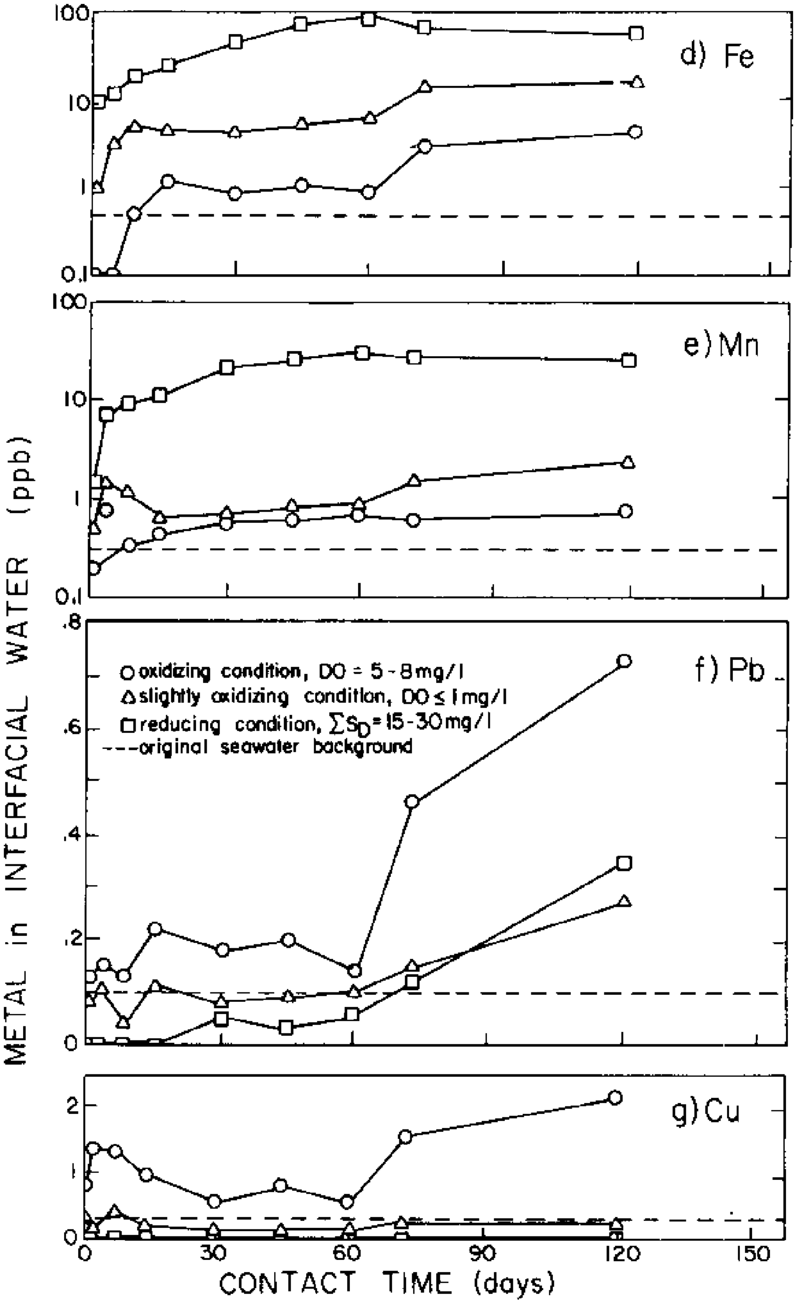


Figure 6.23 -continued-



concentrations of metals in sediments compared to the concentrations in the waste solids. Sediment trap data provide a good handle on this phenomenon for three major reasons: 1. they permit one to analyze exclusively recently sedimented particles before they are altered by chemical or biological processes; 2. they avoid the complications due to mixing processes within the sediments (bioturbation, scouring); 3. even if they do not provide accurate absolute sedimentation data due to difficulties in designing ideal sedimentation traps, they probably provide suitable relative data for comparing natural and waste sediments.

Figure 6.24 (a to f) presents such sediment trap data for some metals. (This figure also contains sediment core data; we are presently concerned exclusively with the sediment trap data shown as line A on the graphs.) The concentration of total volatile solids serves here as a convenient (and reliable) measure of the organic content of the waste and natural particles. By plotting end members corresponding to the waste particles (W) and to the unpolluted sediments (S) on a graph of total volatile solid concentrations vs. metal concentrations, one can draw an ideal mixing line (line A joining W & S). Sediment trap samples that are simply mixtures of waste and natural particles without chemical transformations should provide points situated on line A. Deviations from the line suggest chemical transformations (during sedimentation) while distance from the waste end member (W) is a measure of the dilution by natural sediments. As evidenced by the proximity of the data to the ideal mixing line, little loss or gain of metals (except Ni) or organic matter has taken place. This is expected on the basis of the laboratory experiments which showed little or no release of these metals a day after dilution with seawater (Figure 6.18a) and little oxidation of organic matter over the same time.

Deviations from the ideal mixing line for Ni are maximum at intermediary concentrations (Figure 6.24d). This is consistent with mobilization of nickel in the water column during particle settling. The traps adjacent to the outfall collect rapidly sedimenting sludge particles with little contribution from natural sediments and not enough transport time to release Ni (hence the high points on the graph); vice versa, the traps farthest from the outfall collect mostly natural sediments and yield the low points on Figure 6.24d. In traps at intermediary distance one finds sludge particles that have remained

Figure 6.24 Trace metals in sediments and sediment traps near the Hyperion sludge discharge in the Santa Monica Canyon. From Mitchell and Schafer, 1977 and unpublished data by the same authors (Courtesy of D. Young and SCCWRP).*

* Line A represents a strictly conservative process in which the metal and total organic concentrations reflect a simple mixing of natural sediments (end member S) and waste particles (end member W).

Line B corresponds to sludge end members at various degrees of oxidation, the metals being considered strictly conservative. For example, the 50 percent organic decomposition end member is calculated from

$$\text{Volatile solids} = \frac{65 \times 1/2}{35 + 65 \times 1/2} = 48\%$$

$$\text{Metal} = \text{Metal in Waste} \times \frac{100}{35 + 65 \times 1/2} =$$

$$\text{Metal in Waste} \times 1.48$$

Line C represents an ideal mixing line between the waste end member with 50% organic decomposition and the natural sediments. Metal mobilization processes are exhibited by points lying above this mixing line.

Figure 6.24-continued-

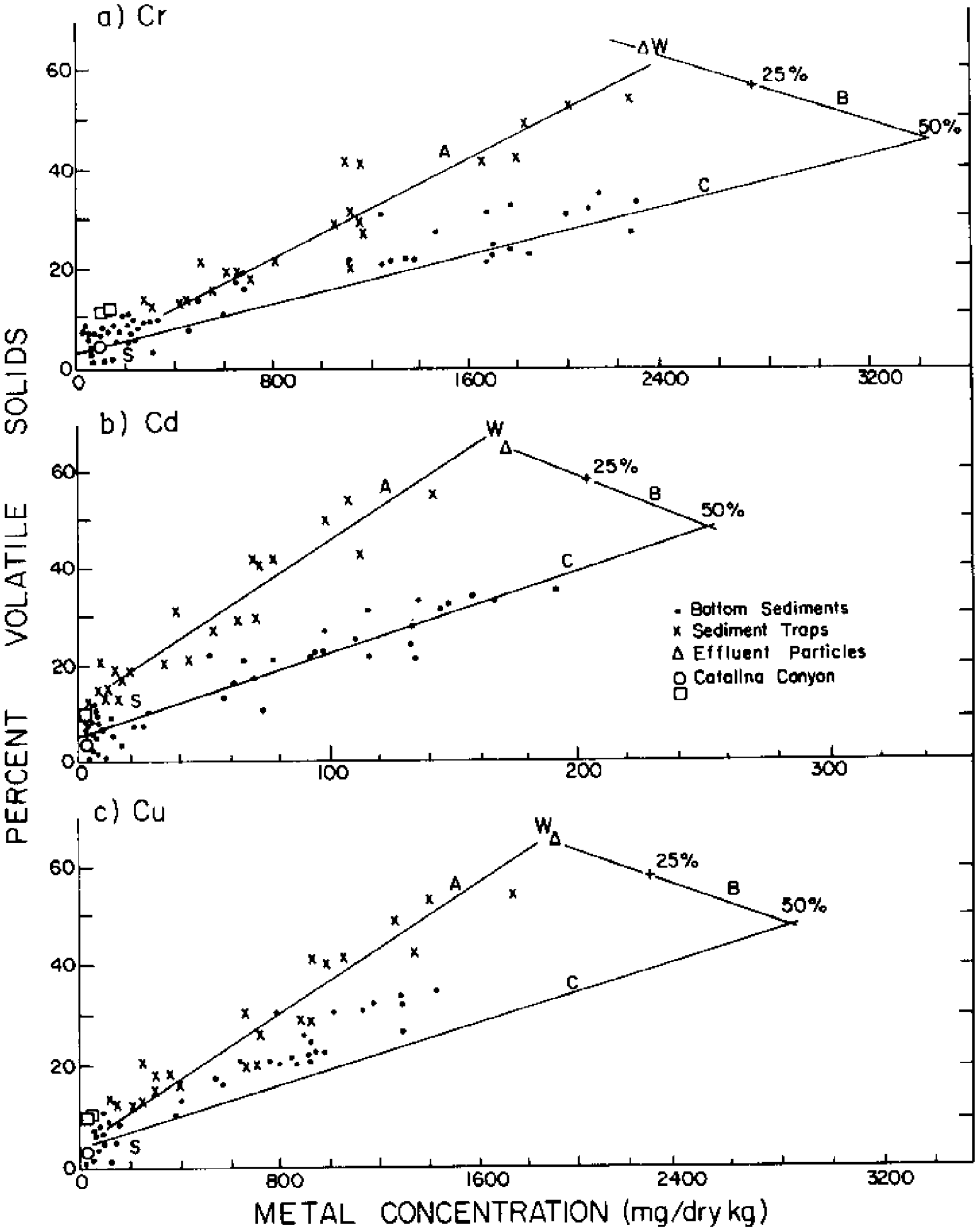
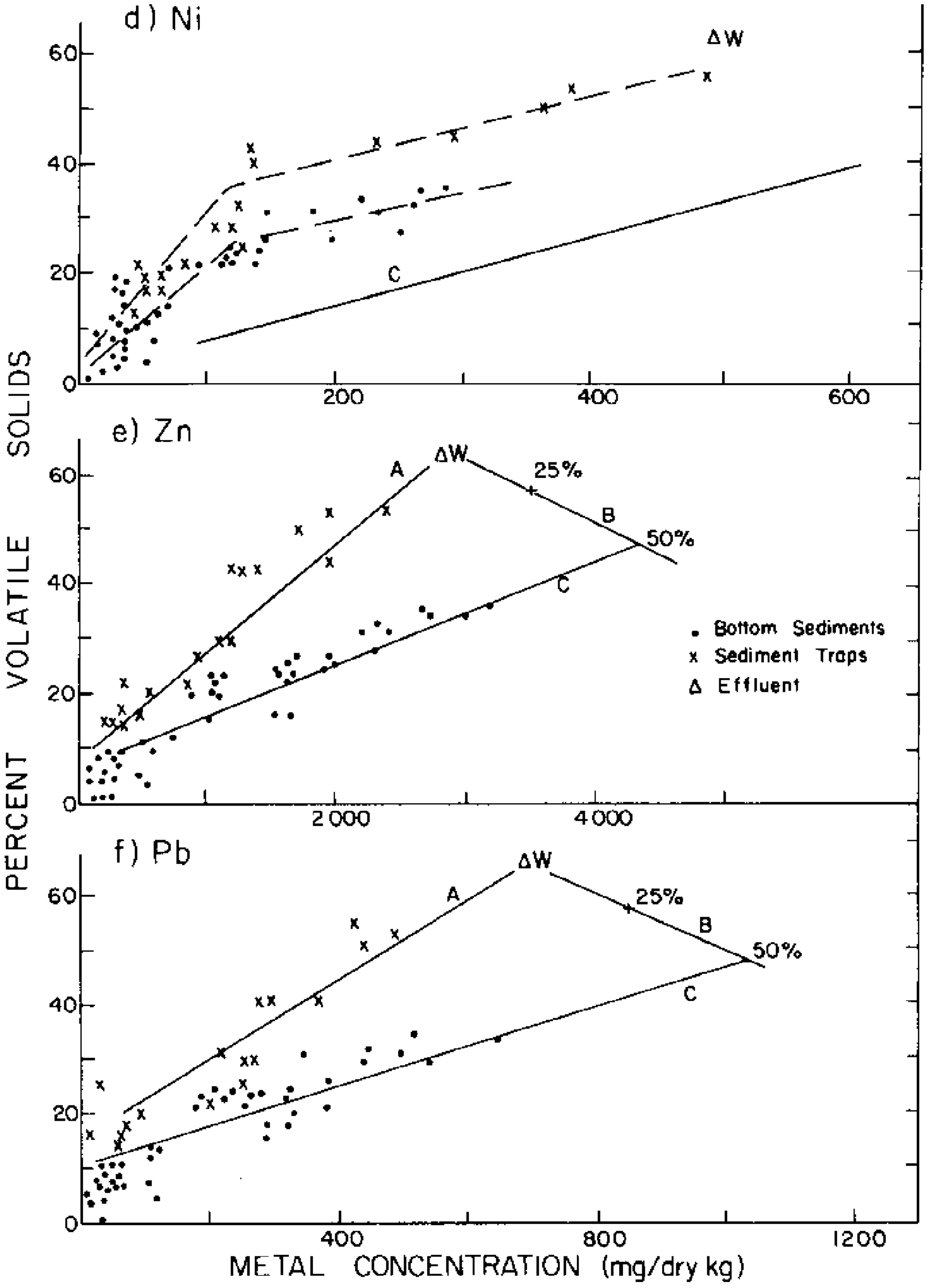


Figure 6.24 -continued-



in the water column long enough (1 to 4 days) to release much of the nickel; the mobilization in the water column is then most evident as a deviation from the middle of the "ideal" mixing line A.

The question of metal mobilization in nearby sediments: Sediment core data. Whether or not trace metals that are deposited in anoxic sediments near disposal sites are in part mobilized (re-released to the water column) or mostly retained in the sediments, has been the object of some debate. On the basis of thermodynamic calculations and of the laboratory experiments presented earlier, one would expect that the sulfide-forming metals would be essentially immobilized in sediments as long as these remain anoxic. This is strongly supported by the remarkable similarity in the concentration profiles of various metals in the sediments as a function of distance from sewage outfalls (Figure 6.25). If metals were markedly released into the water column, one would expect the extent of such metal release to be strongly metal dependent and the similarity of the concentration profiles would then be a highly unlikely coincidence. Taken at face value, the data of Figure 6.25 demonstrate a dominance of transport processes over chemical processes in determining metal concentrations in nearby sediments.

One of the major reasons why metal mobilization has been argued to occur is that metal concentrations in sediments near some major waste source have been found to be much lower than those in the waste solids. This is shown for the L.A. County outfall in Table 6.14: the concentrations of metals such as Cr and Cu are reduced by a factor of approximately two from waste solids to sediments. Intuitively one expects the waste solids to dominate completely the sedimentation process in the immediate vicinity of the outfall. The relatively low concentrations that are measured can then only be explained by hypothesizing some mobilization process. Such "intuition" does not take into account the effect of interactions between natural and waste particles. It appears that coagulation with and dilution by natural sediments can account for the relatively low metal concentrations that are measured. It remains that in the sediments adjacent to the Whites Point Outfall, Cd and Pb are markedly less "diluted" relative to their concentrations in the sewage particulate matter than are Zn, Ag, Cr and Cu (Table 6.14). If indeed none of these metals is significantly mobilized in the water column or in the sediments, the explanation of this

Figure 6.25a Total concentration in sediments vs distance from LACSD outfall. Cobalt, nickel and manganese have been omitted as irrelevant. Data for silver are scattered while those of iron and mercury are not available (Morel et al., 1975).

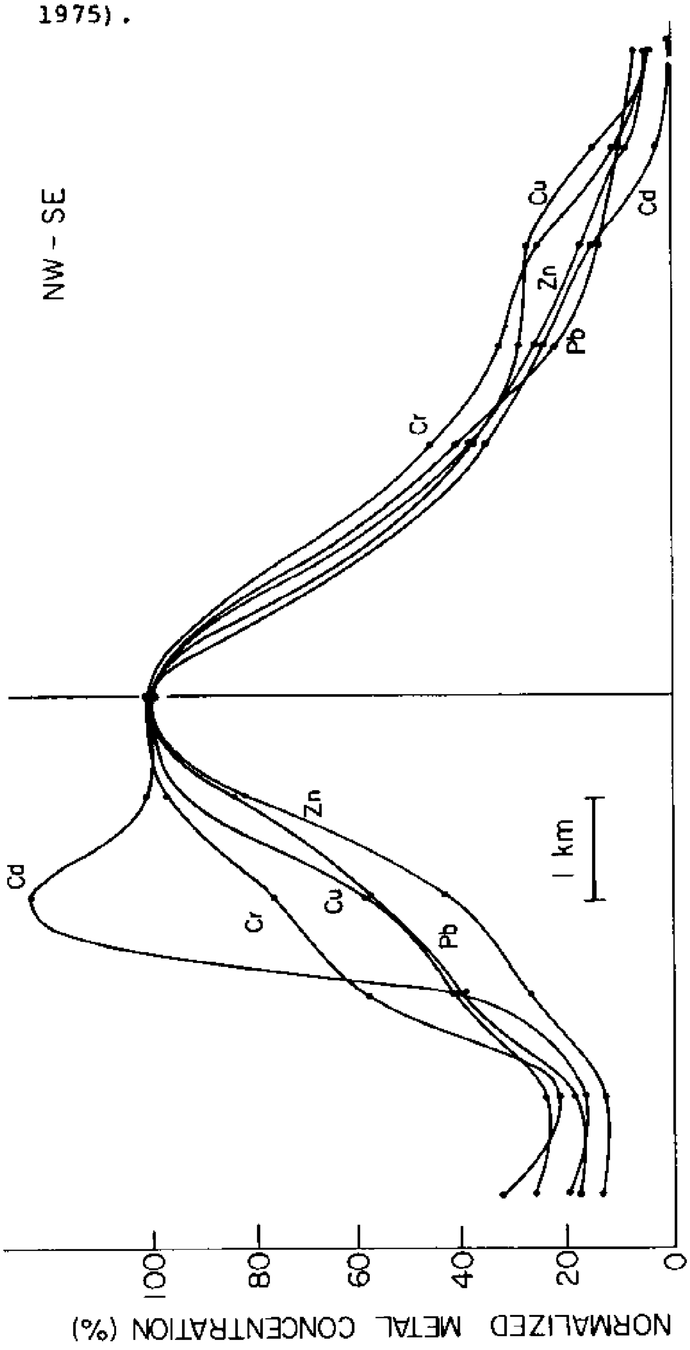
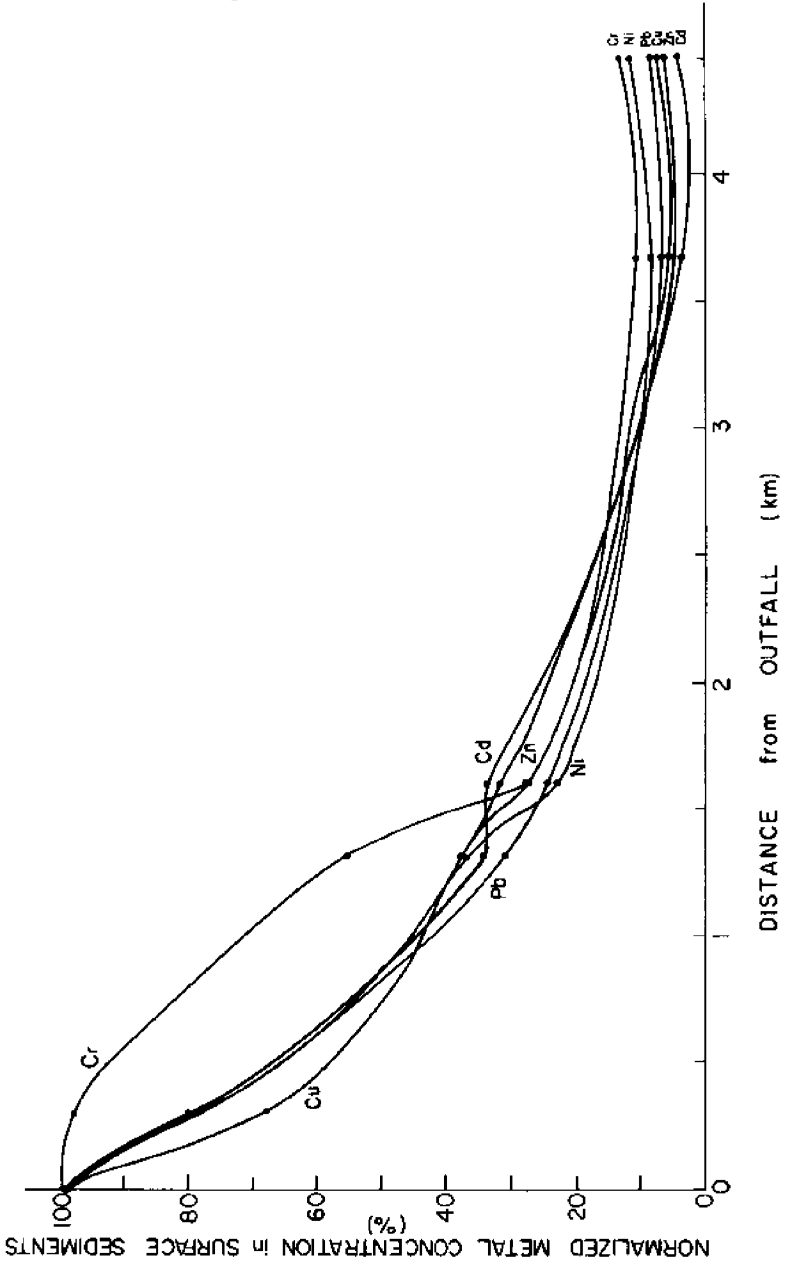


Figure 6.25b Total concentration in sediments vs distance from Hyperion outfall (Mitchell and Schaffer, 1977; and unpublished data by the same authors. Courtesy of D. Young and SCCWRP.).



phenomenon must lie in some differential sedimentation among metals: the fastest sedimenting particles must be relatively enriched in Pb and Cd. Although the data of Figure 6.22 hints that this may be so, it can hardly be taken as unassailable evidence for it.

Table 6.14 Metal Concentrations (mg dry kg^{-1}) in Waste Solids and in Sediments Near L.A. County Outfall

	1971 (SCCWRP, 1973)		1977 (Hershelman et al., 1977)	
	Waste Particles	Box Core (B20) of Nearby Sediments	Waste Particles	Grab Core (7C) of Nearby Sediments
Ag	32	21	46	20
Cd	65	68	92	60
Cr	1700	1000	2640	1170
Cu	1120	660	1444	810
Ni	220	36	564 *	80
Pb	570	460	775	540
Zn	4100	2400	4648	2720

* 50% of the Ni is assumed to be in the soluble fraction. All other metals are assumed to be 100% insoluble.

A key to this problem may be provided by the observation reported earlier that a variable and sizeable proportion of the metals in the waste may be associated with the bacterial floc (Hays and Theis, 1978). This floc can apparently be separated from the other waste solids by suitable adjustment of the overflow rate in an upflow clarifier. This implies that bacterial mass constitutes a large fraction of the rapidly sedimenting waste particles and that a large proportion of the metals that reach the nearby sediments may actually be associated with biological material. The metals may be subsequently released from the organic matter but they would then be immediately precipitated as sulfides and proportions of metals in the sediments would correspond in large part to those originally in the bacteria, not those in the total waste solids. Note also, as has been suggested earlier, that the metals associated with the bacteria may be markedly more mobilizable under the oxic conditions of the plumes than those associated with inorganic sulfides. This creates a very complicated situation and without further experimental data no simple explanation can be provided to relate the metal composition of the nearby sediments to that of the waste solids.

The data most directly pertinent to the question of metal mobilization in sediments come from comparison of concentrations in sediment traps and in actual sediments. Such comparisons are shown in Figure 6.24 for the sludge disposal site in Santa Monica. (Similar data exist for Hg in the Palos Verdes sediments (Eganhouse et al., 1978).) End members corresponding to various levels of oxidation of the waste organics, without metal mobilization, are shown as line B. The oxidaton of organic matter results in a decrease in the total solid mass and, hence, a higher metal concentration than in the waste particles themselves.

Long-term laboratory experiments with mixtures of sewage and sludge with seawater have demonstrated about a 50 percent reduction in the waste organic matter concentrations by oxidation (Myers, 1974; see next section). Oxidation of organic matter in actual sediments might of course be more efficient due, for example, to digestion through the guts of benthic organisms. Nonetheless, the sediment data for Cr, Cd, Zn and Pb (Figure 6.24a,b,e,f) which follow closely the ideal mixing line (C) for the sludge end member with ca. 50 percent loss of organic matter are consistent with the hypothesis that they are not mobilized to any great extent in the Santa Monica sediments. (A similar result is applicable to Hg in the Palos Verdes sediments.) As argued earlier, the nickel data (Figure 6.24d) are largely dominated by mobilization processes in the water column. Perhaps the most surprising result is that of Figure 6.24c which demonstrates a definite mobilization of copper compared to Cd and Cr. This again may be due to copper complexation by organic ligands. Both in the water column (Table 6.13) and in the sediments, copper appears more dissolvable than expected from the stability of copper sulfide.

Transformation by organisms: Methylation. Ever since the infamous methyl-mercury poisoning at Minamata in the 1950s and the subsequent discovery of natural methylation by microorganisms in sediments, there has been much interest in the question of "biomethylation" of metals in natural waters. Many review articles have covered this topic (D'Itri and D'Itri, 1977); here we only mention a few essential facts and present some field data relevant to municipal waste disposal in coastal waters.

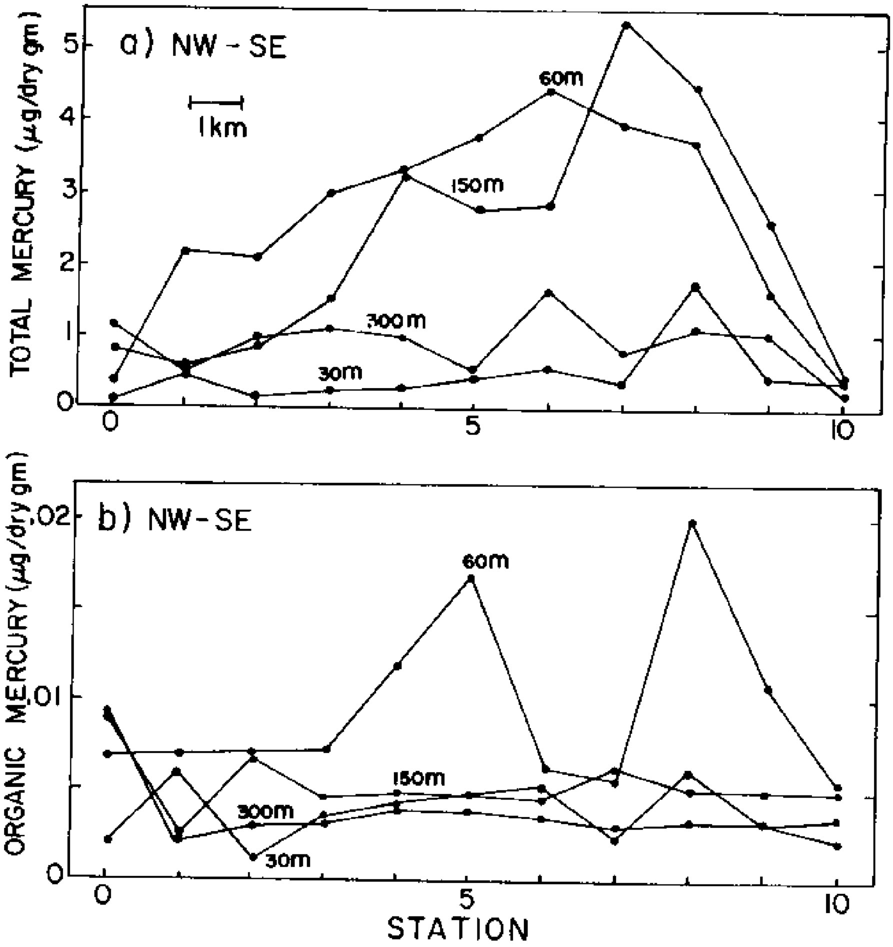
Methylated metals and metalloids have physical, chemical and biological properties drastically different from those of the unmethylated elements: they are volatile, they are readily accumulated by organisms, they are markedly more toxic, usually affecting the nervous system. The list of elements that have been demonstrated to be methylated by organisms includes the metals Sn and Pb, in addition to Hg, and the metalloids As, Se and Te. Various mechanisms have been proposed for the biomethylation process, relating it to the redox chemistry of the elements (Ridley et al., 1977).

Contrary to early expectations, it now appears that methylation occurs not only in reduced sediments and in the guts of organisms, but in the water column as well (Andreae, 1979). There is also evidence that "demethylation" processes are effective and that methylated compounds are not normally accumulated in the environment.

In a study of organic mercury in the sediments adjacent to the Los Angeles County outfall, methyl-mercury concentrations (taken to be the total organic mercury concentrations) were measured to account for less than 0.5 percent of the total mercury (Figure 6.26). Analysis of the local fauna demonstrated no mercury accumulation (Eganhouse et al., 1978). As suggested by the data of Figure 6.26, it appears that in regions of highest total mercury concentrations, there is in fact an inhibition of the methylation process. This may be related to the formation of the highly insoluble mercuric sulfide in the reduced sediments.

Taken as a whole, existing data on the fate of trace metals from municipal waste disposal in coastal waters demonstrate relatively little measurable impact outside of the obvious accumulation in sediments directly adjacent to the disposal sites. In the coastal basins off southern California, the sedimentary record indicates a measurable increase in

Figure 6.26 Mercury in surface sediments of Palos Verdes shelf, September 1975. a. Total mercury; b. total organic mercury. Outfalls are located at stations 8 and 9 at about 60 m depth (Eganhouse et al., 1978)/



metal fluxes with time that is probably associated with human activities (Bruland et al., 1974; Bertine and Goldberg, 1977). However, the small enrichments measured for some of the metals in the sediments of the outer basins have been, in fact, attributed mostly to eolian transport rather than waste disposal (Bertine and Goldberg, 1977).

On the basis of the results presented here, one may be tempted to conclude that the disposal of trace metals in coastal waters does not, in general, pose an important environmental threat. Certainly, one has difficulty demonstrating toxic effects due to waste metals in any marine organisms (except perhaps for the benthos in the sediments immediately adjacent to disposal sites). There is, however, a possibility that important, subtle modifications in the ecology of planktonic organisms may result from even very small changes in trace metal concentrations in coastal waters. It has been hypothesized that metals such as copper, zinc and iron may control the phytoplankton species assemblages in the sea. Copper may be naturally toxic to some algal species; zinc and iron may be naturally limiting. If this is the case, even very modest changes in the trace metal composition of coastal waters could result in a shift of planktonic species. Neither the plausibility nor the gravity of such a process is assessable at this time.

TRACE ORGANIC COMPOUNDS

Production of synthetic organic chemicals in the United States is increasing at an exponential rate with a doubling time of approximately 8 years (Metcalf, 1977). The daily manufacturing rate exceeds 1,000 metric tons and it has been estimated that 3,000 new chemicals are introduced into the environment every year. Many of these compounds are toxic, resistant to degradation and are used in a wide range of applications.

From a variety of sources, organic compounds of varying functions and reactions enter municipal waste systems. Even when direct industrial discharges do not contribute substantially to the waste, potentially hazardous organic compounds may enter as byproducts of manufacturing processes, or from a wide variety of diffuse sources such as domestic products (rodenticides, insecticides, medications, cleaning solvents), agricultural and urban runoff or drainage from land disposal sites. Table 6.15 lists the U.S. production rates for some degradation-resistant organic compounds. It may be anticipated that some proportion of these compounds eventually enters the waste stream and ultimately the oceanic environment.

Table 6.15 United States Production of Some Synthetic Organic Chemicals (Chemical Economics Handbook, 1975)

Class	Compound	Year	Production (10^6 lbs)	Year	Production (10^6 lbs)
Lower molecular weight halogenated hydrocarbons (LMHH)	tetrachloroethylene	1960	209.4	1974	733.2
	1,1,1,-trichloroethane	1966	242.9	1974	590.8
Aromatic hydrocarbons	benzene	1960	3355	1971	8136
	toluene	1960	1981	1971	6194
	naphthalene	1960	517.0	1968	860.7
Chlorinated benzenes (CB)	*o*-dichlorobenzene	1960	24.7	1972	62.4
	p-dichlorobenzene	1960	64.0	1972	77.3
Pesticides	DDT	1960	164.2	1970	59.3
	parathion	1960	7.4	1970	15.3
	2,4-D	1960	36.18	1967	77.14
	Aldrin group*	1960	90.7	1968	116.0

* aldrin, chlordane, dieldrin, endrin, heptachlor, toxaphene

Unfortunately, there is usually a long delay between initial release of an organic compound to the environment and subsequent recognition of its presence or its toxic, carcinogenic, mutagenic, or teratogenic effects. For example, contamination by kepone, a human carcinogen, in the James River went unrecognized for over 10 years. Vinyl chlorides were manufactured for 40 years before their carcinogenicity was documented. Also, it is difficult to separate the individual effects of the waste stream components. Pollution-related, long-term sublethal effects or biological modifications in marine species are difficult to detect, let alone relate to a specific component of a complex mixture. Possible synergistic effects complicate the situation further and it is quasi-hopeless to obtain a cause-effect assessment of the biological impact of a mixture as complex as municipal sewage. *In situ* transformation processes may yield components of greater environmental hazard than that presented by the parent compounds. The absence of demonstrated effects or causalities is not equivalent to the absence of effects or causalities.

Routine analyses of synthetic organic compounds in municipal wastewaters is complicated by the large number of compounds, by the extremely large range of their concentrations, and by the amplitude of the daily variations in these concentrations. The cost of monitoring all chemicals on a toxic substances list on a routine basis may seem prohibitive but, unless some estimate of mass emission rate is obtained, potential environmental or health hazards cannot be assessed.

Due to the large number of organic components in waste effluents, a systematic discussion of the properties, the transport, and the transformations of each compound or even families of compounds, is clearly beyond the scope of this section. Instead we have attempted to present a general framework for understanding the environmental pathways of organic compounds. A general classification is initially proposed within which the chemical and physical properties governing the environmental transport and transformations of organic compounds are examined. Emphasis is placed on the importance of the relative time scales, the relative biological activities and the methods of waste disposal. Subsequently, a few subclasses and a few specific examples are analyzed with regard to salient physical and chemical features in order to achieve an estimate of environmental persistence and to determine the probable ultimate sinks. It is hoped that this general framework may be helpful in the preliminary assessment of the potential environmental danger posed by a new or newly monitored compound.

Organic Components of Wastewater Effluents

The degree of oxidation and the types of organic compounds present in effluent wastewater released to the oceanic environment reflect in part the treatment process, as well as the composition of the influent waste. Initial settling processes remove the large particulate matter. Anaerobic digestion is a two-step process: the first group of anaerobic bacteria (*Pseudomonas*, *Flavobacterium*, *Alealigenes*, *Enterobacter*) decomposes complex lipids, proteins and carbohydrates into organic acids, amino acids, ammonia, and a refractory residue; conversion of organic acids and amino acids into CH_4, CO_2, NH_3 and H_2S by bacteria such as Methanobacterium, Methanosarcina, Methanococcus is the second stage. Production of methane precursors such as formic acid, acetic acid, propionic acid and higher carboxylic acids is also evidenced. In aerobic secondary treatment the remaining organic compounds are partially oxidized biochemically. Easily oxidized functional groups such as aldehydes, alcohols, carboxylic acids, or amines degrade readily, resulting in the evolution of CO_2. Secondary treated wastewaters are therefore typically less susceptible to microbial degradation than wastes from primary treatment. This is reflected in the higher chemical oxygen demand (COD)/biological oxygen demand (BOD) ratios for secondary wastes relative to primary wastes (Table 6.16).

Table 6.16 Comparison of COD* and BOD* in mg l^{-1} for Municipal Wastes (Mueller et al., 1976)

	COD	BOD_5	COD/BOD_5
Raw sewage	328	131	2.5
Primary effluent	395	158	2.5
Secondary effluent	169	36	4.7
Sludge	93,000	17,000	5.5

* COD = Chemical oxygen demand
BOD = Biological oxygen demand

Chlorination. The majority of municipal wastewater discharges to the marine environment are treated with a biocide immediately prior to release. Chlorine is the dominant disinfectant, consuming 1 to 2 percent of the U.S. annual production of Cl_2. During treatment of wastes with chlorine, two parallel processes occur, oxidation and chlorination. Typically effluents are chlorinated to a free chlorine residual to ensure disinfection. Chlorine hydrolyzes almost instantly in water to form hypochlorite.

$$Cl_2 + H_2O \rightleftarrows HOCl + H^+ + Cl^- \quad pK = 3.35 \qquad (25^{\circ}C)$$

Since the alkalinity of sewage is high, the system is well-buffered and the pH change is slight.

The major portion of the added chlorine is consumed in oxidation reactions with both inorganic and organic compounds and in the formation of chloramines. Stable chlorine-containing organic components, such as chlorinated phenols, amino acids, and aromatic acids have been quantified at the microgram per liter level in effluents after chlorination to a 1 to 2 mg l^{-1} chlorine residual (Jolley, 1975). Chloro-derivatives of benzene, toluene and benzyl alcohol have been noted (Glaze et al., 1975), as have volatile low molecular weight halogenated compounds such as haloforms (Rook, 1974, 1977; Bellar et al., 1974). Reactions of chlorine with ammonia or amine compounds yielding chloramines are very fast:

$$HOCl + RNH_2 \rightleftarrows RNHCl + H_2O$$

$$HOCl + NH_3 \rightleftarrows NH_2Cl + H_2O$$

In seawater the chlorine residual promotes very rapid (less than 1 minute) oxidation of bromide to hypobromite (Helz and Hsu, 1978):

$$HOCl + Br^- \quad HOBr + Cl^-$$

As a result, brominated organic compounds may also be end products of the disposal of a chlorinated effluent in seawater. In general (but with many exceptions), an increase in chlorination of an organic compound decreases its susceptibility to microbial and chemical degradation and increases its toxicity to marine organisms.

Classification. Due to the large numbers of organic compounds present in municipal wastewaters, many at low concentrations ($< 10^{-8}$M), the task of identification and quantification of individual components is formidable. Classification schemes have been proposed to deal with this problem and can be based on operational definitions, environmental hazard, or environmental reactivity. An operational scheme (Rebhun and Manka, 1971) partitioned the organic compounds in secondary effluents into the following classes: ether-extractable, anionic detergents, carbohydrates, proteins, tannins, and humic substances. The relative proportions of each class in a secondary effluent from Israel are given in Table 6.17. The ether-extractable category contains many compounds of concern with regard to human health: aromatic esters, hydrocarbons, pesticides, and chlorinated and alkyl substituted aromatic compounds.

Table 6.17 Characterization of Soluble Organic Fractions in Secondary Effluents

	Rebhun and Manka, 1971	Manka et al., 1974
Ether extractables	8.3%	13.4%
Anionic detergents	13.9%	16.6%
Carbohydrates	11.5%	5.9%
Proteins	22.4%	21.6%
Tannins	1.7%	1.3%
Humic substances	40-50%	45.6%

*plus lignins

Classification of organic compounds by environmental hazard involves:

1. the acute and chronic toxicity of the organic compounds;
2. the quantity produced, especially in relation to the amount expected to funnel into municipal wastewater systems;
3. the persistence or biodegradability of the compound;
4. the availability of transport/transformation processes;
5. the tendency to accumulate in the aquatic food web;
6. the tendency to be recycled or mobilized at a future date.

In addition, it is useful to distinguish between a xenobiotic compound (i.e., a compound which is foreign to an organism's unperturbed environment) and a compound similar in reactivity, functionality and concentration to other biogenic organic compounds already present in the environs. Human fecal material is not appreciably different from fecal wastes produced by marine animals. Off southern California, the excretion of fecal matter by the 6 million metric tons of anchovies alone is equivalent to that of some 90 million people--a population ten times that of Los Angeles (Bascom, 1974). Some organic compounds present in sewage--amino acids, vitamin B_{12}, thiamine and urea--may also act as nutrients for phytoplankton growth as discussed earlier. The existence of natural compounds similar in functionality and reactivity increases the probability of an already existing degradative pathway. On the other hand, many xenobiotic compounds rely on their dissimilarity with natural compounds in order to act as herbicides, insecticides, and rodenticides.

Due to the large number of considerations, environmental hazard is difficult to quantify, and hence difficult to use as the basis of a classification scheme for waste organic components. As a result, the general classification proposed in Table 6.18 is based primarily on reactivity or on residence time (which is a function of reactivity) in the marine environment as determined from the following considerations of the physical and chemical properties.

Physical and Chemical Properties

The physical and chemical characteristics of effluent organic compounds govern the transport and transformation processes that are ultimately responsible for the environmental fate of these compounds. These characteristics control the partitioning of the organic waste component between atmosphere, surface microlayer, water column, organisms, suspended particles and sediments, and the mobility and stability within each phase.

Physical state. Obviously, advective transport of a constituent is largely governed by its partitioning between particulate and soluble phases. Less obvious is the fact that some transformation processes also are affected by this partitioning. For example, adsorbed compounds may be stabilized against loss by vaporization or their rates of chemical or biological degradation may be altered.

A study of carbon in the Los Angeles Whites Point effluent (Myers, 1974) showed that about 35 percent of the 450 mg l^{-1} particulate matter is organic carbon. (The effluent also contained 40 mg l^{-1} dissolved organic carbon.) Incubation of the waste under aerobic conditions lowered the organic carbon content of the solid to a stable value (ca. 25 percent) in two months while no change was observed under anaerobic conditions. A first order oxidative

Table 6.18 Classification Schemes for Organic Components in Wastewater

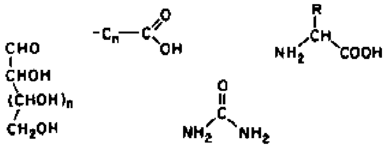
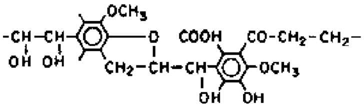
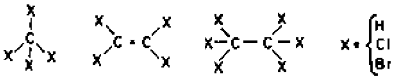
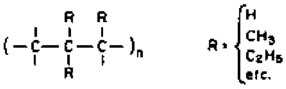
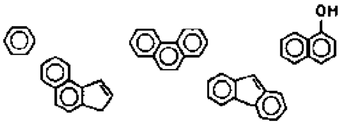
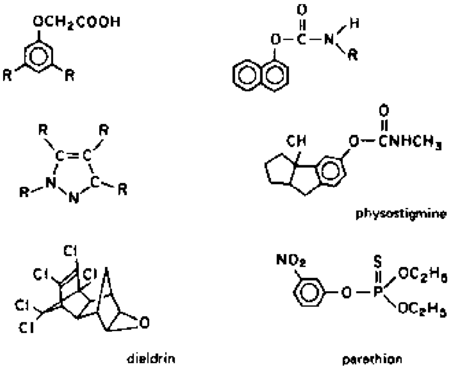
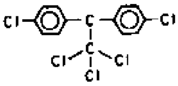
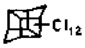
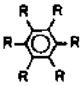
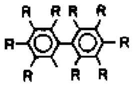
Family of Compounds	Examples of Structure	Examples of Compounds
Class I. Easily Degraded: Used by living organisms for energy and building components. (Environmental half-life < ½ year.)		
amino acids volatile acids sugars urea fatty acids		– glycine – acetic acid, propionic acid, butyric acid – glucose – oleic acid
Class II. Moderately Resistant Compounds. (Environmental half-life ½ to 5 years.)		
a. biogenic humic acids lignin chitin		diagenetically produced polymers/ naturally synthesized polymers
b. xenobiotic LMHH – lower molecular weight halogenated hydrocarbons		chloroform, CCl_4, 1,1,1-trichloroethane, tetrachloroethane, CH_3Br, dichloroethanes (some of these may be produced by algae)
PHC – petroleum hydrocarbons		alkanes, branched or cyclic hydrocarbons
aromatic hydrocarbons		benzene, alkylbenzenes, naphthalene, anthracene, 3,4-benzopyrene, benzafluoroanthenes, dibenzanthracenes, idenopyrenes, phenols, chrysenes, cresols
HPHC – halogenated petroleum hydrocarbons		chlorinated paraffins, polyvinyl chloride
some pesticides		methoxyclor, heptachlor, chlordane, endosulfan & metabolites, endrin & metabolites, aldrin, dieldrin, 2,4,D-silvex

Table 6.18-continued-

Class III. Very Resistant to Environmental Degradation. (Environmental half-life > 5 years.)			
a. non-xenobiotic kerogen			diagenetically produced polymers; few reactive functional groups
b. xenobiotics some pesticides		 mirex	DDT, DDE and metabolites, kepone, mirex
CB—chlorinated benzenes and higher chlorinated aromatic compounds		$R = \begin{cases} Cl \\ H \end{cases}$	
PCB's—polychlorinated biphenyls			Arochlor 1254, Arochlor 1242

decay rate of .02 day^{-1} (17° C) was obtained for the particulate organic matter that is oxidizable under these experimental conditions. If we consider that carbon accounts for 55 percent of the total particulate organic mass (i.e., the solid is originally 64 percent organic; Mitchell and Schafer, 1977), we can calculate that some 50 percent of the waste particulate organic matter was actually oxidized during these experiments. (Verify that 100 mg of solid mass [64 mg organic + 36 mg inorganic] is then reduced by oxidation to 68 mg [32 mg organic + 36 mg inorganic], about 17.5 mg of which is carbon.) Although this result may not apply to all primary effluents (recall that most of the solids in the Whites Point effluent originate from the centrate of the sludge), it is consistent with the field observations on the fate of digested sludge in Santa Monica (see previous section). It appears then that the organic fraction of anaerobically stabilized waste solids is typically about 50 percent refractory, 50 percent oxidizable under aerobic conditions.

The total organic carbon (TOC), a common effluent measurement, typically yields values between 100 and 300 mg C l^{-1} (Metcalf and Eddy, 1972) in municipal wastewaters. In the New York area, average TOC values from 26 wastewater treatment plants decrease from primary to secondary treatment in direct parallel with the decrease in total suspended solids (TSS), as shown in Table 6.19. The increase in TOC from raw sewage to primary effluents most likely reflects an organic carbon contribution from the bacterial floc.

Table 6.19 Concentrations of TOC and TSS (mg l^{-1}) in Municipal Waters (Mueller, et al., 1976)

	TOC	TSS
Raw sewage	83	139
Primary effluent	107	93
Secondary effluent	34	43
Sludge	9,200	39,000

The water solubilities of some common xenobiotic compounds are given in Table 6.20. Water solubility, which is a controlling factor in the association of hydrophobic colloids and particles generally decreases with increasing molecular weight (log solubility is a linear function of molar volume within each homologous series (McAuliffe, 1966)), and increases with nitrogen and oxygen functional groups. The high ionic strength of seawater depresses the water solubility of most organic compounds below the values listed in Table 6.20 (Eganhouse and Calder, 1976 and references therein) in a manner mathematically described by the Setchenow equation:

$$\log S_i^o/S_i = K_s C_s$$

where S_i is the molar solubility in salt solution, $S_i{}^o$ is the molar solubility in pure water, K_s is the empirical salting parameter, and C_s is the molar salt concentration. In addition to the hydrophobic character of many organic molecules, their adsorption on particles is influenced by specific surface processes: Van der Waal's forces, hydrogen bonding, formation of coordination complexes, and chemical bonding with exposed functional groups (e.g., condensation reactions). There is some evidence for micelle formation in sewage. Micelles are subcolloids of organic compounds that result in the increased apparent solubility of hydrophobic compounds, especially in concentrated effluents. Upon dilution and rapid, large increases in ionic strength, these micelles tend to dissociate, causing rapid precipitation or particulate adsorption of their hydrophobic components.

Complexation reactions can also alter the water solubility of complex polyelectrolyte organic compounds. Complexation with cations (particularly major seawater cations during the initial dilutions) may decrease solubility by simple neutralization of negatively charged hydrophilic functional groups on a hydrophobic carbon chain. In polyelectrolytes, complexation also neutralizes the electrostatic repulsive forces (from charged functional groups) that serve to extend the molecule. A coiling of the organic molecule may ensue, causing hydrophilic compounds to become slightly hydrophobic, with inherent loss of water solubility. Cross-complexation of organic compounds with a central metal may also promote precipitation, especially in regions of high organic material concentration, such as the surface microlayer.

Table 6.20 Water Solubility of Common Xenobiotic Compounds

Class	Compound	Water Solubility (ppm)	Temperature (°C)	Ref.
Petroleum hydrocarbons (PHC)	n-butane	61	(20)	6
	n-hexane	9.5	(20)	6
	n-octane	0.66	(20)	1
	2,2,4-trimethylpentane	2.44	(20)	6
Aromatic compounds	benzene	1780	(20)	1
	toluene	515	(20)	1
	ethylbenzene	161	(25)	5
	n-butylbenzene	12	(25)	5
	naphthalene	30	(25)	1
	2-methylnaphthalene	25	(25)	7
	phenanthrene	1.0,1.3	(25)	8,9
LMHH	chloroform	7950	(20)	4
	tetrachloroethylene	400	(25)	4
	1,1,1-trichloroethane	1300	(25)	4
CB	o-dichlorobenzene	100	(20)	1
	p-dichlorobenzene	79	(25)	1
Pesticides	DDT	0.0012	(25)	3
	Methoxychlor	0.1-0.4	(25)	2
	2,4-D	400-900	(25)	2
	Dieldrin	0.23-0.51	(25)	2
	Parathion	24	(25)	2
	Lindane	10	(25)	2
Polychlorinated biphenyls (PCB)	Arochlor 1242	0.24	(25)	3
	Arochlor 1248	0.054	(25)	3
	Arochlor 1254	0.012	(25)	3
	Arochlor 1260	0.0027	(25)	3

[1] Verschueren (1977)
[2] Gunther et al. (1968)
[3] McKay and Leinonen (1975)
[4] Dilling et al. (1975)
[5] Sutton and Calder (1975)
[6] McAuliffe (1966)
[7] Eganhouse and Calder (1976)
[8] May et al. (1978)
[9] McKay (1977)

Rate of evaporation. The rate of evaporative removal of organic compounds from natural waters is a function of many variables including the Henry's Law constant of the organic compound, the concentrations of the substance in the liquid and gaseous phases, and the local weather conditions (particularly wind speed and temperature). Utilizing Fick's First Law of Diffusion, these factors have been included in equations that model evaporation rates by Kanwisher (1963) and Broecker and Peng (1974). The system is conceptually viewed as two large homogeneously mixed reservoirs (i.e., the atmosphere and the natural water body) separated by a stagnant aqueous boundary layer. The rate of exchange of organic compounds between these phases is assumed to be controlled by the rate of diffusive transfer across the stagnant film. Thus:

$$\text{Flux} = \frac{D[C_\ell - C_g/H]}{Z}$$

where the flux is computed in $\text{gm}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$,
D is the molecular diffusion coefficient in water ($\text{cm}^2\cdot\text{sec}^{-1}$),
C_ℓ is the concentration of the organic solute in water ($\text{gm}\cdot\text{cm}^{-3}$),
H is the Henry's Law constant (wt/vol/wt/vol),
C_g is the concentration of the organic vapor in air ($\text{gm}\cdot\text{cm}^{-3}$),
and Z is the thickness of the stagnant boundary layer (cm).

Although this model is adequate for organic compounds with high Henry's Law constants (≥ 0.1 wt/vol. air/wt/vol. water), a better description of evaporative transfer is obtained using a two-film model (Liss and Slater, 1974; MacKay and Leinonen, 1975; Sauer, 1978) for compounds that more favorably partition into the aqueous phase (e.g., cyclohexanol, DDT, PCB). These compounds appear to encounter additional resistance to transfer from water to air from a stagnant gaseous boundary layer. Thus:

$$\text{Flux} = K_i\ (C_\ell - C_g/H_i)$$

where the flux is computed in $\text{gm cm}^{-2}\cdot\text{sec}^{-1}$,

K reflects the combined resistance to transfer across both films (cm sec^{-1})
and the other parameters have the same meaning as above.

K is computed from the mass transfer coefficients of water into air (assuming no liquid resistance to transport) and of CO_2 into air by the following:

$$K_i = \frac{H_i K_{gH_2O}\left(\frac{mwH_2O}{mwi}\right)^{1/2} \quad K_{\ell CO_2}\left(\frac{mwCO_2}{mwi}\right)^{1/2}}{H_i K_{gH_2O}\left(\frac{mwH_2O}{mwi}\right)^{1/2} \quad K_{\ell CO_2}\left(\frac{mwCO_2}{mwi}\right)^{1/2}}$$

Liss and Slater (1974) estimate K_{gH_2O} as 3000 $cm \cdot hr^{-1}$ and $K_{\ell CO_2}$ as 20 $cm \cdot hr^{-1}$. Thus when H is large, $K_{\ell i}$ reduces to $K_{\ell CO_2}$ $(mwCO_2/mwi)^{1/2}$, which is the same as D/Z in the single stagnant film model above. Table 6.21 presents evaporation half-lives for some common xenobiotic compounds calculated using the two-film model. Times represent evaporative removal to half the original concentrations from a 1 m deep-water body. The calculations assume that the atmospheric concentrations are negligible and that the bulk water and atmosphere are well-mixed. Dilling (1977) found agreement between model predictions and observations in laboratory evaporation experiments for many chlorinated light hydrocarbons.

Evaporation is especially important for certain situations where the introduction of organic compounds results in high surface concentrations, for example, barge dumping operations. Also for compounds that have long half-lives in the aqueous phase, transfer to the atmosphere is very important because they become subject to photochemical transformation processes and available for eolian transport. Thus, depending on their susceptibility, photochemically-sensitive compounds will be degraded while more resistant forms will be globally redistributed. (It is important to note here that evaporation is not the only process that transfers compounds from the ocean to the atmosphere. Depending on the wind and wave action, aerosol formation may be very important [MacIntyre, 1970].)

Chemical hydrolysis. Chemical hydrolysis is a common reaction involving the replacement of a functional group on an organic compound by an -OH substituent. Examples of hydrolysis reactions include cleavage of ester, amide, sulfide, and halide linkages. Hydrolysis, then, is a degradative mechanism usually producing smaller molecules.

Table 6.21 Evaporation Half-lives from 1-m-deep Water Calculated Using Two-layer Model

Class	Compound	Evaporation Half-life	Conditions T(°C), ionic strength, wind	Ref.
PHC	propane	11.5 hr	(17), sw, wind=6.3 m/sec	3
		18.7 hr	(17), sw, wind=6.3 m/sec	3
	n-octane	5.5 hr	(25), fw	1
	2,2,4-trimethylpentane	18.7 hr	(17), sw, wind=6.3 m/sec	3
	n-dodecane	22.3 hr	(17), sw, wind=6.3 m/sec	3
	benzene	4.8 hr	(25), fw	1
	toluene	5.2 hr	(25), fw	1
	naphthalene	7.2 hr	(25), fw	1
LMHH	chloroform	6.6 hr	(25), fw	2
	trichloroethylene	6.4 hr	(25), fw	2
	tetrachloroethylene	6.9 hr		
Pesticides	DDT	3.1 days	(25), fw	1
	lindane	191 days	(25), fw	1
	dieldrin	530 days	(25), fw	1
	aldrin	7.7 days	(25), fw	1
	2,4-D(methylester)	13.8 days	(25), fw	4
PCB	Arochlor 1242	12.1 hr	(25), fw	1
	Arochlor 1248	9.5 hr	(25), fw	1
	Arochlor 1254	10.3 hr	(25), fw	1
	Arochlor 1260	10.2 hr	(25), fw	1

[1] McKay & Leinonen (1975)

[2] Dilling et al. (1977)

[3] Sauer (1978)

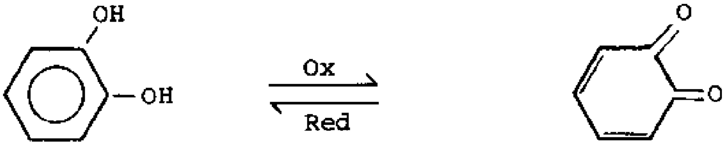
[4] Physical data from Zepp et al. (1975)

Examples of hydrolysis half-lives for some xenobiotic compounds are given in Table 6.22. These rates may differ greatly from those in the environment where factors such as pH, ionic strength, temperature, and the presence of catalysts may be important.

Hydrolysis rate constants are typically quoted for dissolved species and should be modified if the compounds are partitioned between the aqueous and the suspended phases. Although many chemical hydrolysis products are formed in the waste stream itself, hydrolysis is a common microbially-mediated reaction and should continue in the marine environment. Note that the hydrolysis rate constants given in Table 6.22 are for chemical hydrolysis only. Microbially-mediated hydrolysis rates may differ substantially depending on the species, substrate concentration and other environmental conditions. The hydrolysis of condensed organic molecules may enhance their water solubility and susceptibility to microbial attack.

<u>Chemical oxidation.</u> Although organic carbon compounds are thermodynamically unstable in aerobic environments with CO_2, NO_3^- , SO_4^{2-} as the end oxidation products, chemical oxidation is usually a very slow process. Susceptibility to chemical oxidation varies with the nature of the functional groups on the carbon skeleton and few of these will be chemically oxidized upon dilution of sewage with seawater.

One group of easily oxidized organic compounds is the phenols. Phenols and quinones form reversible redox couples; their interconversions are rapid enough to yield reproducible electrode potentials. In reducing environments such as sediments proximal to outfalls, phenols are often found. Catechol, a phenolic component detected at low levels in sewage effluents, exhibits this behavior:



catechol o-quinone

Another group of readily oxidized compounds are the mercaptans, which form disulfides with mild oxidants such as air and ferric salts.

Table 6.22 Hydrolysis Half-lives

Class	Compound	Products	Half-life		Conditions (°C)	Ref
Pesticides	DDT	DDE	12	yrs.	(27), pH5	1
	methoxychlor	anisoin/anisil/DMDE	1	yr.	(27)	1
			0.74	yr.	(25)	3
	2,4-D(methylester)	2,4-D	44	days	(28), pH6	4
		2,4-D	1.1	hr.	(28), pH9	4
	2,4-D(1-buthylester)	2,4-D	220	days	(28), pH6	4
		2,4-D	17	hr.	(28), pH9	4
LMHH	CH_3Cl	CH_3OH	2.5	yrs.	(20)	2
			14	yrs.	(10)	2
			88	yrs.	(0)	2
	CH_3Cl	CH_3OH	0.93	yrs.	(25)	3
	CH_3CH_2Cl	CH_3CH_2OH	0.10	yrs.	(25)	3
	CH_3Br	CH_3OH	0.05	yrs.	(25)	3
	CH_3I	CH_3OH	0.30	yrs.	(25)	3
	CH_3F	CH_3OH	30	yrs.	(25)	3
	CH_2Cl_2		704	yrs.	(25)	3
	$CHCl_3$		3500	yrs.	(25)	
	CCl_4		7000	yrs.	(25), 6 M	3
Phthalate	$o-C_6H_4(C(O)OCH_2CH_3)_2$		22	yrs.	(25)	3

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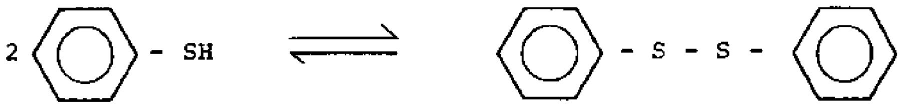
[1] Wolfe et al. (1977)
[2] Zafiriou (1975)
[3] Mabey and Mill (1978)
[4] Zepp (1975)



thiophenol

(Disulfides are commonly more toxic than the parent sulfur compound.)

Most compounds, however, require extreme conditions in order to undergo oxidation. For example, aromatic hydrocarbons are oxidized only by strong oxidants such as chromic acid or permanganate (as are used in the analysis of COD).

Microbial degradation. Microbial degradation is the dominant transformation process in the environmental fate of organic constituents. This is due to the high number and diversity of the organisms present in effluents and receiving waters and to the efficiency and the versatility of their metabolic pathways. Microbial transformations are relatively specific processes. Although the details of microbial pathways are outside the scope of this section, structural reactivity relationships are helpful in determining the general susceptibility of a compound to microbial attack (see Alexander, 1965 for review). Highly branched compounds are frequently fairly resistant to biodegradation. Increased branching and substitution hinders β-oxidation, the usual mechanism for microbial destruction of alkyl chains. Ease of degradation thus increases from highly branched to straight carbon chains. Alkanes are more liable to biological degradation than aromatic compounds. Aldehydes, carboxylic acids, and primary amines are readily metabolized. Chlorination or fluorination generally increases the environmental lifetime of organic compounds. These general biodegradability relationships are indicated in Figure 6.27.

Metabolism and degradation of synthetic organic compounds by aquatic organisms typically involve the conversion of a lipid-soluble component to a more water-soluble component with the aid of microsomal oxidases. Direct enzyme-mediated attack of the OH radical may be followed by rearrangement or further degradation. Some general reaction types are shown in Figure 6.28.

Figure 6.27 Biodegradability relationships.

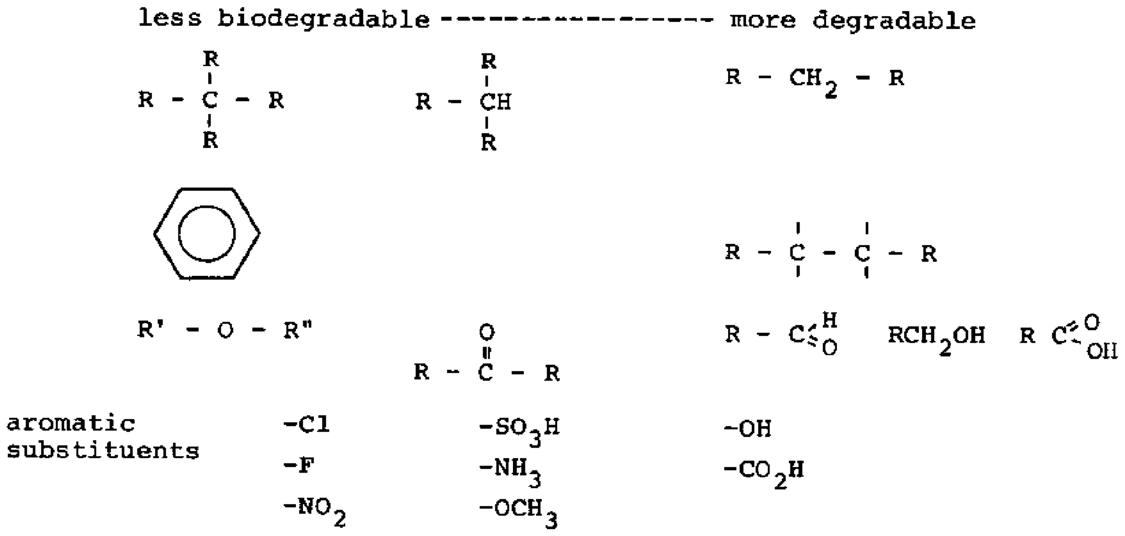
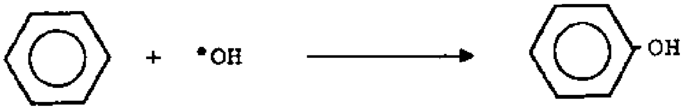
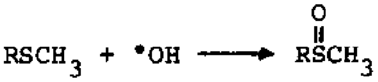


Figure 6.28 Several general reaction types of direct enzyme-mediated attacks of the OH radical.

1. Ring hydroxylation:



2. Sulfoxidation:

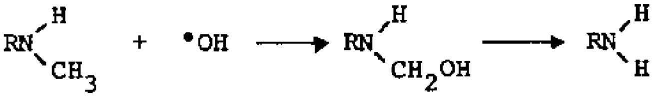


$RSCH_3 + {}^\bullet OH \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{S}CH_3$

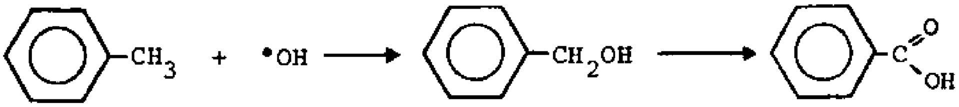
3. O-Dealkylation:

$R\text{-}OCH_3 + {}^\bullet OH \longleftrightarrow R\text{-}OCH_2OH \longrightarrow ROH$

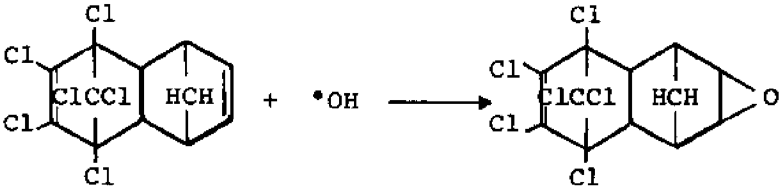
4. N-Dealkylation:



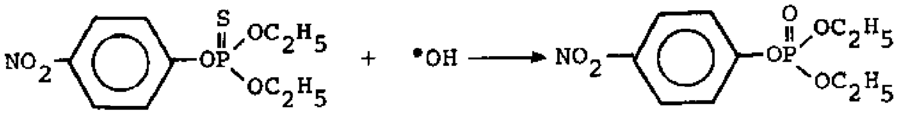
5. Side chain oxidation:



6. Epoxidation:



7. Desulfuration:



Rarely does full oxidation to mineral phase (CO_2) occur. Partial oxidation is characterized by a mass increase as oxygen-containing substituents are introduced into the molecule.

Metabolism and transformation of trace organic compounds by organisms other than bacteria may be important especially in aerobic sediments. Processing of organic compounds in the digestive tracks of benthic organisms may permit a more rapid or complete oxidation than would be obtained in the water. However, the relative importance of such processes in the overall degradation of waste organic materials is poorly understood as are their rates and the nature of the metabolites produced.

Photochemical transformation. Photochemical reactions may heighten or diminish the toxicity of organic compounds in the marine environment and concomitantly increase or decrease their susceptibility to biological degradation. For example, photolysis of 2,4-D produces many compounds (including a polymeric substance from the intermediate 1,2,4- trihydroxybenzene, see Figure 6.29) that may have toxic properties and longer environmental half-lives than the parent compound. Although photolysis may not immediately seem a major transformation pathway for pollutants in submerged sewage plumes, it could be an important degradative mechanism for environmentally persistent compounds such as polycyclic aromatic compounds, DDT, pesticides and PCBs.

Photochemical transformations can occur in the euphotic layer, in marine aerosols, in the surface microlayer or at the sediment-water interface in shallow waters. More light is absorbed by the sea than by the entire troposphere where important photochemical reactions are known to occur (Zafiriou, 1975, 1977). Photons reaching the sea have energies from 14.0 to 33.5 x 10^3 cm^{-1}, in excess of activation energies for most common chemical reactions. (Figure 6.30) In oligotrophic ocean waters, the average chemical excitation rates for a water column of 40 meters ranges from 1/2 to 1/5 the value of near surface rates, depending on the transparency of water. Average excitation rates are, of course, reduced in coastal and productive oceanic waters. Photochemically induced chemical reactions include dimerization, elimination, dissociation, isomerization and free radical formation. Excitation of lone electron pairs on oxygen, nitrogen and sulfur

Figure 6.29 Photolysis of 2,4-dichlorophenoxy acetic acid (Crosby and Tutass, 1966).

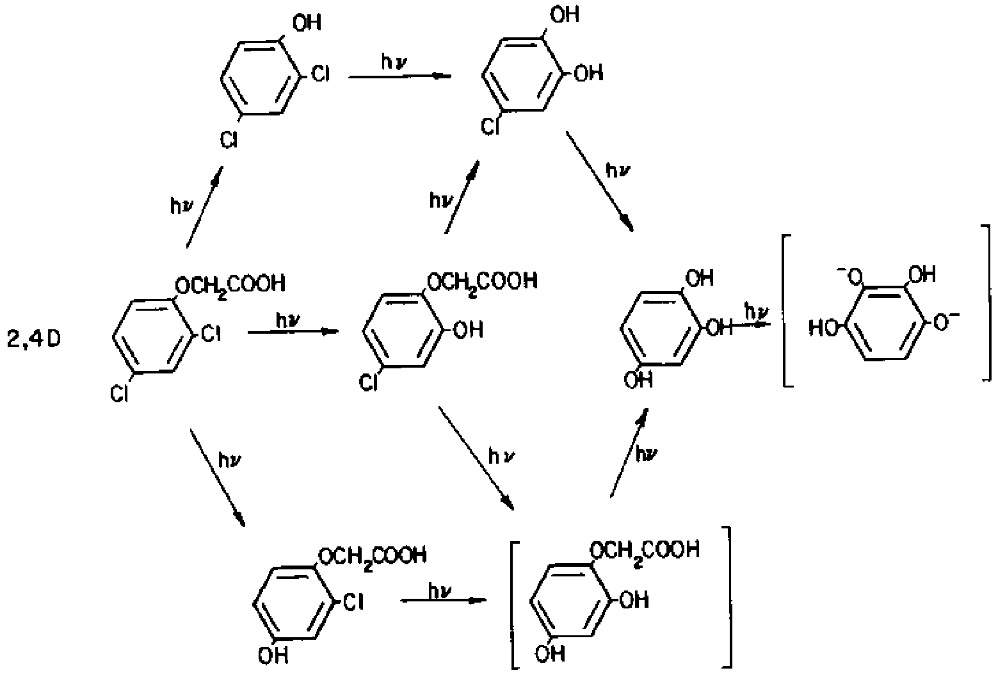
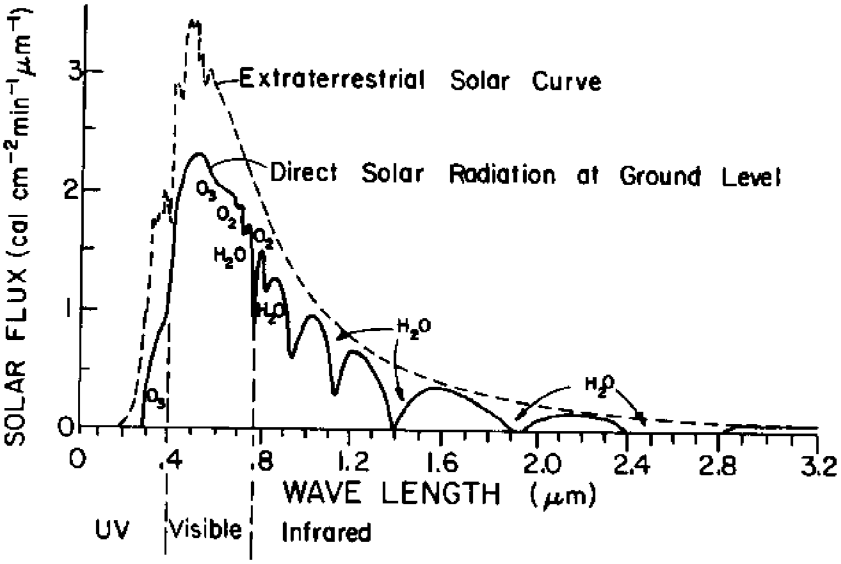


Figure 6.30 Extraterrestrial solar flux and solar flux at the surface of the earth with major absorption bands from atmospheric O_2, O_3 and water vapor (Wetzel, 1975).



is facile, and can lead to reactions such as cyclization or hydrogen abstraction. Direct photochemical reactions of many aromatic compounds do not occur because the ozone layer effectively screens the necessary energies (<280 nm). An electronically excited molecule however, may act as a photochemical sensitizer by promoting excitation in a second acceptor molecule. Photosensitization enables compounds that do not normally absorb within the UV range to receive photochemical energy. Recently large concentrations of singlet oxygen, a product of direct photochemical reactions, have been shown to exist in surface waters (Zepp, 1977). The effect of the presence of this powerful oxidant is still undetermined but it appears that deactivation in aqueous medium is rapid (~2 μs).

The critical parameter describing the efficiency of a photochemical process is the quantum yield, $\emptyset$. ($\emptyset$ is equal to the number of the unit process of interest resulting from absorption of a given quantity of photons. Theoretically the sum of all primary quantum yields from all deactivation processes is equal to one. Secondary processes, such as free radical chain mechanisms, may result in a very large experimental $\emptyset$. A small $\emptyset$ results if a quencher or rapid reverse mechanism is present.) For direct photolysis, first order kinetics are usually obeyed (Hedlund and Youngson, 1971):

$$-\left(\frac{d\ C}{dt}\right) = \emptyset\, k\, C$$

where C is the concentration, and k is the photolysis rate constant. The photolysis half-life, $t_{1/2}$ (the time required to achieve 1/2 of the initial concentration), is given by:

$$t_{1/2} = \frac{\ln 2}{\emptyset\, k}$$

It is important to note that the half-life is concentration independent. If all the incident light is absorbed by the compound, however, the photolysis kinetics become zero order. The half-life is then dependent on initial compound concentration and depth of the water sample. Often, in the laboratory where high pollutant concentrations are used, the resultant half-lives are longer than those experienced in the natural environment. Thus, without an estimate of in situ $\emptyset$, a minimum photolysis rate is calculated. The determination of $\emptyset$ for a very dilute solution is governed by the solubility criteria of the organic pollutant. Generally, $\emptyset$ is assumed to be independent of the absorption wavelength. $\emptyset$ can also be estimated in the laboratory by comparison to a reference pollutant (DDE is common) or from the slope of a first order plot of ln C versus exposure if the light intensity, extinction coefficient and path length are known. Some photolysis half-lives are given in Table 6.23. Translation of laboratory direct photolysis data into environmental half-lives for organic compounds under natural sunlight has been developed with considerations of season, latitude, time of day, depth of water, and thickness of ozone layer (Mancini, 1978; Zepp and Cline, 1977). Not included in these models, however, are the presence of sensitizers, daily variations in cloud and ozone layers, and the effects of light scattering.

Bioconcentration of organic pollutants. Organisms have been shown to concentrate and accumulate high concentrations of lipid-soluble compounds, either directly from the water or as a result of a contaminated food source. The bioconcentration of the pesticides DDT and dieldrin by fish, especially in cold waters where major detoxification processes are insignificant, is a linear function of the age of the fish (Metcalf, 1977). The concentration of organic compounds by organisms is analagous to the analytical technique of solvent extraction. Estimation of the partition of an organic compound between lipid and aqueous phases has been accomplished in the laboratory by a solvent system of n-octanol and water. The partition coefficient, $K_{o/w}$ is defined as the equilibrium ratio of constituent activity in the organic phase, a_o, to the activity in the aqueous phase, a_w:

$$K_{o/w} = \frac{a_o}{a_w}$$

An unknown partition coefficient can be estimated from partition coefficients of comparable carbon skeletal arrangements and addition of constants due to modification by corresponding substituents.

$$\log K_{o/w}^{\text{unknown}} = \Sigma \log K_{o/w}^{\text{sub}} + \log K_{o/w}^{\text{c skeleton}}$$

Additivity constants are listed in Table 6.24 (Hansch et al., 1972; Leo, 1971).

The log of the bioconcentration factor (defined as K_1/K_2, where K_1 is the rate of uptake and K_2, the rate of excretion) in the muscle of the rainbow trout, _Salmo gaindneri_, has been correlated

Table 6.23 Photochemical Half-Lives

Class	Compound	Photochemical Half-life	Reference
Pesticides	DDT	150 yr	1
	Methoxychlor	4.5 months	1
	2,4-D (Methylester)	29 days	2
Polycyclic Aromatic Hydrocarbons	naphthalene	71 hrs.	3
	1-methylnaphthalene	22 hrs.	
	phenanthrene	8.4 hrs.	
	anthracene	6.75 hrs.	
	pyrene	0.68 hrs.	
	fluoranthene	21 hrs.	
	benzo(a)pyrene	0.54 hrs.	

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[1] Wolfe et al., 1977.
[2] Zepp et al., 1975.
[3] Zepp and Schlotzhauer, 1979.

Table 6.24 Additivity Constants for Partition Coefficents (Leo, et al., 1971)

Calculation Step or Group	Additivity Constant(logs)	Uncertainty Units (uu)*
1. $-CH_2-$	0.50	0.02
2. Branching		
in C chain	-0.20	0.02
of functional group	-0.20	0.05
ring closure	-0.09	0.02
3. Double bond	-0.30	0.03
4. Folding of aliphatic chain	-0.60	0.05
5. Intramolecular H-bonding	0.65	0.10
6. Aliphatic groups	on aliphatic	chains
-COOH	-0.65	0.03
-OH	-1.16	0.03
$-NH_2$	-1.16	0.03
-C=O	-1.21	0.03
-CN	-0.84	0.04
-O-	-0.98	0.05
$-CONH_2$	-1.71	0.05
-F	-0.17	0.03
-Cl	0.39	0.04
-Br	0.60	0.04
-I	1.00	0.05
7. Cl on benzene	0.70	---
Cl on phenol	0.73	---
-ortho	0.73	---
-meta	1.04	---
-para	0.98	---
8. Aromatic groups		
-benzene	2.13	---
-phenol	1.46	---

*Uncertainty units are assigned by considering the average deviation in logK values of solutes with the required structural differences. They are not standard deviations in the strict sense.

with the log of the partition coefficient for 6 organic compounds as shown in Figure 6.31a (Neeley et al., 1974). Biconcentration has also been correlated with partition coefficients for mosquito fish Gambusia affini (Lu and Metcalf, 1975; Figure 6.31b). Thus in a first approximation, octanol/water partition coefficients may indicate the bioconcentration expected for a given lipid-soluble compound. Other important considerations include the rate at which the organic compound is degraded in vivo into excretable metabolites and the environmental stability of the organic compound in water.

Similarly water solubility is related to bioconcentration since water solubility and partition coefficient are correlated (Chiou et al., 1977). Figure 6.32 shows this correlation over 8 orders of magnitude in solubility and 6 orders of magnitude in $K_{o/w}$. The figure covers a wide range of organic classes: hydrocarbons, aromatic acids, pesticides, PCBs and organic halides encompassing differences in polarity and physical state. The thermodynamic basis for this relationship has been discussed (MacKay, 1977; Chiou et al., 1977) and involves considerations of solute activity coefficients and solubility effects of octanol in water and water in octanol.

Simple input-output models of pollutant concentrations in organisms can be formulated. For example the absorption rate may be taken as proportional to the environmental concentration and the "deconcentration" processes (excretion, degradation, dilution through growth) as proportional to the internal concentration:

$$\frac{dC_{org}}{dt} = \frac{C_{env}K_{ab}}{V} - K_{ex}C_{org}$$

(where C_{env} and C_{org} are the concentrations of the pollutants in the environment and the organism respectively; K_{ab} is the absorption constant; K_{ex} is the sum of rate constants for excretion, degradation and dilution.) Integrating for a constant C_{env}, yields:

$$C_{org} = \frac{C_{env}K_{ab}}{K_{ex}\ V}\ [1 - \exp(-K_{ex}t)]$$

At steady state:

$$C_{org} = \frac{C_{env}K_{ab}}{K_{ex}\ V}$$

Figure 6.31a Linear regression between logarithms of partition coefficient and biconcentration of various chemicals in trout muscle (Neeley et al., 1974).

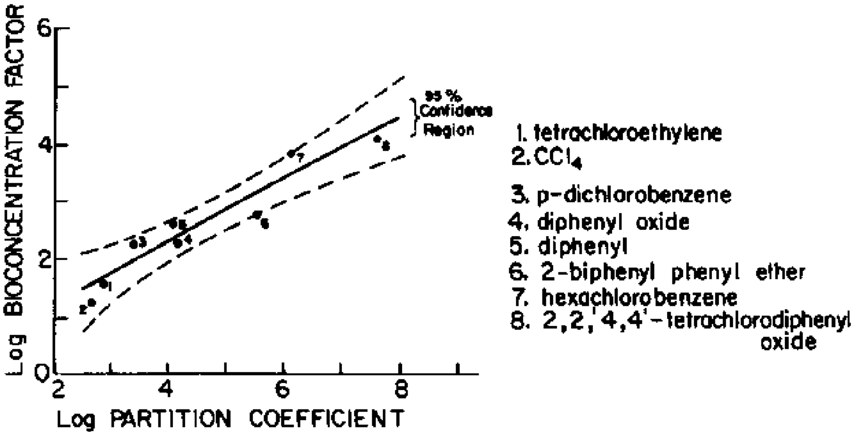


Figure 6.31b Relationship of $K_{o/w}$ to bioconcentration of various organic compounds in the fish <u>Gambusia affinis</u>.

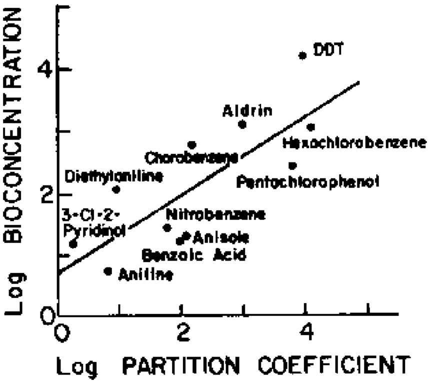
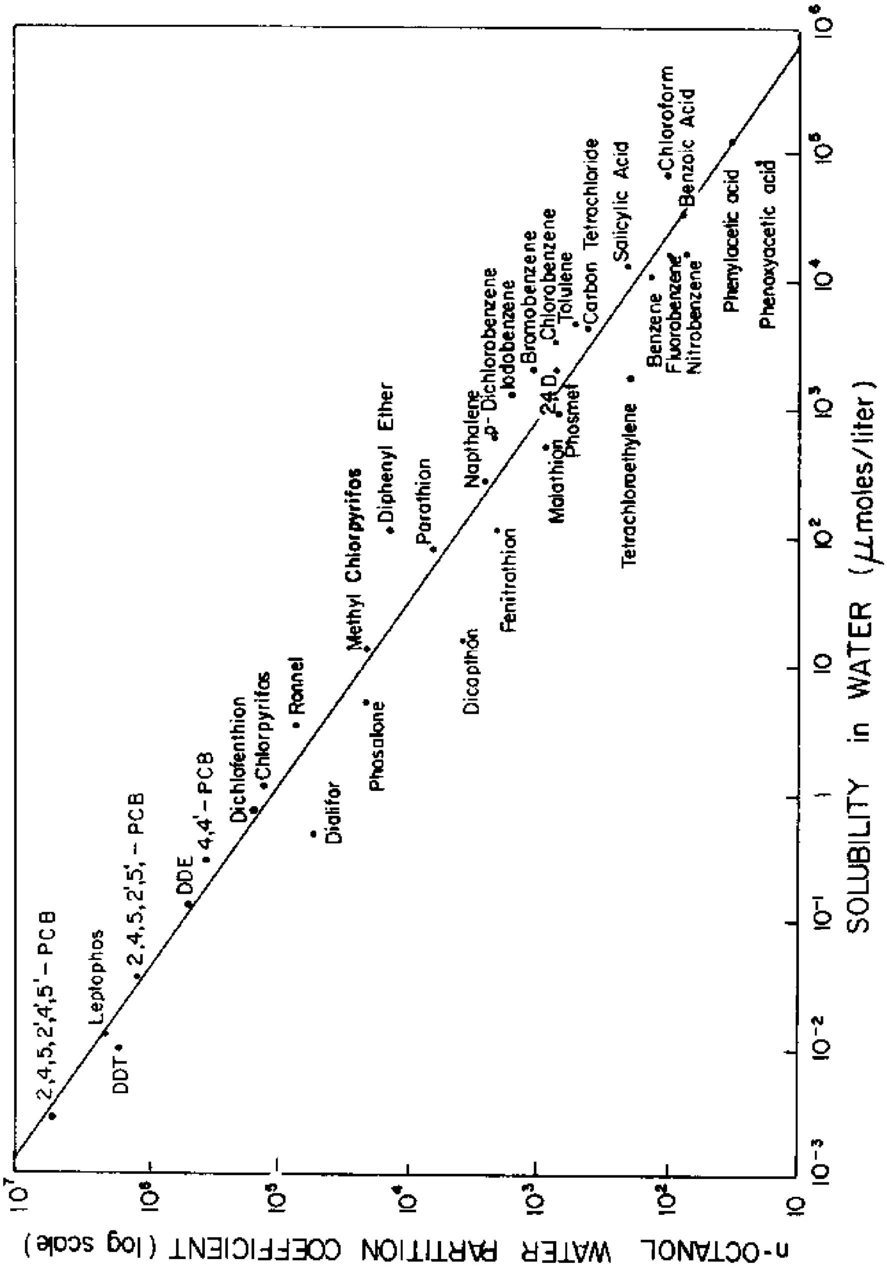


Figure 6.32 Partition coefficients and aqueous solubilities of various organic chemicals at room temperature (Chiou et al., 1977).



If the excretion rate is slow compared to the longevity of the organism, the cellular concentration never reaches a steady state and it increases approximately linearly with age. Similar models can be formulated for bioconcentration from food intake although the rate constants are not well quantified for most organisms.

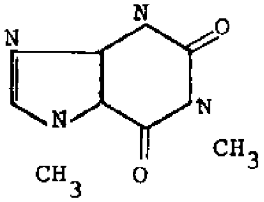
Surface microlayer. At the sea surface, a microlayer averaging typically 40 μm in thickness in the open ocean (Peng et al., 1979), and enriched with respect to fatty acids, hydrocarbons and trace metals has been observed (for review see MacIntyre, 1970). Enrichment of surface-active compounds may or may not be evidenced by a visible surface slick. Stratification exists within the microlayer. Nearer the interface, particulate matter and a substantial bacterial population are noted; below lie autotrophic cells and dissolved elements. Photochemical reactions are maximized at the surface. Chemical and biological activity is also intensified due to increased concentrations of reactants, substrates, trace metals, catalysts, and nutrients. Evaporation rates of compounds could, in principle, be affected by the microlayer, although neither *in situ* measurements nor wind tunnel experiments have as yet demonstrated this effect.

Since aerosol formation at the sea surface should yield particles that are more representative of the surface microlayer than subsurface waters, airborne particles may be enriched with respect to bulk seawater in organic materials and metals. Enrichment factors in the top 100 to 150 μm, compared to subsurface water, have been obtained in Narragansett Bay waters (Duce et al., 1972). If a surface microlayer of 5 molecular layers is assumed, enrichments of 4×10^4 in PCB or approximately 60 ppm PCB, was found. The overall importance of the microlayer in governing physicochemical transformations is not yet fully ascertained.

Case Examples

Physical and chemical characteristics were used to establish the classification scheme presented in Table 6.18, with regard to the fate and persistence of waste organic fractions. The members of each class have several physical and chemical factors in common. In the following discussion, certain subgroups and some specific examples will be isolated in an attempt to illustrate these features.

Biogenic compounds. The components of Class 1 are either found in the marine environment or are similar in structure and concentration (after dilution) to compounds already present. Thus, microbial degradation pathways have already been established and marine organisms are adapted to the presence of the components. Caffeine, a compound of chiefly anthropogenic origin in the sea, is found at an analytically detectable level in sewage, yet it cannot be used as an effluent tracer due to the availability of a rapid microbial degradation pathway. Although caffeine demonstrates a large degree of aromatic character, the presence of a variety of functional groups facilitates microbial attack.



caffeine

A tracer that has been used for sewage studies is coprostanol, a sterol exogenous to the marine environment (Hatcher, 1970). Coprostanol has been found at levels of 8 μg l^{-1} in activated sludge effluent and 100 μg l^{-1} in trickling filter sludge. Although a microbial degradation pathway is postulated since this compound has the same basic carbon skeleton as other sterols such as brassicasterol (a phytoplankton-derived sterol) or cholesterol (a common crustacean sterol), the kinetics of removal are slow enough to permit monitoring of coprostanol as a sewage tracer in the marine environment.

Oil and grease. The standard analytical component of municipal wastewater effluent labelled "oil and grease" constitutes a significant discharge to the marine environment. Table 6.25 compares oil and grease fractions for raw wastewater, primary and secondary effluents. The standard engineering method for determining this fraction involves sample extraction with hexane (hexane-extractable material; H.E.M.) yielding non-polar aromatic, paraffinic, cyclic and alkyl-substituted hydrocarbons. The oil and grease fraction constitutes from 20 to 50 percent of the total organic carbon content of municipal wastes, the larger percentages being obtained if urban (street) runoff is included in the wastewater system. The annual input of petroleum products to coastal regions of the United States from marine waste disposal is large. This input amounts to 60 percent, on a tonnage basis, of the input from oil spills, or 31,000 metric tons in 1974 (Van Vleet and Quinn, 1977). The following discussion distinguishes between non-aromatic petroleum hydrocarbons (paraffins, cycloalkanes, etc.,) and aromatic hydrocarbons.

Table 6.25 "Oil and Grease" and TOC Concentrations ($mg\ l^{-1}$) in Municipal Wastes (Mueller et al., 1976)

	TOC	Oil & Grease	Oil & Grease / TOC
Raw sewage	83	36	.43
Primary effluent	107	23	.21
Secondary effluent	34	15	.44
Sludge	9,200	1,900	.21

Non-aromatic hydrocarbons. The adsorption of hydrocarbons onto settling particulate matter results in an important environmental sink for heavier petroleum components from natural waters. Over 95 percent of the hydrocarbons entering Providence Bay from the Providence River are reported to be in suspended solids that must eventually settle to the sediments (Van Vleet and Quinn, 1977). The same is true of more than 95 percent of the oil and grease fraction of the sludge barged into the New York Bight.

Adsorption increases with increasing molecular weight in n-alkanes, isoalkanes, and monoalkenes, but not necessarily in polyunsaturated or aromatic compounds. N-alkanes and n-alkenes are adsorbed to a similar extent, but less than isoalkanes. Much like in chromatography, these differences in adsorption characteristics may enhance the fractionation among petroleum components in aquatic systems, especially during advective transport. For example a loss of aromatic character has been noted in petroleum fractions moving down river or in coastal currents. Since adsorption appears to be highly correlated with the amount of organic matter in particles (Karickhoff et al., 1979), the high organic content of waste solids should facilitate hydrocarbon sedimentation.

The degree to which hydrocarbons dissolve in water may be a controlling factor in their biodegradation. Although hydrocarbons are readily metabolized microbially, their low solubility limits the amount of hydrocarbon substrate available for attack by free living bacteria, and presumably much of the decomposition must take place at the surface of particles. The presence of benthic organisms which induce bioturbation and resuspension of sediments, also greatly enhances microbial degradation rates. Although phytoplankton do not appear to metabolize hydrocarbons, uptake of lower molecular weight components may result in ultimate deposition in the sediments. It has been estimated that 20 percent of the particulate oil in an oil spill may be sedimented via ingestion of oil droplets by zooplankton and subsequent excretion in faecal pellets. Some copepods have enzymes capable of metabolizing hydrocarbons to various excretable hydroxylated metabolites. Fish take up hydrocarbons in gill membranes, from ingested food, or by direct absorption of more volatile hydrocarbons from water.

Aromatic hydrocarbons. Aromatic hydrocarbons are unsaturated ring structures which may also contain alkylated substituents. They include benzenes, naphthalalenes, phenanthrenes, chrysenes, benzopyrenes, indenopyrenes, dibenzanthracenes and many more. 3,4-benzopyrene is perhaps the most widely studied due to its known carcinogenic properties. Aromatic hydrocarbons may also be formed *in situ* in the marine environment (Laflamme and Hites, 1978; Wakeham et al., 1980; Laflamme and Hites, 1979).

Aromatic hydrocarbons have a tendency to accumulate at the air-water interface and photo-oxidation may result in the formation of highly toxic water soluble compounds.

Neff (1979) has recently reviewed the literature on metabolism of polycyclic aromatic hydrocarbons. In animals, the metabolism of aromatic hydrocarbons involves hydroxylation without ring cleavage. The excreted products thus retain the initial aromatic ring. The operative metabolic oxygenase system often results in the formation of arene oxides, phenols and diols as the first intermediates. The presence of this enzyme system is evidenced in marine fish, crabs and worms. Fish exposed to petroleum products demonstrate increased liver mixed function oxygenase activity, resulting in increased water solubility of the ingested parent compound, and thus facilitating compound excretion. Bacteria can utilize aromatic hydrocarbons as a carbon source, inducing ring cleavage with CO_2 as the eventual product. Bacteria typically produce cis-diols, whereas animals produce trans-diols, from aromatic hydrocarbons.

The toxicity of aromatic hydrocarbons to organisms decreases with the ring size--the monoaromatics being the most toxic (Blumer, 1971). The decrease in toxicity is due to the large molecular size, which inhibits direct uptake, and an extremely low water-solubility. In the benzene, napthalene and phenanthrene series, toxicity increases with an increasing degree of alkylation. Arene oxides, as well as some phenols and diols, have necrotic, mutagenic and carcinogenic properties.

Low molecular weight halogenated hydrocarbons. Low molecular weight halogenated hydrocarbons (LMHH) include compounds such as chloroform, carbon tetrachloride, di-, tri- and tetrachloroethylenes. LMHH concentration in the Los Angeles City wastewater discharge is estimated to be one order of magnitude higher than chlorinated benzenes (CB), or about 2 orders of magnitude above DDT or PCB residues. DDT and PCB are the components comprised in the familiar engineering term "total identifiable chlorinated hydrocarbons", while CB and LMHH concentrations are not routinely monitored. LMHH are produced in extremely large quantities annually, constituting approximately 90 percent of the total 1971 production of halogenated hydrocarbons. LMHH may also be formed during chlorination of wastewater prior to release, especially in anaerobically digested effluents with high methane, and lighter n-alkane or alkene concentrations.

Unfortunately, very little is known about the environmental fate and effects of LMHH. The high vapor pressures characteristic of this class of compounds enable facile partitioning to the atmosphere. Evaporation half-lives are generally around a few hours from a 1 m water depth, and volatilization followed by chemical degradation in the atmosphere probably constitutes the principal elimination mechanism. The high-water solubilities of these compounds correlate with low bioaccumulation factors, 100 to 1,000 times smaller than those of common pesticides, resulting in aquatic toxicities at approximately 10^2-10^3 ppm compared to 0.1-1 ppm for most chlorinated aromatic compounds.

Chlorinated benzenes. In 1976, southern California municipal wastewater analyses for chlorinated benzenes (CB), showed CB effluent concentrations one order of magnitude greater than PCB or DDT concentrations (Young et al., 1978), a manifestation of the extensive industrial and domestic use of these compounds. Five chlorinated benzenes are of concern: p-dichlorobenzene (p-DCB), o-dichlorobenzene (o-DCB), 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, and hexachlorobenzene (HCB). The widespread use of p-DCB as the mitostatic poison in deodorizer cakes placed in public urinals constitutes a major contribution to wastewater treatment plants. O-DCB and the trichlorobenzenes are used as cleaning solvents, rust-proofing and degreasing agents, oil additives and insecticides. Trichlorobenzene is also the dominant metabolic degradation product of the common domestic alicyclic pesticide, lindane. In 1976, approximately 9,000 kg of p-DCB and o-DCB were discharged through the Los Angeles County submarine outfalls (Young et al., 1978). The 1975 and 1976 effluent samples that were analyzed for CB were not subject to disinfection by chlorination, thus these concentrations reflect influent loads, not chlorination products. (Chlorinated benzenes are formed during the aqueous chlorination of petroleum products such as diesel fuel; Reinhard et al., 1976).

The chlorinated aromatic character of CBs results in a high resistance to degradation during primary and secondary treatment processes. Both microbial degradation and hydrolysis rates appear to be very slow. In the Whites Point area, CBs have been found to accumulate 3 orders of magnitude less than DDT and 2 orders of magnitude less than PCB in Dover sole livers. This is consistent with a higher aqueous solubility and an octanol-water partition coefficient approximately twenty times lower for CB than for PCB or DDT. Not much is known of the biological effect of CBs, but they have been shown to damage liver cells and p-DCB is a strong mitotic inhibitor. At present, the long-term fate and effects of CB in marine waters and sediments cannot be assessed. The scarcity of research on this subject reflects the long delay in the identification of CBs as significant pollutants in municipal wastewater.

Hexachlorobenzene has been cited as a pollutant of special concern by the National Academy of Science (1975), due to its mitotic inhibitory effects. Concentrations of HCB are roughly one order of magnitude lower than CB in southern California municipal effluents analyzed in 1975 (Young and Heesen, 1978). Bioaccumulation of HCB in rainbow trout, however, has been determined as 37 times the accumulation of PCB, thus indicating the need for more research into environmental transport and transformations of HCB.

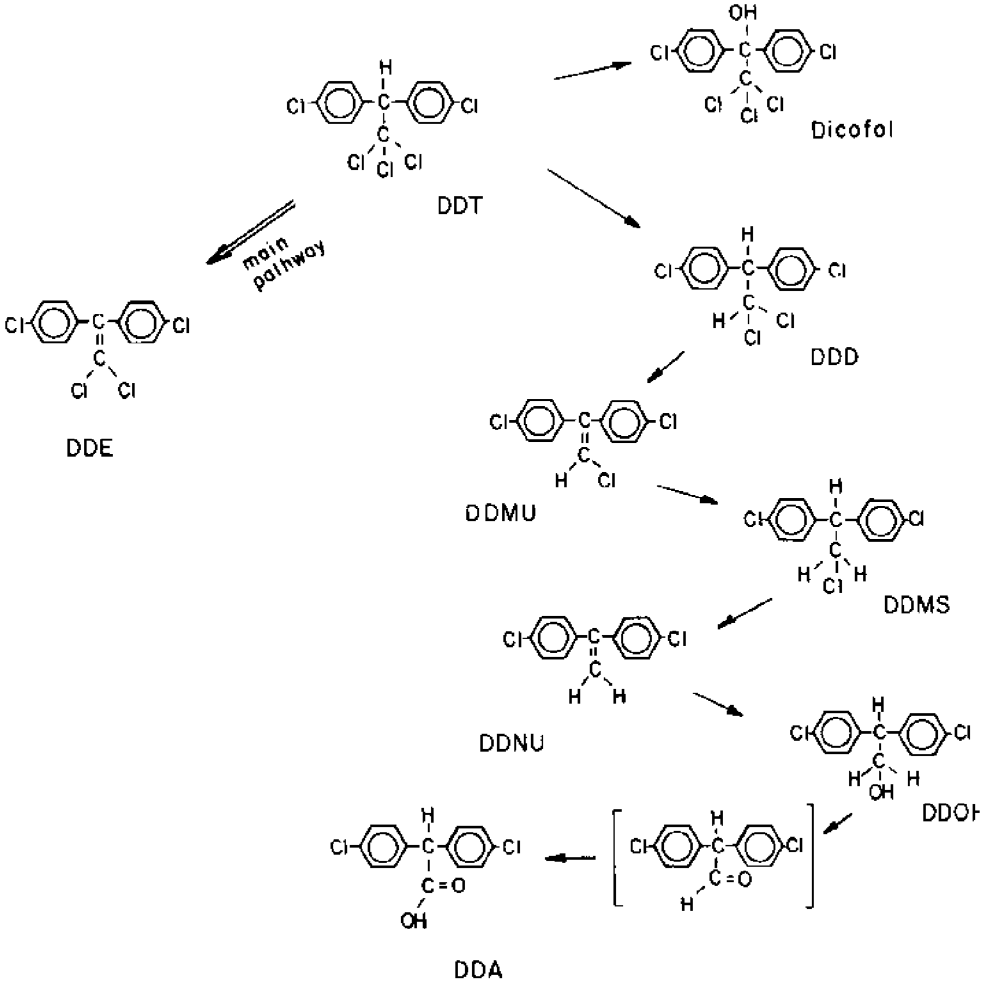
DDT. DDT has become a ubiquitous anthropogenic contaminant in the environment. The pesticide has been suspect in the decline in reproductive success in bald eagles, peregrine falcons south of Alaska and brown pelicans on the California coast. The presence of DDT in Antarctic penguins further illustrates the widespread dispersion of DDT and the necessity of elucidating transport/transformation pathways for important anthropogenic compounds and corresponding metabolites. DDT degrades in the environment to the more biochemically stable DDE. Of the two metabolic pathways shown in Figure 6.33, DDE is the predominant one over p, p-DDA which is excretable. The half-life of DDT increases with decreasing temperatures and DDT may thus be accumulating particularly in cold water fish. Both DDT and DDE have low water solubilities and high octanol/water partition coefficients.

The major hydrolysis product of DDT is also DDE. The hydrolysis rate increases with pH over the pH range of natural aquatic environments (pH 5-9) with an increased hydrolysis rate exhibited in alkaline media. At 27 , pH 7, the half-life of DDT with respect to hydrolysis is approximately 8 years (Wolfe et al., 1977). The hydrolysis reaction exhibits a pseudo first order rate. A second order dependence on hydroxide concentration is expected due to a second order elimination (dehydrochlorination) reaction. The pseudo first order rate constant is thus represented as:

$$K_{\text{observed}} = K_{H_2O} + K_{OH}[OH^-]$$

Catalysis or the presence of other compounds and microorganisms in natural environments can alter the rate and the mechanism of hydrolysis. Since degradation follows pseudo first order kinetics, the half life of DDT is concentration independent. The degradation product, DDE, is resistant to further hydrolysis.

Figure 6.33 Metabolic degradation pathways of DDT.

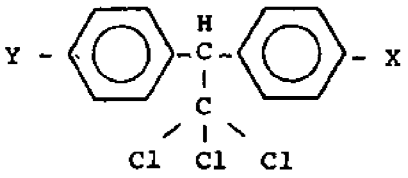


The increased environmental stability of the DDT metabolite, DDE, illustrates the need to elucidate and study degradation products of xenobiotic compounds present in waste streams. Structure-reactivity relationships between parent and degradation/ transformation products may be employed to predict rates for accumulation and persistence. For DDT, the replacement of electron-withdrawing Cl by H increases the dehydrochlorination half-life of the resultant compound by a factor of 5 (Wolfe et al., 1977). Chemical reactivity relationships are well quantified for common organic reaction mechanisms, and involve considerations of steric effects, electronic effects, resonance effects and charge.

Biodegradability of organic pesticides may be increased upon incorporation of substituents that easily undergo microbial attack. This is evidenced in the DDT series. Substitution of the two para chloro substituents (as shown by positions x and y in Figure 6.34) by methoxy groups ($-OCH_3$), as in methoxychlor, greatly enhances biodegradation. Methoxychlor, which is soluble in water at 0.62 ppm, is readily O-dealkylated *in vivo* to produce 2,2-bis-(p-hydroxyphenyl)-1,1,1-trichloroethane, with a water solubility of 76 ppm. Alkyl side chains are readily transformed microbially to carboxylic acids. Attack of methyl side chains on methylchlor (H_2O solubility 2.21 ppm) yields 2,2-bis-(p-carboxyphenyl)-1,1,1-trichloroethane (H_2O solubility 50 ppm). The increase in water solubility upon degradation of methoxychlor and methylchlor results in a decreased octanol/water partition coefficient, and therefore decreased bioaccumulation.

Polychlorinated biphenyls (PCBs). Polychlorinated biphenyls are a complex mixture of homologues and isomers whose stability towards environmental degradation increases with the introduction of additional chlorine atoms. The chlorine content of industrial PCB ranges from 30 to 60 percent by weight. Although 210 theoretical homologues and isomers exist, typically only about 14 major peaks are evidenced on a low resolution gas chromatogram. Common industrial mixtures, which exhibit different gas chromatograph "fingerprints", include Arochlor 1242, 1248, 1254 and 1260 (1242 and 1254 are the analyses most frequently performed although it is important to note that neither analysis is equivalent to *total* PCB).

Figure 6.34 Substituent effects on DDT family series (Kapoor et al., 1973).



X	Y	Compound	Ecological Magnification (ppm fish/ppm H_2O)	$K_{o/w}$ ($x10^{-3}$)	H_2O Solubility (ppm)
Cl	Cl	DDT	84,500	9.49	0.002
CH_3O	CH_3O	methoxychlor	1,545	2.05	0.62
C_2H_5O	C_2H_5O	ethoxychlor	1,536	1.18	0.163
CH_3	CH_3	methylchlor	140	3.74	2.21
CH_3S	CH_3S	---	5.5	7.08	0.57
CH_3S	CH_3O	---	310	0.784	0.189
C_2H_5O	CH_3	---	400	9.19	0.028
CH_3	Cl	---	1,400	29.3	0.10

The aqueous solubility of PCB is low (~56 ppb for Aroclor 1254), the components with the fewer chlorine atoms exhibiting greater solubilities (Haque et al., 1974). Like DDT, PCBs are generally associated with the particulate material discharged from outfalls. Analyses of wastewater during the primary and secondary treatment processes show that PCB accumulation is similar to heavy metal accumulation and virtually all PCB remains in the sludge solids throughout the process (Shannon et al., 1976). Adsorption of PCB to various substrates increases with increasing chlorine substitution due to decreased water solubility (Haque et al., 1974). Binding to solid particles greatly diminishes the loss of PCBs by evaporation.

The industrial applications of PCBs reflect their inherent high chemical stability. Common uses include transformer oils, capacitor dielectrics, hydraulic lubricants, plasticizers, printing inks and surface coatings. The high chemical stability is due to the aromatic character along with the presence of several chlorine substituents: PCBs are stable to hydrolysis with respect to strong acids and bases and their photochemical degradation requires UV light in the region effectively blocked by the upper ozone layer. Evaporation half-lives of PCB are fairly short (10.2 hr. for Arochlor 1260), but since practically all the waste PCB is adsorbed on particulate matter, evaporation does not constitute a major mechanism of elimination from coastal waters. Bacteria capable of using PCB as primary carbon source have been recovered from seawater (Sayler et al., 1978) where they appear to exist in higher concentrations than in the sediments where the particulate-bound PCB settles. The rates and extent of PCB microbial degradation are still to be determined but it has been postulated that the rates are low compared to the influx of PCB into the ocean.

A case study of the Southern California Bight illustrates dramatically a key point in the control of an environmentally persistent compound. In the period 1972 to 1975, the mass emission rates for PCB and DDT in municipal wastewaters were reduced by almost 90 percent (from greater than 19,000 kg/yr and 6,500 kg/yr in 1972 to 2,800 kg/yr and 1,300 kg/year in 1975, respectively (Shafer, 1976) due to control of industrial inputs and general use restrictions. Atmospheric fallout of PCB is now of a magnitude comparable to the sewage input. Despite the emission reduction, only minor decreases have been observed in the concentrations of DDT and PCB in bottom sediments and Dover sole flatfish in the vicinity of the Whites Point outfall. Figure 6.35 compares the decrease in wastewater, sediment and flatfish concentrations from May 1972 to February 1975, normalized to one. (The decreases reported in Dover sole or in sediments since 1972 are not statistically significant given the variations within the sample population.) It has been concluded that the relatively high levels of DDT now evidenced in bottom-feeding fish adjacent to the Los Angeles County submarine outfall will decrease only with a corresponding decrease in sediment concentrations (Young et al., 1976). Approximately 150 metric tons of total DDT are contained in the upper 30 cm of the bottom sediments in a 50 km^2 area off the Palos Verdes Peninsula.

The finding that surface sediment concentrations of DDT and PCBs have not decreased in parallel to mass emission rates suggests that there may be some mechanism for upward transport or concentration of DDT and PCB in the sediments. Sediment trap and sediment data for p,p'-DDE are given in Figure 6.36 similar to trace metal data in Figure 6.24 (see previous section for detailed explanations). The sediment trap data (line A) contain more scatter than the corresponding metal data, probably owing to a greater difficulty in analytical techniques. Also, since DDE is the degradation product of DDT, the scatter may reflect in part the time scale of the degradation processes. The experimental points from actual sediments lie below the ideal mixing line corresponding to approximately 50 percent oxidation of organic solids (line C). Figure 6.37 shows similar sediment trap and sediment data for PCB 1254. The picture is not outwardly as simple. The spread between the ideal mixing line and the sediment data indicates the operation of a secondary process. Past history of discharge into the Santa Monica Bay from Hyperion 7-mile pipe may provide an answer. The concentrations of DDT, total PCB, and PCB 1254 in Hyperion sludge are given in Table 6.26. Total PCB and PCB 1254 concentrations exhibit a substantial decrease from 1972 to 1975, whereas DDT concentrations (unlike total DDT input to the Southern California Bight) remain relatively constant. The sediment trap data obtained in 1975 probably reflect the recent low PCB concentrations of the effluent while homogenized sediment samples presumably reflect the previous sediment history of a few years and, in the case of PCB, the higher waste concentrations prior to 1975. A back calculation of the effluent concentrations necessary to agree with sediment data given a loss of organic matter of approximately 50

Figure 6.35 PCB and DDT in LACSD wastewater, surface sediment and flatfish muscle tissue May 1972 to February 1975 (Young et al., 1977. PCB 1254 May 1972 data are estimated from PCB 1242 May 1972 data using a typical wastewater concentration ratio of 2.5).

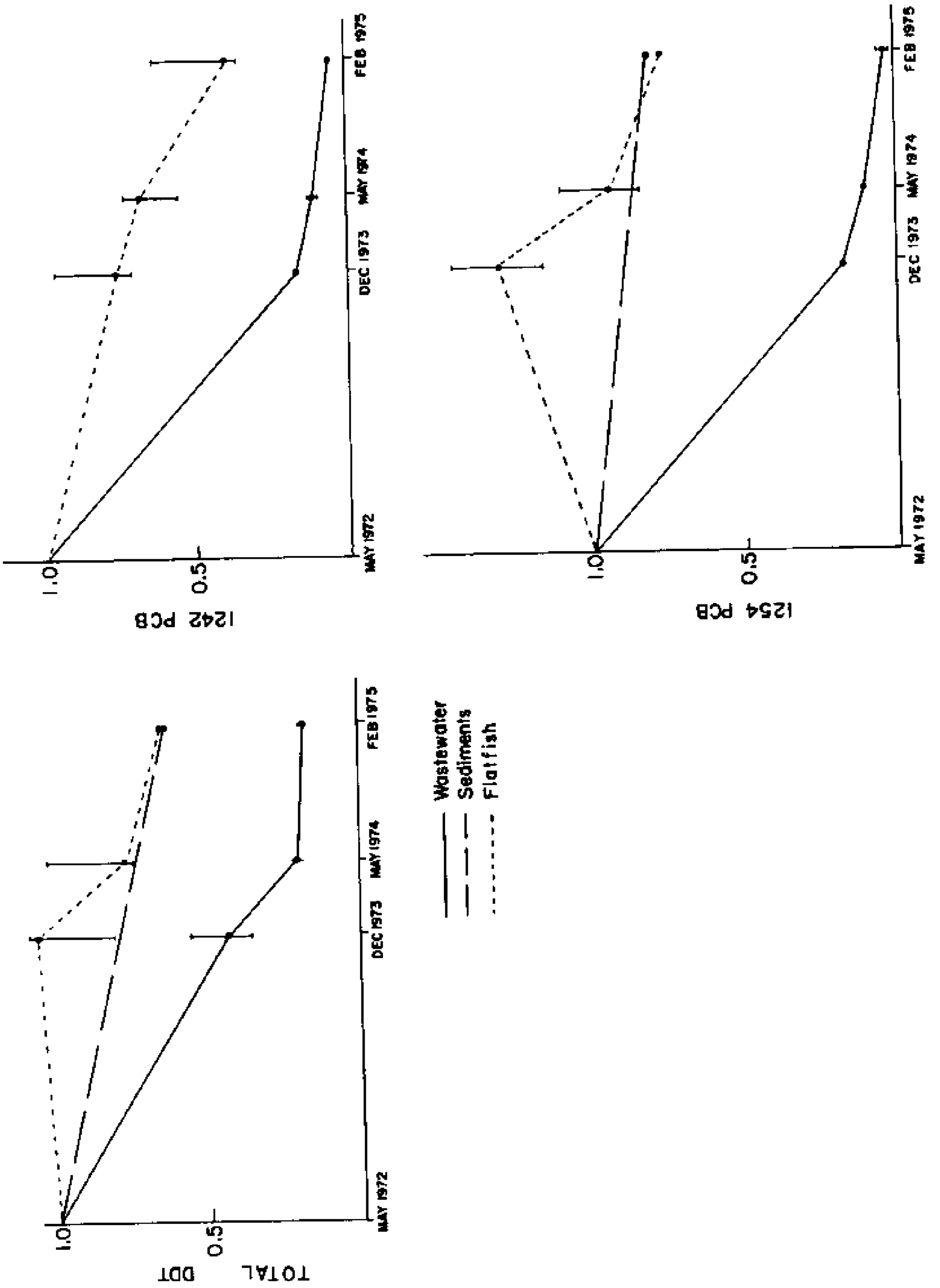


Figure 6.36 Volatile solids vs. DDE concentration (Data courtesy of D. Young and SCCWRP).

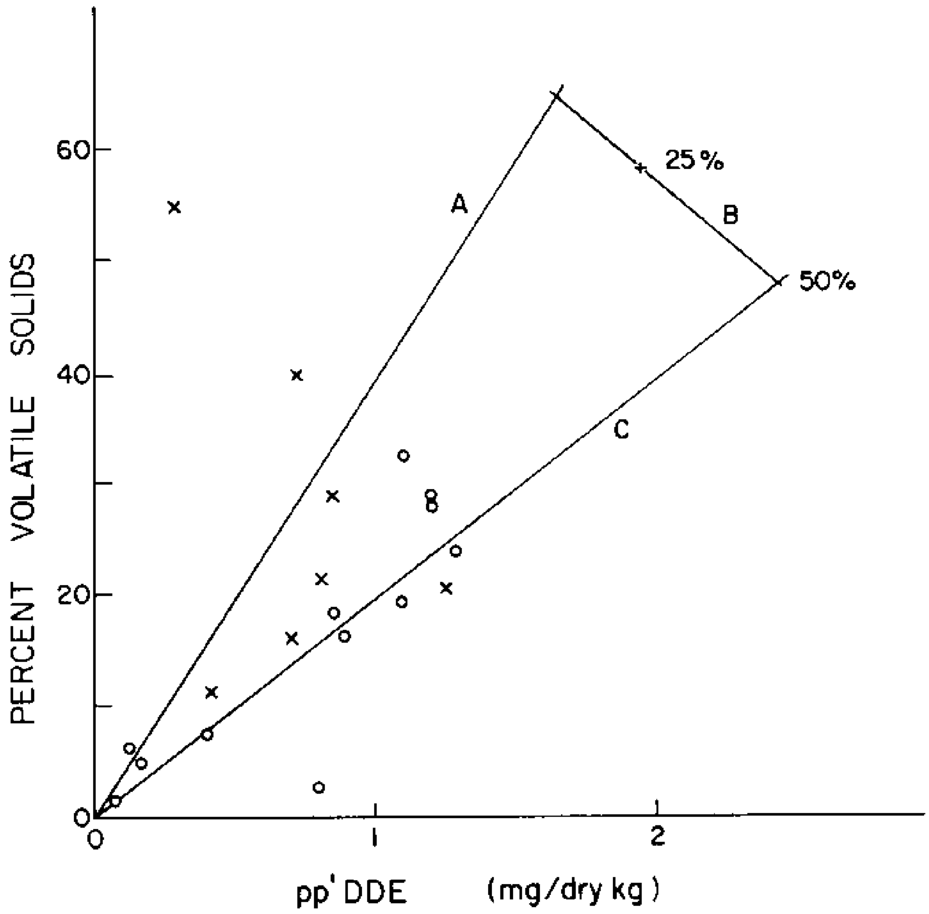
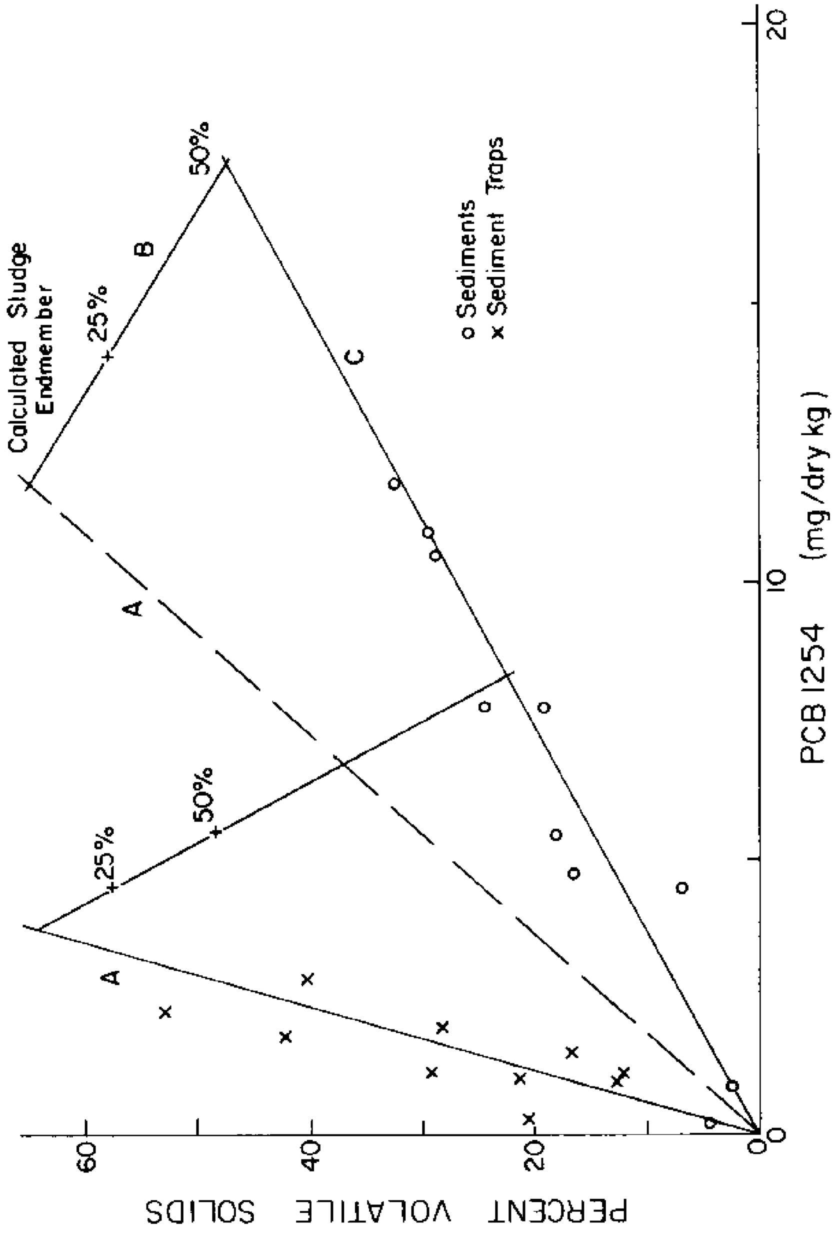


Figure 6.37 Volatile solids vs. PCB 1254 Concentration (Data courtesy of D. Young and SCCWRP).



percent yields an effluent concentration of 77 µg l^{-1}. This is not unreasonable in light of the 1972-1974 values in Table 6.26. Although PCB 1254 concentrations never reach the magnitude of the calculated effluent concentration, total PCB concentrations exceed this value by as much as a factor of 4. It must be remembered here that PCBs are analyzed according to the closeness of fit to a given industrial fingerprint and thus concentrations of a particular mixture may not reflect the total concentration. An analysis of total PCB, if properly handled, is generally a better concentration indicator.

Table 6.26 PCB and DDT Effluent Concentrations and Particulate Concentrations* in Hyperion 7-mile Sludge (Young et al., 1976)

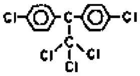
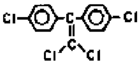
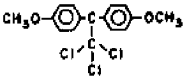
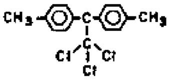
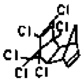
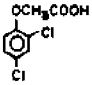
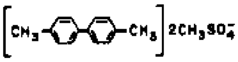
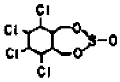
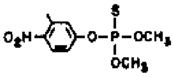
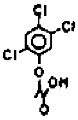
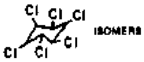
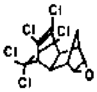
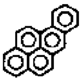
	TOTAL DDT	TOTAL PCB		PCB 1254	
	effluent (µg l^{-1})	effluent (µg l^{-1})	particulate (mg kg^{-1})	effluent (µg l^{-1})	particulate (mg kg^{-1})
1972	5.0	280	43	ND	---
1973	1.4	26	4	26	4
1974	2.6	125	19.2	50	7.7
1975	3.0	40	6.2	20	3.1
calculated sludge end member	---	---	---	77	11.8

* Calculated from an average value of 7470 mg l^{-1}TSS with 87% of TSS associated with particulate phase. DDT, PCB are assumed to be 100% associated with particulate phase.

To a large degree, the adolescent field of organic geochemistry is in an analytical phase. More work is still aimed at identifying and measuring compounds in various environments than at tracing, explaining and quantifying their transport and transformation. While some of the progress will have to come from the application of fundamental sciences such as thermodynamics and chemistry, the largest front in our battle for knowledge in this field is clearly in the experimental realm. Beaches, marshes, estuaries and bights are seeing most of the scientific action. Coastal waste discharges provide unique opportunities for the field experimentalist--such as calculating mass balances; studying processes at high concentrations and tracing historical changes in inputs. These inadvertent experimental systems should thus become the foci for much of our research in explaining and predicting the fate and effects of organic compounds in the aquatic environment. While advancing our fundamental knowledge in this manner, we will at the same time solve one of the outstanding problems of modern society--disposing safely of our wastes.

APPENDIX

SCIENTIFIC NAMES OF COMMON XENOBIOTICS

Trade/Common Name	Structure	Scientific Name
DDT		2,2-bis-(p-chlorophenyl)-1,1,1-trichloroethane
DDE		2,2-bis(p-chlorophenyl)-1,1-dichloroethylene
Methoxychlor		2,2-bis-(p-methoxyphenyl)-1,1,1-trichloroethane)
Methylchlor		2,2-bis-(p-methylphenyl)-1,1,1-trichlorethane)
Aldrin		1,4,5,8-dimethano-napthalene 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexa-hydroendo-exo isomer
2,4-D		2,4-dichlorophenoxyacetic acid
Paraquat		1,1-dimethyl-4-4' bipyridinium dimethyl sulfate
Endosulfan		5-Norbornene-2,3-dimethanol, -1,4,5,6,7,7-hexachloro-cyclic sulfite
Fenitrothion		phosphorothioic acid, O,O-dimethyl O-4-nitro-m tolyl ester
Kepone		1,3,4-metheno-2H-cyclobuta [cd]-pentalen-2-one, decachloroocta-hydro
Silvex		2-(2,4,5-trichlorophenoxy)-propionic acid
Toxaphene		chlorinated camphene industrial mixture containing 67–69% chlorine
Lindane		hexachlorocyclohexane
Dieldrin		1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-dimethanonaphthalene
3,4-benzopyrene		3,4-benzopyrene

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7

Biological Effects

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INTRODUCTION

Knowledge of the biological effects of pollution is often the weak link in assessments of environmental impact. The level of uncertainty tends to increase in models of response from physical to chemical to biological systems. The laws of physics and chemistry operate in physiologically and behaviorally complex biological processes which have evolved to enhance species survival. As a consequence, precise answers cannot often be given to questions regarding the biological effects of man's activities. This review reflects that inability, even though we have attempted to be as thorough and synthetic as possible.

This overview is organized into eight sections in addition to introductory and concluding sections. The first four of these concern effects at the organismic level, including factors governing the availability and accumulation of pollutants and their lethal and sublethal effects. These sections seek to review the assumptions, limitations and utilization of experimental data rather than to present a compendium of values from the literature. The second four sections concern effects observed in nature or in experiments at a community or ecosystem level. In contrast to the approach of the preceding sections, the discussion here attempts to synthesize extensive and diverse observations.

The review is intended to emphasize the mode of biological effects and to address, in particular, several key issues identified as most crucial to management decisions. Those topics on which we focus are: 1. the lethal and sublethal effects of municipal wastewater constituents as evaluated through laboratory tests, 2. the application of experimental data on toxic effects to determine the environmentally safe levels of toxicants, 3. the effects of nutrient enrichment on plankton and its relationship to eutrophication, and 4. the effects of particulate pollution of the sea bed on benthic organisms.

BIOAVAILABILITY

Aquatic organisms are delimited from the external milieu by a semi-permeable integument which allows some materials to enter the organisms while excluding others. For many organisms, much of the integument is nearly impermeable, with specialized areas, primarily the gills, permeable to gases, salts and other chemicals. The entire integument in some organisms, or the gills in others, serve as one route whereby contaminants in the external milieu may enter an organism and cause sublethal or lethal effects.

A second route whereby contaminants may enter an organism is through the digestive tract. If ingested with food, chemical contaminants may then be transported across the gut wall along with the essential foods.

A substance which can enter an organism by either or both of these routes is said to be bioavailable. The bioavailability of a given substance is a function of the permeability of the integument or gills and the gut wall. The degree of permeability depends on various properties or characteristics of the material in question--its concentration, solubility in various solvents, chemical state, degree of sorption to inorganic and organic particles and possibly other factors--as well as the properties of the organisms.

Knowledge of the bioavailability of a particular substance is inferential, based on observable responses of or effects on organisms exposed to the substance in a known form. From the data presently available, which are far from complete, there begins to emerge some general understanding of the concept of bioavailability.

Trace metals, introduced to aquatic environments with sewage effluents and sewage sludge, enter the receiving water in various chemical states: dissolved as ions of various valences, chelated with ligands, precipitated, or sorbed to suspended solids. Once in the receiving waters, the amounts of metals in each chemical state may be changed through various physicochemical reactions, but the metals still exist in these various distinct compartments.

Metals in some compartments are not as readily bioavailable as those in other compartments. For example, copper chelated with various organic ligands has a lower bioavailability than free ionic copper (Brown et al., 1974; Sunda and Gilliard, 1976; Swallow et al., 1978; Gillespie and Vaccaro, 1978). Brown et al. (1974) observed that increased amounts of treated sewage effluent added to a 2 mg l^{-1} copper solution increased the survival rate of rainbow trout, indicating that the bioavailability of copper was reduced. Glycine and humic substances, which can chelate copper, had a similar beneficial effect. Eutrophic marine waters also contain ligands capable of complexing copper (Gillespie and Vaccaro, 1978), produced at least in part by phytoplankton (Swallow et al., 1978).

Complexes of some metals with inorganic components of saline waters have reduced bioavailability; for example, cadmium complexes with chloride ions. Sunda et al. (1978) observed decreased sensitivity of the grass shrimp (Palaemonetes pugio) to total cadmium concentration in 4-day tests as a function of increasing salinty. However, when the survival rates were plotted against measured free cadmium ion concentration, a single curve fit all data independent of salinity. Other metals are also known to form complexes with inorganic ligands which may affect bioavailability (Whittle et al., 1977).

Metals are also sorbed to inorganic minerals, particularly clays and silts, and particulate organics in saline water. Helz et al. (1975) presented evidence that trace metals released in sewage effluent were removed from the water to the sediments near the outfall. Schell (1977) also found evidence of trace metals bound to sediments near a sewage outfall, but speculated that this resulted from dredge spoil or sludge dumping. Lead and cadmium concentrations, however, were elevated in the water but not the sediments. Patterson et al. (1976) observed high lead concentrations in water near a sewage outfall which they believed to result from cation exchange since lead entering seawater with sewage effluent is particulate.

Bioavailability of sediment-bound trace metals will differ greatly from those forms in solution. However, if ingested, the acidic conditions of the gastrointestinal tract could desorb metals from particulate materials, thus making the metals available for passage through the gut.

Speciation of metals in seawater is a complex, not yet fully understood, subject. The various forms of any given metal are in equilibrium, but the equilibrium constants for each possible compartment are unknown. Further, the degree of bioavailability from the various compartments is largely unknown. In theory, at least, metals in each compartment are bioavailable to some degree, each compartment contributing some undefined portion of the total biological effect observed in any given test condition. These considerations make it impossible to make precise predictions of the toxicity of trace metals introduced into saline receiving waters without direct tests of toxicity.

Pesticides are also introduced into receiving waters with sewage and sewage sludge. Cox (1971) suggested that a large share of the DDT in southern California waters resulted from sewage outfalls. Further, Young et al. (1976) attributed high concentrations of DDT in sediments adjacent to sewage outfalls in southern California to industrial wastes discharged through municipal treatment plants.

Organochlorine compounds are of much greater concern than other types of pesticides because they are relatively persistent. In general, they exhibit low water solubility and high lipid solubility, properties which lead to partitioning of these compounds into the biota. Organochlorine compounds are also readily sorbed to fine particulates suspended in the water or associated with the bottom (Stickel, 1968; Huang and Liao, 1970). If ingested, sediment-bound pesticides can contribute to accumulation in the biota. Much of the organochlorine compounds ultimately accumulate in the bottom sediments, especially fine sediments, by sedimentation processes and deposition of dead organisms. The pesticides are then available to the benthic organisms at quite high concentrations.

Chloroorganics may also be sorbed to humic substances in water (Wershaw et al., 1969). Seba and Corcoran (1969) reported high concentrations of pesticides in surface slicks even when undetectable in the underlying water. This accumulation probably reflects sorption to organic materials in the slicks.

Sewage effluent is only a minor contributor of petroleum hydrocarbons to saline waters (Blumer, 1969 and 1971; Whittle et al., 1977). The term hydrocarbons refers to a very diverse group of compounds ranging from very low molecular weight normal alkanes to large aromatic ring compounds, some of recent biogenic origin. Aliphatic compounds, including the n-alkanes, are relatively unimportant because they have few known toxic effects. Aromatic compounds, on the other hand, are known to be toxic and at the same time are a major portion of the water-soluble fraction of petroleum hydrocarbons (Blumer, et al., 1971). Hydrocarbons are also readily sorbed to particulates. Hence toxic hydrocarbons can enter organisms either by absorption across gills and other external tissues or through the digestive system.

BIOACCUMULATION

It has been shown that organisms have the ability to take up various contaminants from either the aqueous medium (Holden, 1962; Ferguson et al., 1966; Emanuelson et al., 1978; and numerous others) or from food and other particulate matter (Bahner et al., 1977; Nimmo et al., 1971; Nimmo et al., 1974; Kobylinski and Livingston, 1975; and others). Organisms may also lose contaminants by degradation, excretion, or diffusion out of the organism across the gills or other membranes. The balance between the processes of uptake and loss defines the amounts of a contaminant which will accumulate within an organism.

Uptake

For aquatic organism, both plant and animal, the rate of uptake from water is a function of the concentration of the contaminant in the water, the diffusion rate across the integument, and the area and thickness of the integument. For most substances, the uptake rate seems to be a zero order process which can be expressed as:

$$C = a + k_u t$$

where: C = chemical concentration in animal (g g^{-1})
t = time (hr)
a = C at $t = 0$
k_u = uptake rate (μg g^{-1} hr^{-1})

Uptake from food and other particulate matter through the gut is a more complex process involving not simply transfer rates across the gut wall, but concentration in the food, ingestion rates, solubilization within the gut, biotransformations within the gut and possibly other processes. Uptake of a few materials from food and other particulates has been measured (Bahner et al., 1977; Nimmo et al, 1971; Kobylinski and Livingston, 1975). A general rate model for uptake from food was suggested by Metcalf (1977):

$$\frac{dC}{dt} = \frac{a(C_pW_p)}{V} - k_dC$$

where C = concentration in predator ($\mu g\ g^{-1}$)
C_p = concentration in prey ($\mu g\ g^{-1}$)
W_p = weight of prey consumed per unit time ($g\ hr^{-1}$)
V = weight of predator
k_d = depuration rate ($\mu g\ g^{-1}\ hr^{-1}$)

Clearance or Depuration Rate

The rate of clearance of a contaminant by an organism can be determined by measuring the concentration in the contaminated organisms after they are held in clean water for various time intervals. In general, the depuration rate can be expressed as a first order function of the initial concentration in the organism:

$$C_t = C_o\ e^{-k_dt}$$

where C_t = concentration at time t,
C_o = initial concentration
k_d = depuration rate

The depuration rate constant, k_d, is the rate of clearance by all processes of loss and is in fact a mixed order rate function.

Bioconcentration Factor

As indicated earlier, the concentration found in an organism is a function of the balance between the uptake rate and the depuration rate. At equilibrium, the concentration in an organism can be expressed as a bioconcentration factor (BCF); i.e., the ratio of the concentration within the organism to the concentration in the source (water or food). In the simplest case in which there are two compartments, water and organism, in equilibrium, this ratio is equal to the ratio of the uptake to depuration rates. Thus,

$$BCF_e = \frac{C_a}{C_w} = \frac{k_u}{k_d}$$

where C_a = concentration in organism ($\mu g\ g^{-1}$)

C_w = concentration in water ($mg\ l^{-1}$)

k_u = uptake rate

k_d = depuration rate

assuming C_w is constant (Hamelink, 1977). Regardless of the pathways of uptake or loss and the factors regulating these processes, there must exist some concentration at which the uptake rate equals the loss rate.

BCF values have been determined for numerous organisms (though mostly freshwater species) and compounds. Some general patterns have emerged, although considerably more study is needed before we can accurately predict the degree of accumulation to be expected without recourse to direct measurement.

Woodwell et al. (1967) measured the concentrations of DDT residues in a series of estuarine organisms ranging from primary producers to carnivores. They observed a stepwise increase in the concentration from one trophic level to the next. This observation has led to the concept of biomagnification, which is based on the premise that the major route of uptake is food and the amount of a substance available in food controls bioaccumulation. However, since the basic observations were made on wild populations, there was no proof that the observed data on the higher trophic levels were the result solely of intake through food.

Hamelink et al. (1971) postulated that the residue of chlorinated hydrocarbons present in each trophic level of a food chain results from the dynamic balance between adsorption and differences in solubility operating through exchange equilibria. They presented data from pond studies describing DDT accumulation in algae, invertebrates and fish to substantiate their hypothesis. They observed the stepwise increase in organismic concentrations between trophic levels even when the uptake route could not have been the food chain. The results could, however, be explained on the basis of partitioning between water and body fat.

This concept led to comparison of the partitioning coefficient of various pesticides between water and various solvents and the degree of accumulation observed in fishes (Neely et al., 1974; Metcalf et al., 1973; Lu, 1974; Metcalf, 1977). A strong correlation between the n-octanol/water partition coefficient and bioconcentration for various chlorinated hydrocarbons has been shown. The higher the partitioning coefficient, the greater the tendency for bioconcentration. A correlation between water solubility and bioconcentration has also been demonstrated, with greater bioaccumulation of compounds with low water solubility than high (Metcalf, 1977; Whittle et al., 1977). One can, then, predict the order of magnitude to which a particular chlorinated hydrocarbon will be bioconcentrated from a knowledge of its water or lipid solubility.

BCFs for chlorinated hydrocarbons are reported to range from between 1 x 10^5 and 1 x 10^6 for DDT (Hamelink, 1969; Reinert, 1969) to 1 x 10^4 for dieldrin (Chadwick and Brocksen, 1969) to 1 x 10^2 for lindane (Gakstatter and Weiss, 1967). Theoretically, the BCF at equilibrium should be a constant for any given species and chlorinated hydrocarbon, independent of the medium of concentration. This has been confirmed for Kepone uptake in marine organisms (Bahner et al., 1977) and dieldrin uptake by oysters (Emanuelsen et al., 1978).

Various bioconcentrated organic substances are generally localized within organisms, often in lipid-rich tissues such as the liver and gonadal tissues (Whittle et al., 1977; Sheridan, 1975; Macek and Korn, 1970; and numerous others). Metals also concentrate more in some tissues than others (Hardisty et al., 1974), although the physiological/biochemical basis for such partitioning within an organism is not known.

While pesticides in marine organisms have been monitored for over a decade (Butler, 1973), little data concerning bioconcentration of pesticides in animals near sewage outfalls has been collected. Young et al. (1976) reported greater accumulation of DDT in benthic crabs and flatfish taken near the Palos Verdes sewage outfall than in those from control areas. DDT levels in mussels held in the water column receiving sewage effluent decreased significantly over the study period due to source controls, but levels in the Dover sole increased. They concluded that sediments containing large reservoirs of DDT served as the dominant source for accumulation in the benthic animals.

The concentration of chlorinated benzenes and PCBs in Dover sole collected near the Palos Verdes outfall was reported by Young and Heeson (1978). While these compounds are not used as pesticides, they are chloroorganics. The chlorobenzenes were more abundant in effluents than either DDT or PCBs, but these low molecular weight compounds were not greatly accumulated by Dover sole. There was considerable accumulation of PCBs, but the levels accumulated correlated more closely to sediment levels than effluent levels, as observed for DDT (Young et al., 1976). Petroleum hydrocarbons also appear to be bioconcentrated but are not biomagnified through the food chain (Whittle et al., 1977). In general, the hydrocarbons concentrate in lipid-rich tissues. Little seems to be known about rates of uptake and loss or bioconcentration factors for specific hydrocarbons. This is not surprising given the difficulties of experimentation and analysis with petroleum hydrocarbons and the vast number of compounds to be considered.

Trace metals can be bioconcentrated by various organisms (Eisler, 1977a; Nimmo et al., 1977a; Huggett, 1977; Mearns, 1975, 1977; and many others). Sedentary molluscs have been shown to be especially efficient concentrators of metals (Eisler, 1977a; Huggett, 1977; Steele et al., 1973). There is no evidence of biomagnification of trace metals through the food chain (Whittle et al., 1977). Thus, the metal concentrations of bivalve molluscs are good indicators of metal pollution in an area.

Eisler (1977a) measured metal uptake by the softshell clam Mya arenaria from six metal mixtures. He observed significant uptake of lead, copper, zinc, manganese and nickel (in order of BCF) in the summer, but only copper, manganese, zinc and lead (in order of BCF) in the winter. Field observations must be interpreted with considerable care to account for seasonal differences in uptake.

Several studies of trace metals in biota have been conducted near sewage outfalls off southern California. Mearns (1975 and 1977) concluded that fish concentrated little or no trace metals from primary effluents discharged into southern California waters. McDermott et al. (1976) found no relationships between concentrations of silver, cadmium, chromium, copper, nickel, lead and zinc in selected organs of Dover sole and proximity to the Palos Verdes outfall. Jan et al. (1977) analyzed six invertebrates and six fish species for the same seven metals plus mercury. Again, no apparent metal accumulation was found in the fishes. However, several invertebrates, notably the scallop from the outfall areas, did concentrate one or more trace metals above levels found at control sites. Young et al. (1979) analyzed the trace metal content of mussels from both harbors and outfall areas in southern California. They observed greater accumulation of cadmium, chromium, copper, lead, tin and zinc in mussels from harbors than those from coastal waters. They also observed accumulations of silver, cadmium, chromium, copper, nickel, lead and tin in mussels near sewage outfalls.

Marine organisms from various ocean disposal sites in the Middle Atlantic Bight have also been analyzed for trace metals (Greig et al., 1977). With few exceptions, no differences in trace metal levels in the animals from various sites and a control site were observed. The few exceptions could not be clearly explained on the basis of the wastes dumped at or near the collection sites. However, primary species studied were windowpane flounder (Scophthalmus aquosus) and rock crabs (Cancer irroratus), both motile species and not known to be great accumulators of trace metals. Channeled welk (Busycon canaliculatum) collected from Long Island Sound, did exhibit significant accumulation of cadmium and silver when compared to specimens from control sites. However, whelks were not collected at all dump sites.

Taken together, these studies demonstrate that selection of species for field monitoring studies of bioconcentration is important, with molluscs being better than fish or decapods. Further, sewage outfalls and sludge disposal sites are not the only sources of high concentrations in biota.

BIOTRANSFORMATIONS

Biotransformation refers to chemical modification of contaminants through metabolic processes and is significant primarily for organic contaminants. In this process, relatively water insoluble/lipid soluble substrates are converted to water soluble compounds which may then be more readily excreted. Microsomal oxidases seem to be the primary enzymes involved in detoxification by biotransformation (US National Academy of Sciences, 1972). Metcalf (1977) has reviewed the principal types of reactions mediated by microsomal oxidases as they relate to chlorinated hydrocarbons. In general, the degradation products have reduced toxicity, but this is not universally the case. For example, aldrin may be degraded to highly toxic dieldrin and some phosphothionates of low toxicity may be converted to highly toxic phosphates.

Metcalf (1977) pointed out that, in general, microsomal oxidase systems are apparently less well developed in aquatic species than in terrestrial forms. The relative importance of detoxification by biotransformation in aquatic species may therefore be questioned. Further, very few data are available regarding microsomal oxidases in marine species.

Other enzyme systems may also produce biotransformations. DDT has been shown to be dehydrochlorinated by an enzyme (called DDT'ase by Metcalf) in some organisms, yielding DDE and other products (Metcalf, 1977). These products of DDT degradation are frequently observed in marine species exposed to DDT (Sheridan, 1975; Butler, 1973; Young et al., 1976). However, the mere presence of DDE in a given test organism cannot be taken as evidence that that organism possesses DDT'ase since DDE may have been produced by microbial species in the water or in the gut of the test animal (Whittle et al., 1978).

Mechanisms for the metabolism of petroleum hydrocarbons have been discussed in US National Academy of Sciences (1975) and Malins (1977). Most attention has been directed at metabolism of aromatic hydrocarbons by marine animals. However, not all organisms have this ability. Further, many petroleum hydrocarbons are quite resistant to enzymatic degradation as compared to biogenic hydrocarbons of recent origin. This is another area in which research is greatly needed to yield a clearer picture of biological capabilities for detoxification.

LETHAL EFFECTS

Acute Toxicity

In the following discussion, the term acute toxicity will refer to lethal effects observed following brief exposure to a contaminant. The usual unit for expressing acute toxicity at some specified time of exposure is the LC50 or the concentration causing 50 percent mortality of an exposed population. Methods to estimate LC50s for various organisms are presented in various general references (American Public Health Association (APHA), 1975; Stephan, 1975; Sprague, 1969) and need not be reviewed here.

In general, the longer a population of organisms is exposed to a given contaminant, the greater the proportion of individuals affected. Similarly, the higher the exposure concentration, the more individuals will be affected in any given time interval. Thus, the degree of effect is a function of both time of exposure and concentration of a contaminant. Longer exposure periods result in lower LC50s, down to some level often called the incipient lethal level (Sprague, 1969). The incipient LC50 is generally not specifically determined. Care must be exercised in assessing the significance of reported LC50s, since the relationship of any reported value for a specified exposure time to the incipient LC50 is not known.

Known Acute Toxic Effects

It is well known that trace metals are toxic to aquatic organisms when present at concentrations in excess of those necessary to metabolic requirements. For marine species, most trace metals must be present at relatively high total concentrations before acute toxic effects are noted, levels which are often greater than those customarily found in marine waters even adjacent to many point sources of trace metals.

There is considerable variability in 96 hr LC50 values for various metals even when the same or related species are compared, partly because of variations in test method, source of animals and, in some cases, poor technique (Becker and Thatcher, 1973; Eisler, 1977b). It is therefore difficult to specify a sequence of the relative toxicity of trace metals of marine organisms.

In an attempt to avoid problems arising from variable technique in determining LC50s, several studies were selected in which several trace metals were tested using consistent methods for single marine species by single researchers, summarized in Table 7.1. The most complete metal series was tested with oyster embryos (Calabrese et al., 1973). The metals are arranged in the table from most to least toxic based on oyster embryo response. For all these species, mercury is the most toxic metal, but the degree of sensitivity varies greatly with polychaetes being much more tolerant than bivalves, even as embryos. The ranking of the other metals by toxicity for the several species tested is not consistent, however, even within the molluscs.

Table 7.1 LC50 Values (in mg l^{-1}) for Selected Marine Invertebrates. (Test duration for tests with larvae was 48 hr, with adults and juveniles, 96 hr.)

Metals	*Crassostrea virginica*[1]* embryos	*Mya arenaria*[2] adults	*Mercenaria mercenaria*[3] embryos	*Neanthes arenaceodentata*[4] adult	juvenile	*Capitella capitata*[4] adult	embryo
mercury	0.0056	---	0.0048	0.022	0.1	<0.1	0.014
silver	0.0058	---	0.021	---	---	---	---
copper	0.103	0.035	---	0.3	0.3	0.2	0.18
zinc	0.31	1.55	0.166	1.8	0.9	3.5	1.7
nickel	1.18	>50.0	0.31	---	---	---	---
lead	2.45	8.80	0.78	>10.0	>7.5	6.8	1.2
cadmium	3.80	0.150	---	12.0	12.5	7.5	0.22
arsenic	7.50	---	---	---	---	---	---
chromium (III)	10.3	---	---	---	---	---	---
manganese	16.0	330.0	---	---	---	---	---
chromium (IV)	---	---	---	>1.0	>1.0	5.0	8.0

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[1] Calabrese et al., 1973.

[2] Eisler, 1977b.

[3] Calabrese and Nelson, 1974.

[4] Reish et al., 1976.

*Artificial seawater test medium; results may not be realistic for natural seawater.

These comparisons, while less tenuous than compilations of data from more diverse sources which introduce variations in test protocol, end point, experimental conditions, etc., are still dubious since the chemical form of the metals is unknown and the metal concentrations are based on calculations rather then measurements. The use of artificial seawater in two studies (Calabrese et al., 1973; Calabrese and Nelson, 1974) may also have affected the rank order of metal toxicity.

Sunda et al. (1978) in a study to determine cadmium toxicity to the grass shrimp, *Palaemonetes pugio*, demonstrated that for cadmium at least, mortality results from responses to the free metal ion, not from cadmium complexed with chloride. The effect of similar complexes, formed with various other metals (Whittle et al., 1977) on toxic responses is not reported in the literature. Further, complexation of metals with organic ligands also occurs, which may reduce the toxicity of metals to aquatic species. Unspecified components of sewage effluent itself have been shown to form complexes with copper, reducing the toxicity of copper to rainbow trout (Brown et al., 1974).

The valence state of metals also affects their toxicity. Trivalent chromium has low toxicity compared to the hexavalent form (Oshida and Wright, 1976; Oshida, 1977). Some metalloorganic compounds also have different toxicity than the metal itself. For example, metallic mercury has lower toxicity than its methylated form (Whittle et al., 1977).

Many of the more complete data sets on trace metal toxicities were collected for species which are relatively tolerant, such as cyprinodont fishes (Eisler, 1967 and 1971; Eisler and Gardner, 1973) and the grass shrimp, *Palaemonetes* sp. (Sunda et al., 1978). Some metals, at least, have high LC50 values relative to typical oceanic concentrations even for species presumed to be sensitive. For example, the LC50 values for polychaetes, echinoderms and crustaceans exposed to hexavalent chromium were about one thousand times the levels customarily found in seawater (Reish et al., 1976; Okubo and Okubo, 1962; Oshida and Wright, 1976).

In summary, *acute* toxic effects of trace metals on organisms in the water column are unlikely to result from treated sewage inputs, either in coastal or estuarine waters given the dilution rates commonly required. Little can be said about acute effects on benthic forms exposed to contaminated sediments since toxicity studies on these species have not been performed. The well-documented accumulation of trace metals in bottom sediments might produce toxic effects in benthic organisms, but direct demonstration of acute effects is wanting.

There exists extensive data on the acute toxicity of pesticides to various marine organisms. Differences in test procedures and conditions, test end points and uncertainties in many cases regarding actual exposure concentrations render generalizations difficult.

Korn and Earnest (1974) determined the 96 hr LC50 of twenty pesticides to striped bass at salinities of 27 to 30 parts per trillion (ppt) and temperatures of 13 to 18°C (Table 7.2). Fish differed significantly in size between tests. Ignoring these factors, which could bear on relative toxicities of the pesticides, Endrin, Endosulfan, DDT and Durban were the four most toxic pesticides tested, with 96 hr LC50s ranging from about 0.1 to 0.6 µg l^{-1}. Carbaryl and Abate were least toxic with 96 hr LC50s of 1000 µg l^{-1}. In general, the chloroorganic pesticides were most toxic.

Table 7.2 Toxicity of Insecticides to Striped Bass (Kern and Earnest, 1974)

Insecticide	96 hr LC50 (µg l^{-1})	95% Confidence Limits
Endrin	0.094	0.045 - 0.19
Endosulfan	0.1	0.048 - 0.21
DDT	0.53	0.38 - 0.84
Dursban	0.58	0.35 - 0.97
DDD	2.5	1.6 - 4.0
Heptachlor	3	1.0 - 6.0
Methoxychlor	3.3	2.1 - 5.1
Toxaphene	4.4	2.0 - 9.0
Aldrin	7.2	3.4 - 15.2
Lindane	7.3	4.5 - 11.9
Chlordane	11.8	5.7 - 24.0
Malathion	14	13.0 - 15.0
Parathion	17.8	4.8 - 65.7
Dieldrin	19.7	9.8 - 33.4
EPN	60	25.0 - 150.0
Fenthion	453	216.0 - 955.0
Dibrom	500	100.0 - 2,400.0
Methyl Parathion	790	170.0 - 1,400.0
Carbaryl	1,000	---
Abate	1,000	---

Estuarine species appear to exhibit considerable differences in sensitivity to specific pesticides. Only rarely does a single research team test several species against a single pesticide. Parrish et al. (1976) tested the response of five estuarine species representing three phyla to Chlordane (Table 7.3). The pink shrimp, _Penaeus duorarum_, was most sensitive, the fish, _Cyprinodon variegatus_, least sensitive. The other three species (oyster, shrimp and fish) were comparable in sensitivity. The range in 96 hr LC50s spanned about two orders of magnitude. However this rank order for species sensitivity does not hold for other pesticides tested, including Heptachlor

Table 7.3 Relative Sensitivity of Selected Estuarine Species to Several Pesticides.

	96 hr LC50s (µg l^{-1})				
Species	Chlordane	Endosulfan	Toxaphene	Kepone	Heptachlor
Crassostrea virginica (shell deposition)	6.2	---	16.0	11.6-43.9[d]	1.5
Penaeus duorarum	0.4	0.04	1.4	28.1*[d]	0.11
Palaemonetes pugio	4.8	1.3	4.4	121[e]	1.06**
Callinectes sapidus	---	---	---	>>210[e]	---
Cyprinodon variegatus	24.5	---	1.1	69.5[e]	3.68
Lagodon rhomboides	6.4	0.3	0.5	---	3.77
Leiostomus xanthurus	---	0.09	---	6.6[e]	0.85
Mugil cephalus	---	0.38	---	---	---

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[a] Parrish et al., 1976

[b] Schimmel et al., 1977a (S., Patrick & Wilson)

[c] Schimmel et al., 1977b (S., Patrick & Wilson)

[d] Butler, 1963

[e] Schimmel and Wilson, 1977

[f] Schimmel et al., 1976

*Penaeus aztecus

**Palaemonetes vulgaris

(Schimmel et al. 1976), Endosulfan (Schimmel et al., 1977a), Toxaphene (Schimmel et al., 1977b) and Kepone (Butler, 1963; Schimmel and Wilson, 1977) (Table 7.3).

The limited input of pesticides with treated sewage suggests that acute effects are unlikely except perhaps when effluents from pesticide manufacturers are included in the waste as occurred with DDT at Los Angeles County's treatment plant that discharges offshore at Palos Verdes, California (Young et al., 1976). Even in the Kepone incident in the James River, Virginia, in which Kepone was released to the Hopewell Sewage Treatment Plant and thence to the James River, no instances of acute mortalities attributable to Kepone were observed.

The acute toxicity of petroleum hydrocarbons has been studied using both crude and refined hydrocarbons as test material. Since the water soluble fractions in crude or refined oil may differ radically in composition from the petroleum hydrocarbons released in sewage waste, the applicability of these results in more than the most general sense is limited. In general, the aromatic hydrocarbons are more soluble in water and more toxic to marine species than the straight chain aliphatics (Whittle et al., 1977; Malins, 1977). The specific fractions producing the toxic effects noted, however, are rarely, if ever, definitively identified.

Chlorine is commonly added to treated sewage effluents as a disinfectant (White, 1972). The resultant oxidants when chlorinated sewage is mixed in seawater, while not precisely known chemically, have been shown to be highly toxic to various marine organisms (Esvelt et al., 1973; McLean, 1973; Galtsoff, 1946; Roberts et al., 1975; Roberts, 1978; Bender et al., 1977; Eppley et al., 1976; Middaugh et al., 1977; Capuzzo et al., 1976 and 1977; and others). Copepods (*Acartia tonsa* and *Eurytemora affinis*) and oysters (*Crassostrea virginica*, larvae and juveniles) are especially sensitive with 48 hr or 96 hr LC50s near 20 $\mu g\ l^{-1}$ total residual "chlorine" (Heinle and Beaven, 1977; Roberts and Gleeson, 1978). Phytoplankton exposed to chlorine exhibited a 24 hr EC50 (effective concentrations producing 50 percent reduction in photosynthesis) as low as 10 $\mu g\ l^{-1}$.

Total "chlorine" residuals exceeding these values have been reported near sewage outfalls. Residuals as high as 2 mg l^{-1} were reported near two sewage outfalls in the James River during a 1973 fishkill attributed to chlorine (Bellanca and Bailey, 1977). More recently, residuals of 10 to 50 μg l^{-1} were observed near the James River Sewage Treatment Plant (LeBlanc et al., 1978), still high enough to produce acute toxic effects on phytoplankton, copepods and oyster larvae. One the other hand, no evidence of acute effects on phytoplankton were observed by Eppley et al. (1976) near the San Diego sewage outfall, though effects were noted near the cooling water outfall of the San Onofre Nuclear Generating Station (total chlorine residuals not reported). Presumably, the levels at the San Diego site were below 10 μg l^{-1} as a result largely of high dilution rates or lack of chlorination.

One solution to possible problems arising from release of chlorinated waste is dechlorination. Esvelt et al. (1973) and Ward and DeGraeve (1978) demonstrated that dechlorination with sulfur dioxide eliminated the toxicity to freshwater species attributable to chlorine. Dechlorination with sodium thiosulfate eliminated chlorine-produced toxicity in treated sewage added to seawater (Roberts, 1980b).

A second approach to eliminating problems of chlorine toxicity would be application of an alternative disinfectant. Of several proposed alternate disinfectants, toxicity of only bromine chloride has been tested in saline waters to any extent. Roberts and Gleeson (1978) found bromine chloride to be slightly less toxic than chlorine to a series of estuarine invertebrates and fishes. Similar results were observed by Burton and Margrey (1978) and Liden and Burton (1977). LeBlanc et al. (1978) and Roberts (1980b), however, in a pilot plant study, found bromine chloride slightly more toxic than chlorine using spot (Leiostomus xanthurus) as the test organism. The primary advantage to bromochlorination lies not in its lesser toxicity, but in its possibly greater disinfection potential and more rapid decay than chlorine (Mills, 1975; Roberts and Gleeson, 1978; LeBlanc et al., 1978; Roberts, 1980b).

While the major contaminants in treated sewage other than chlorine occur in concentrations and forms which seem unlikely to produce acute toxicity, published accounts of direct tests of sewage effluent toxicity are few. Esvelt et al. (1973) in their studies of chlorine toxicity, determined the toxicity of various treated effluents prior to chlorination. Toxicity was noted in mixtures containing about 45 percent sewage (no chlorine) tested with Notemigonus chrysoleum (golden shiner) and Gasterosteus aculeatus (three-spined stickleback) in fresh water. However, Ward et al. (1976 and 1977), using several freshwater fishes and invertebrates, found sewage mixtures to be non-toxic to freshwater fishes. LeBlanc et al. (1978) and Roberts (1980b) observed no mortalities among spot (*Leiostomus xanthurus*) exposed to mixtures containing 5 or 40 percent treated sewage. It should be noted that the James River Sewage Treatment Plant, at which the latter study was performed, receives only 15 percent industrial waste and is not representative of large sewage treatment plants in general.

Interaction Effects

While most experimental studies have dealt with single substances, actual effluents include complex mixtures of potential contaminants. There is the possibility, therefore, for changes in the magnitude of response to one component in the mixture as a function of interactions with a second component.

Synergism may be defined as an interaction between two or more substances which results in a response greater than the sum of responses to each substance by itself (Warren, 1971). Antagonism, on the other hand, may be defined as an interaction between two or more substances yielding a less-than-additive response (Warren, 1971).

Several models have been proposed for development to define strictly additive responses (Muska and Weber, 1977). These models are not statistically or conceptually equivalent. At present, there is no clear basis for selecting one model over another.

The conceptual model of Warren (1971), when experimentally applied to two toxicants necessitates a factorial design with a large number of treatments. Marking (1977) has proposed a simpler experimental design using a fixed ratio of two toxicants with varied total concentration of toxicants. The predicted sum of the biological response (strict additivity) is taken to be

$$S = \frac{A_m}{A_i} + \frac{B_m}{B_i}$$

where s = additive response

A_i and B_i = LC50s of substances A and B acting alone

A_m and B_m = apparent LC50s of substances A and B in the test mixture.

This equation can be expanded for additional substances by adding new terms to the equation. An index is then defined such that:

$$I = \begin{cases} \frac{1}{s} - 1.0 & \text{for } s \leq 1.0 \\ s(-1) + 1.0 & \text{for } s \geq 1.0 \end{cases}$$

Thus, for s = 1, representing a strictly additive response, I = 0. If $s < 1.0$ representing a synergistic effect, $I > 0$, whereas if $s > 1.0$ (antagonistic effect), $I < 0$. Marking (1977) reported several applications of this method applied to two-substance mixtures with several freshwater species.

Another experimental approach is to expose a species to a series of mixtures with varying ratios of two toxicants and a fixed level of total toxicants. The treatment series ranges from 0 percent to 100 percent (the LC50) for substance A and from 100 percent (the LC50) to 0 percent for substance B. If the response is strictly additive, a 50:50 mixture will result in 75 percent mortality, whereas if the compounds act synergistically, the response to a 50:50 mixture will exceed 75 percent. If all treatments produce a 50 percent response, there is no interaction. Buikema (1977) used this method to assess the interaction of various trace metals against the freshwater crustacean Daphnia magna.

Eisler (1977a) examined the interaction of six metals (manganese, zinc, lead, nickel, copper and cadmium) in a fixed ratio. The study was designed primarily to examine metal uptake by the softshell clam Mya arenaria. However, LC50s for the metal mixture were determined for five species, rock crab (Cancer irroratus), mummichog (Fundulus heteroclitus), softshell clam (Mya arenaria), quahog (Mercenaria mercenaria) and mahogany clam (Arctica islandica). Rock crabs and mummichogs were much more sensitive to the metal mixture than the three mollusc species. However, no attempt was made to analyze the data for interaction effects.

SUBLETHAL EFFECTS

Chronic Toxicity

A chronic toxicity test can be defined as a test in which the exposure period exceeds one complete life cycle. The responses measured customarily include fecundity, egg hatchability, larval growth and survival, and juvenile growth. Procedures for this type of experiment have been developed for a few aquatic species, only two of which are marine, the sheepshead minnow, *Cyprinodon variegatus* (Hansen and Parrish, 1977; Hansen et al., 1977) and the mysid shrimp, *Mysidopsis bahia* (Nimmo et al., 1977b).

A major objective of chronic tests is to determine the maximum acceptable toxicant concentration (MATC) or that concentration having no measurable effect over the life cycle. To date, only few such determinations have been completed with marine species. For example, Hansen and Parrish (1977) reported MATCs of five pesticides (Endrin, Heptachlor, Methoxychlor, Malathion and Carbofuran) determined for the sheepshead minnow.

Isolated portions of the life cycle, especially larvae, have frequently been tested, involving measurements of egg hatchability, survival and growth of larvae, and normality of development. These tests are often referred to as partial chronic tests.

This approach has been used with a variety of marine species representing several invertebrate phyla as well as fishes. No attempt is made here to review the extensive literature concerning partial chronic tests, but a few examples are listed (Table 4). This small sampling indicates the variety of applications possible for partial chronic tests. These studies at times may provide MATCs when full chronic studies are impractical or impossible. For example, Reish (1977) showed that partial chronic effects of Cr^{+6} were observable in *Capitella capitata* at levels above about 0.02 $\mu g\ l^{-1}$. This led him to suggest that the Cr^{+6} levels in sewage effluents in southern California were too high.

The results of acute and chronic (or partial chronic) tests can also be used to set application rates for wastes in receiving waters. An application factor is defined as that fraction which, when multiplied by an acute toxic concentration (LC50), yields an estimate of an MATC or "safe concentration"

Table 7.4 Taxa with Which Partial Chronic Tests Have Been Conducted.

Taxon	Toxicant	Source
Hydroids		
Campanularia flexuosa	Hg^{+2}, Cu^{+2}, Cd^{+2}	Stebbings, 1976
Annelids, Polychaetes		
Capitella capitata	Cr^{+6}	Reish, 1977
Nereis virens	Cu^{+2}, Cr^{+6}	Raymont & Shields, 1963
Molluscs		
Mytilus edulis	pesticides	Roberts, 1975
bivalve larvae	metals	Okubo & Okubo, 1962
Crustaceans		
Uca pugilator	PCB	Vernberg et al., 1977
Uca pugilator	Hg^{+2}	
Rhithropanopeus harrisii	malathion	Bookhout & Monroe, 1977
Callinectes sapidus	malathion	Bookhout & Monroe, 1977
Cancer magister	methoxychlor	Armstrong et al., 1976
Echinoderms	metals	Okubo & Okubo, 1962
	chlorinated benzenes	Oshida, 1977
	petroleum hydrocarbons	Allen, 1971
	Li	Runnstrom 1935
Chordates, Fish		
(flounder)	Cd^{+2}	Westernhagen & Dethlefsen, 1975
(garpike)	Cd^{+2}	Westernhagen et al., 1975
(herring)	Cd^{+2}	Westernhagen et al., 1974
Clupea harengus pallasi	Cu^{+2}	Rice & Harrison, 1978

in the receiving water. Formerly, the application factors were unsubstantiated numbers. However, if the acute and MATC concentrations of a given substance are known for one species, the ratio of these values can then be used as an application factor to be applied for other species when only the acute toxicity is known. Hansen and Parrish (1977), for example, reported application factors for five pesticides experimentally derived, using the sheepshead minnow. Using this approach, one makes the assumption that the value of the application factor is unique for a given compound and independent of species. Hansen and Parrish (1977) presented limited data for three pesticides compiled from several sources which seem to support this notion.

Physiological Effects

Increasingly over recent years, researchers are examining other kinds of organismic responses to toxicants in order to estimate concentrations which produce no effects. The traditional method of chronic testing examines whole organism responses which are time consuming to determine. Often estimates are made with insensitive species and lack precision.

Two physiological responses are frequently assessed: blood serum constituents, especially in reference to osmoregulation and metabolic rates of whole animals or selected organs or tissues.

For example, Miller and Kinter (1977) measured sodium and potassium levels in blood plasma and gut water absorption in the mummichog, *Fundulus heteroclitus*, exposed to DDT. They found slight evidence of a disruption of osmoregulation at higher doses. Metabolic rate changes have been observed in response to low levels of various biocides including pesticides (Leffler, 1975) and metals (Gould, 1977; Thurberg et al., 1977).

Enzymatic effects have also been reported in several recent studies. Various enzyme systems have been affected. Gould (1977) observed stimulation in production of carbonic anhydrase and leucine aminopeptidase in winter flounder (*Pseudopleuronectes americanus*) exposed to cadmium at sublethal levels. He suggested that low levels of cadmium affect metalloenzymes and perhaps other enzymes. Thurberg et al., (1977) observed increased ATPase activity in lobsters (*Homarus americanus*) exposed to cadmium and mercury.

Numerous other studies showing physiological responses could be cited. These are characterized by great variety in methods of exposure, responses observed, method of response measurement and other features. At present, it seems premature to attempt to generalize on the types of responses elicited by any defined type of toxicant. Further, it is difficult given the present state-of-the-art to attempt to predict population effects based on physiological data. Nevertheless, these types of studies not only provide information regarding mode of action, but also can be used to define toxicant concentrations which produce no measurable response.

Pathological Effects

Various types of pathological effects have been noted during toxicity tests. Perhaps most frequently observed are necrotic and other effects on the gills of fishes (Middaugh et al, 1977; Nimmo et al., 1977a). The effects are often observed only at or near concentrations producing significant mortality.

DiMichele and Taylor (1978) exposed the mummichog, Fundulus heteroclitus, to various levels of naphthalene for 1, 4, or 15 days and recorded both mortality and histopathological effects on gills, sensory organs, pancreas, liver, brain, renal system, intestine and muscles. They observed gill hyperplasia in 30 percent of the controls and 80 to 100 percent of all exposed fishes, even at doses causing no mortality. Neurosensory cells at all doses showed some signs of necrosis except at 0.002 mg l^{-1} after 15 days or less. Effects were observed in other tissues at doses causing mortality or at the highest non-lethal doses after prolonged exposure (15 days). They concluded that pathological effects on neurosensory structures are perhaps diagnostic for sublethal exposure. Observations of Gardner and LaRoche (1973) with several fish species support this suggestion.

Several reports indicate that organisms exposed to toxicants, even at low levels, may exhibit increased prevalences of disease. This has been shown in penaeid shrimp (Couch and Nimmo, 1974; Couch and Courtney, 1977) and southern California field studies on fishes (Mearns and Sherwood, 1977; Sherwood and Mearns, 1977). In the latter studies, increased incidence of fin erosion was observed in marine fishes collected near sewage outfalls.

As with physiological effects, it is presently difficult to extrapolate from observable pathological effects to specific changes at the population level resulting from these sublethal effects. However, they are clear evidence of a deleterious effect on the exposed population.

Behavioral Effects

One of the earliest studies dealing with a behavioral response to pollutants was that of Sprague (1964) which demonstrated avoidance of copper-zinc solutions by salmon (in fresh water). Other avoidance tests have shown that various aquatic species can detect and avoid toxicants at concentrations below acutely toxic levels (Middaugh et al., 1976; Hansen, 1969; Meldrin and Fava, 1977). Avoidance responses are affected by temperature, salinity, pH, light levels and oxygen concentration (Meldrin and Fava, 1977). Further, responses are not always consistent, with avoidance of low concentrations and apparent preference for higher concentrations (Hansen, 1969).

Qualitative changes in feeding behavior have also been observed. Mearns et al. (1976) observed reduced feeding activity in the sand dab (*Citharichthys stigmatus*) exposed to Cr^{+6} at levels well below the LC50 level. Cappuzzo and Sasner (1977) reported reduced filtration rates in the blue mussel, *Mytilus edulis* and the softshell clam, *Mya arenaria*, exposed to low levels of hexavalent chromium, both dissolved and sorbed to particulates. Keck et al. (1978) observed reduced food consumption in hard clams, *Mercenaria mercenaria*, exposed to sublethal levels of the water soluble fraction of a crude oil. Rubenstein (1979) observed significant differences in feeding behavior of the lugworm (*Arenicola cristata*) exposed to Kepone at 2.8 $\mu g\ l^{-1}$, which is approximately 1/10 the acutely toxic level. Jacobson and Boylan (1973) observed chemotaxic effects on *Nassarius obsoletus* exposed to kerosene in seawater. McLeese (1973) observed changes in olfactory responses of the lobster, *Homarus americanus*, exposed to bleached kraft mill effluent.

Thus, behavioral responses are very sensitive indicators of effects of a pollutant. The nature of the behavioral changes observed is often such that one can foresee a significant population effect. Only a limited number of available studies yield adequate information to make reliable ecological predictions. There is no clear experimental evidence that any species responds behaviorally to sewage effluent, although some field observations have been interpreted to imply avoidance or preference of regions receiving sewage effluent.

Sublethal Effects Versus Population Survival

Two objectives for sublethal tests are to provide rational bases: 1. to predict levels for specific toxic substances which will produce no effect on exposed populations (MATCs) and ; 2. to predict the magnitude of effects on populations at somewhat higher but non-lethal exposure levels. It is important to consider whether or not sublethal tests of various kinds can in fact yield results appropriate to make either prediction with any desired level of assurance.

Chronic tests, as defined herein, are designed to measure specific population parameters which bear directly on population survival when acute mortality is not at issue. These tests measure growth rates for individuals in the population (time necessary to reach reproductive maturity), fecundity (including both the number of eggs produced per female and the number of spawning events) and hatching rates for fertilized eggs produced by organisms exposed to various levels of toxins.

Chronic tests are performed, however, under rigorously defined and restricted (non-natural) environmental conditions. Temperature, salinity, dissolved oxygen level, pH and other water quality parameters are generally maintained near optimal levels. Suspended particulate materials are often excluded. The food provided is rigidly prescribed and does not correspond qualitatively or quantitatively to the natural food for the species. Predation on the test organism is eliminated. Natural bottom substrates are excluded, eliminating one possible factor changing the concentration of the toxin under test, but also providing, by default, an unnatural substrate for the test species. Dose levels of the toxic substance are controlled within prescribed limits which may not reflect patterns of exposure for a natural population.

Thus, in these and other ways, the populations in chronic tests are not subjected to a toxic substance in a manner comparable to a wild population. The restrictions placed on the exposure system in the laboratory are necessary to produce interpretable and repeatable results. Such experimental precision is achieved, however, at some expense in terms of direct and accurate applicability to the prediction of effects on naturally exposed populations. On the other hand, the tests can contribute to the unraveling of effects observed in natural populations where several sources of exposure (dissolved, suspended particulate and sedimentary) and several potentially toxic substances are available. The same arguments apply to the more limited observations of partial chronic tests.

Other types of sublethal studies involving measurement of various physiological/biochemical parameters, behavioral responses and pathological changes can demonstrate biological effects at very low exposure levels in many, though not all, cases. Yet no direct estimate of parameters of population success, such as growth and reproduction can be made from these data. We presume that if an effect can be shown in such sublethal studies, then there is some corresponding effect on the population success parameters even though the magnitude of such effects cannot be defined.

In applying the results of all types of sublethal experiments to the prediction of effects on natural populations, there remains the further complication that such tests typically involve single toxic substances rather than mixtures. Thus, there is no inherent consideration of interaction effects which might occur with a complex waste such as sewage effluent or sludge. Neither is there any consideration of sublethal effects under less ideal environmental conditions.

In summary, chronic tests are useful in predicting exposure levels producing no effect, given the assumption that interaction effects with other toxins and the suite of environmental conditions are insignificant. Sublethal effects studies are also useful in unraveling the causes of effects observed in natural populations. One must bear in mind, however, that the level of certainty associated with predictions of population effects based solely on laboratory studies is low but unspecified.

EFFECTS ON PELAGIC SYSTEMS

It is convenient both for the sake of organization and because of differences in the mode of effects to discuss separately effects on pelagic and benthic ecosystems. Dissolved constituents of wastes have been of primary concern in the pelagic realm, whereas particulate, settleable constituents are the prime mode of impact on the benthos.

Biostimulation

Municipal wastes contain materials which may be inhibitory or stimulatory to pelagic organisms. Inhibition may be through direct toxic effects, such as discussed in preceding sections; it may be due to increased turbidity caused by suspended particulate wastes; or it may be the result of competitive or predatory adjustments in community structure. Most attention has, however, focused on the stimulation of phytoplankton by nutrient additions and on the subsequent effects on oxygen dynamics and consumer food chains.

Primary production by photoautotrophs requires light, water, CO_2 and essential nutrients. Nitrogen and phosphorus are the major nutrient elements required and their role in photosynthetic production or organic matter may be stoichiometrically represented (Richards, 1965):

$$106\ CO_2 + 122\ H_2O + 16\ HNO_3 + H_3PO_4 \xrightarrow{\text{Light}} (CH_2O)_{106}(NH_3)_{16}\ H_3PO_4 + 138\ O_2$$

Other nutrients which may be required in smaller amounts include silicon, trace metals and certain organic compounds, such as vitamins. Municipal wastes contain substantial quantities of inorganic or organic nitrogen and phosphorus which may stimulate productivity if either is limiting phytoplankton production in the receiving waters.

Nitrogen and Phosphorus. Although the classic oceanographic view was that nitrogen (N) was microbially fixed to balance the phosphorus (P) available in the sea, Ryther and Dunstan (1971) demonstrated, based on field observations and laboratory experiments, that N is generally the limiting nutrient in coastal marine environments. They concluded that about twice the amount of phosphate ($PO_4^{=}$) as can be used is normally present because of: 1. the low nitrogen-to-phosphorus ratio in terrigenous contributions and human wastes and 2. the more rapid regeneration of phosphorus than ammonium (NH_4^+) from decomposing organic matter.

The ratio of N to P in unicellular marine algae varies with species and growth conditions; values between 5:1 and 15:1 are common and a reasonable working value is 10:1. Sewage effluent following secondary treatment contains on the average 118 μg-atom l^{-1} NH_4-N, 24 μg-atom l^{-1} NO_3-N and 26 μg-atom PO_4-P for an atomic ratio of N:P of about 5:1 (Dunstan and Menzel, 1971). Thus this nutrient input is phosphorus rich with respect to the N:P nutritional requirements of phytoplankton.

Ryther and Dunstan (1971) presented data on the distribution of inorganic nitrogen and phosphate away from input sources in Moriches Bay, Long Island (duck farms) and the New York Bight apex (Figure 7.1) to show that nitrogen is quickly assimilated, whereas phosphate diminishes from the source primarily as a function of dilution. Thus the N:P ratio declines drastically beyond the zone of intense stimulation of primary productivity. Experiments with the addition of N (as ammonia) and phosphate to monospecific cultures of the flagellate Nannochloris atomus from Moriches Bay and the diatom Skeletonema costatum from the New York Bight showed stimulation of growth with N-enrichment but no significant stimulation of growth over controls with P-enrichment (Figure 7.2).

Vince and Valiela (1973) also found greater stimulation in growth and increase in chlorophyll a with the addition of NH_4-N to natural phytoplankton poulations from Vineyard Sound, Massachusetts, than in controls or in similarly PO_4-P enriched populations. However, enrichment with NH_4^+ and $PO_4^=$, regardless of the N:P ratio, resulted in even greater growth. They suggested that under favorable conditions and rapid growth, phytoplankton absorb more phosphorus than Ryther and Dunstan's N:P ratio of 10:1 would predict. Similar "luxury" assimilation of $PO_4^=$ has been observed in the San Francisco Bay estuary (Di Toro et al., 1977) and in the Oslofjord (Baalsrud, 1967).

Other investigators have inferred phytoplankton limitation by phosphorus based on field observations (e.g., Björn-Rasmussen, 1975; Blanc et al., 1975), but there has been relatively little experimental evidence of phosphorus limitation in marine waters. Again in the New York Harbor region, Mahoney and McLaughlin (1977) found growth stimulation by inorganic and organic phosphate enrichment of cultures of three phytoflagellates, Massartia rotundata, Olisthodiscus luteus and Prorocentrum micans, responsible for intense, potentially noxious blooms in summer.

Figure 7.1 The distribution of particulate organic carbon (POC), inorganic nitrogen (N) and phosphate (P) in surface waters along a section running southeast from New York Harbor to the edge of the Gulf Stream (Ryther and Dunstan, 1971).

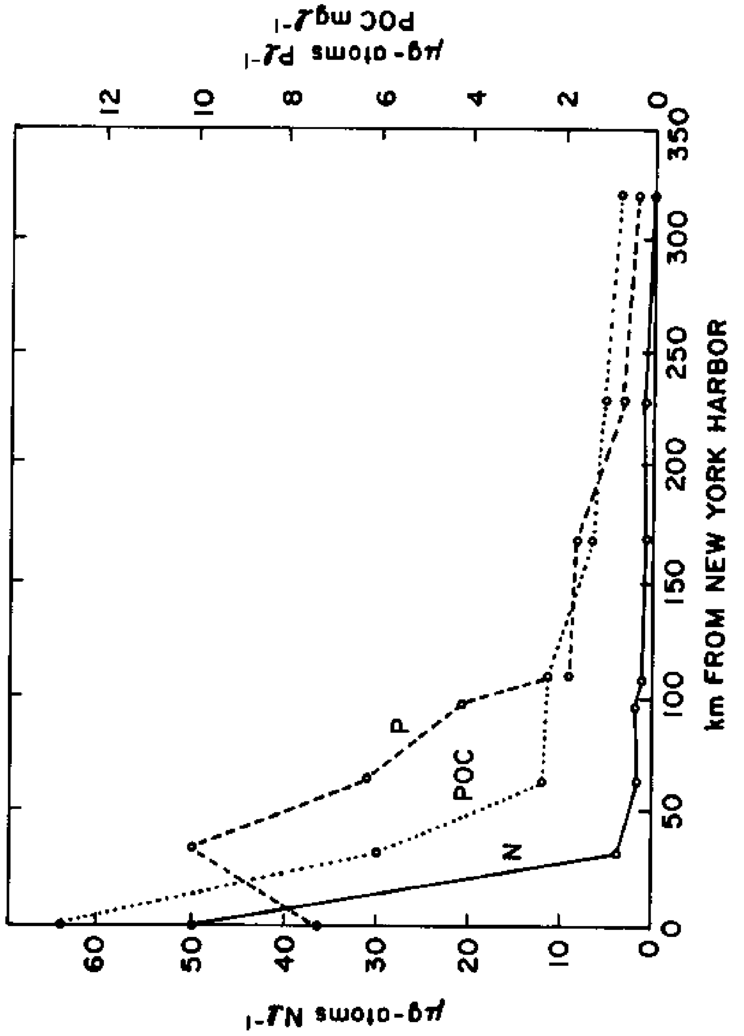
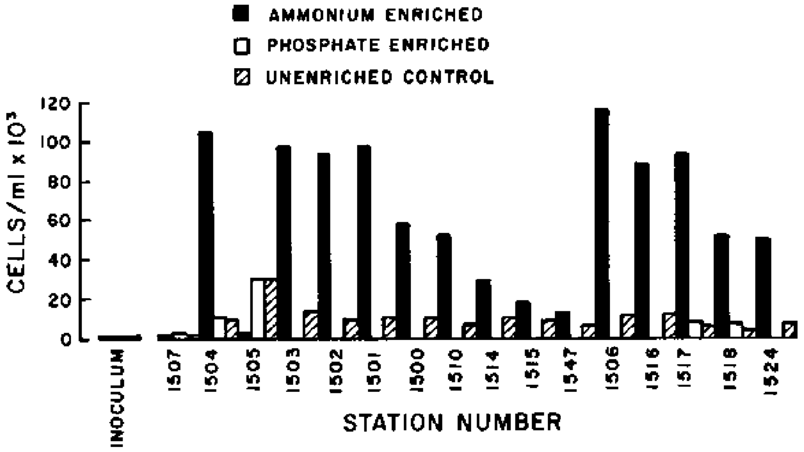


Figure 7.2 Growth of the diatom Skeletonema costatum in unenriched, ammonium-enriched, and phosphate-enriched water from the New York Bight (Ryther and Dunstan, 1971).



Phosphate limitation of the intense chlorophyte-blue-green algal blooms which cause serious oxygen depletion in the Potomac River estuary has been demonstrated by the reduction of chlorophyll levels following the institution of phosphorus removal at Washington, DC sewage treatment plants (Jaworski et al., 1972).

In addition to the concentration of N and P, their molecular form may also affect their ability to stimulate phytoplankton production. Traditionally, attention has been focused on nitrate (NO_3^-) and inorganic phosphate ($PO_4^=$). It has now been widely shown that marine phytoplankton prefer NH_4^+ and organic N in the form of urea over NO_3^- (Conway, 1977; McCarthy et al., 1977; MacIsaac et al., 1979). McCarthy and Eppley (1972) and McCarthy et al. (1977) found that when NH_4^+ concentrations exceed 0.5-1.0 μg-atom N l^{-1}, the utilization of NO_3^- is almost totally inhibited. Urea is used after NH_4^+ , NO_3 is used only when the sum of NH_4^+ and urea is insufficient to meet phytoplankton demand. This must lead to a rethinking of the nitrogen limitation question, as NO_3-N often constitutes the bulk of the nitrogen pool. Much of the nitrogen pool in non-oligotrophic coastal systems must not be of direct consequence to primary production. Instead, stimulation will depend largely on regeneration (through mineralization and waste excretion) of nitrogen in the ammonium or dissolved organic nitrogen pools. Nitrogen limitation may not take place if NH_4^+ and NO_3^- levels are above 0.4 and 0.5 μg-atom N l^{-1}, respectively (Caperon and Meyer, 1972). Thus, Malone (1976) observed that in the New York Bight apex, the dissolved inorganic nitrogen (DIN) concentration was never less than 1 μg-atom l^{-1} and phytoplankton assimilation was highest during summer when DIN concentrations were lowest but the proportion of NH_4-N to total DIN was at a peak. Malone concluded that it is unlikely that phytoplankton growth was nutrient-limited and that high summer phytoplankton demand could not be satiated by estuarine (New York Bay) discharge and had to be supplemented by regenerated ammonium.

Evidence is also forthcoming that other forms of phosphate are available for phytoplankton nutrition. Taft et al. (1975) showed that dissolved organic phosphorus was present in Chesapeake Bay waters in concentrations usually in excess of those of soluble reactive (inorganic) phosphorus. Taft et al. (1977) demonstrated the utilization of phosphomonoesters which were found to be present in significant concentrations in Chesapeake Bay. Mahoney and McLaughlin (1977) found stimulation of growth of 3 bloom flagellates from lower New York by 6 to 8 of the 8 organic phosphate compounds tested. This stimulation could, however, have resulted from heterotrophic uptake.

Other Factors. A host of other factors may act in controlling primary productivity by marine phytoplankton. Some serve to naturally limit production to below a level supportable by available N or P, so that nutrient enrichment will cause no stimulation. Others are usually not limiting but may become so during intense growth stimulated by nutrient enrichment. The enormous reservoir of bicarbonate in seawater generally prevents depletion of CO_2 required in photosynthesis, although CO_2 may become limiting during intense algal blooms (Mahoney and McLaughlin, 1977). More probably, CO_2 availability may regulate the qualitative nature of the phytoplankton but not gross production (Shapiro, 1973; Caperon and Smith, 1978). The presence of a wide variety of organic substrates was shown to stimulate the growth of 3 bloom flagellates studied by Mahoney and McLaughlin (1977). The stimulation may be the result of the autotrophic utilization of organic C or, more probably, the facultatively heterotrophic uptake of an organic substrate. In any case, the complex mix of organic compounds may sustain or prolong noxious blooms.

Silicon is required for diatom growth as it is for frustule formation. Paasche (1973) examined the silicate-uptake kinetics for several species of diatoms and suggested that species may compete for available silicate and that growth limitation by silicate may be effective in N and P enriched, highly productive waters. This may shift competitive advantage to other phytoplankton not requiring silicon, e.g., flagellates.

Trace metals, usually thought of as toxicants, are necessary plant nutrients in small concentrations. Dunstan (1975) observed widely different stimulation of several monospecific algal cultures by effluent from different sewage treatment plants in New England matched in concentration of inorganic nitrogen. All batches of sewage tested stimulated best growth in some species and poorest in others. He demonstrated that the disparities were at least in part due to differences in trace metal concentrations of the effluents. Metals and other trace factors, such as chelation potential, organic load and vitamins, may only become important when phytoplankton populations escape nitrogen limitation. Furthermore, trace metals and other potential toxicants in sewage effluents may serve to inhibit nutrient uptake and production near the discharge (MacIsaac et al., 1979).

Physical factors often limit natural phytoplankton production to below the level supportable by available nutrients. Zooplankton grazing may also be important in this regard (Winter et al., 1975; Di Toro et al., 1977). Photosynthesis, as with all metabolic processes, is temperature dependent. Malone (1976, 1977a) found that assimilation, expressed as the rate of carbon fixation per unit chlorophyll a, was exponentially related to temperature between 8°C and 24°C. Below 8°C, assimilation was higher than expected, perhaps reflecting temperature acclimation. Primary production in the New York Bight apex in winter is thus limited to levels far below that which could be sustained by nutrient inputs. The differences in assimilation efficiency in relation to temperature between size fractions of phytoplankton could account for the dominance of the nanoplankton fraction during the summer bloom period.

Light limitation is also a very common occurrence in coastal waters. Light limitation may occur because of high concentrations of inorganic particulates or by self-shading. Light limitation has been shown to exert important control on nutrient stimulation in virutually every coastal environment studied, notably the lower Hudson River estuary and the New York Bight (Malone, 1976; Garside et al., 1976), Puget Sound (Winter et al., 1975) and the Chesapeake Bay system (Flemer, 1970).

Turbulent mixing and advection of water masses exert important effects on nutrient-phytoplankton relationships. Highly stable water masses will tend to suffer loss of nutrients and phytoplankton due to sinking of algal cells. Alternatively, intermittent water mass stability may favor motile flagellates which migrate to surface layers causing noticeable blooms. Turbulent mixing serves to keep algal cells suspended and drive the flux of nutrients from deeper waters into the euphotic zone. Mixing is especially important in stratified water masses such as coastal plain estuaries (Flemer, 1970: Haas, 1977), fjords (Winter et al., 1976) and the seasonally stratified coastal ocean (Yentsch, 1977; Walsh et al., 1978). In these systems, the pycnocline in the surface-mixed layer serves as a barrier to replenishment of nutrients in high concentrations in bottom waters because of sinking or benthic regeneration. Wind-forced advection and upwelling is important in the vertical transport of nutrients especially along the Pacific but also along the Atlantic (Walsh et al., 1975) coasts. Turbulent mixing due to tidal current exchange has been shown to be important in destratification and vertical transport of nutrients in the Chesapeake Bay (Haas, 1977).

Community Structure Modifications. In addition to the biostimulatory effects of nutrient additions, it is necessary to consider the effects of enrichment on the composition and structure of the phytoplankton community. Enriched areas typically support phytoplankton populations dominated by nanoplankton and phytoflagellates (chlorophytes and dinoflagellates) in particular. The summer phytoplankton of lower New York Bay and the nearshore zone off New Jersey and Long Island is dominated by chlorophytes, particularly Nannochloris atomus (= didymtocystis of some earlier authors) and occasionally Calycomonas gracilis (Malone, 1977b). Dinoflagellates, Prorocentrum micans and Peridinium spp., are also important and may be responsible for noxious blooms. The phytoplankton of the outer New York Bight is, on the other hand, dominated by diatoms, e.g., Rhizosolenia setigera, Leptocylindricus danicus, Guinardia flaccida and Chaetoceros spp. Similarly and on a more local scale, Tasiakian and Hardy (1976) found blue-green algae (Oscillatoria, Spiralina, Phormidium and Synochococcus) and dinoflagellates (Gymnodinium and Prorocentrum) associated with zones of nutrient enrichment by sewage off the coast of Lebanon, while diatoms generally dominated the phytoplankton outside the enriched areas.

On the other hand, Eppley and Weiler (1979) have cautioned against oversimplified models relating phytoplankton cell size and nutrient enrichment or other pollutant effects. They present examples of dominance by large phytoplankters (usually dinoflagellates) under enrichment conditions and many examples of nanoplankton dominance in pristine areas.

There is surprisingly little experimental evidence of the effects of nutrient addition on phytoplankton community structure, although many authors speculate on selective effects of nutrient enrichment. Dunstan and Menzel (1971) and Vince and Valiela (1973) both enriched natural phytoplankton populations from Vineyard Sound, Massachusetts and found little change or adjustment of species after 16 and 6 days, respectively. Rather, the species prevalent in the natural population generally tended to remain dominant and grow in enriched continuous cultures. This may be a result of inability to simulate natural conditions which favor shifts in community structure in these controlled culture experiments.

Predicting Biostimulatory Effects. In summary, it can be concluded that the degree to which stimulation of primary production will occur depends on complex and interacting factors. In open coastal systems where dilution is great, stimulatory effects will be transient and localized. Off the southern California coast, for example, sewage discharges were found to stimulate primary productivity to two to three times the normal seasonal averages but within the range of upwelling episodes (Eppley et al., 1972). Associated with the enhanced production were high concentrations of chlorophyll *a*, adenosine triphosphate (ATP) and particulate organic carbon and nitrogen, but no appreciable increases in nutrients or dissolved organic constituents. This suggests rapid uptake and regeneration of nutrients (Harrison, 1978) and effective dispersal in the large ocean volume off southern California. The total impact of the enrichment on the southern California Bight is small and localized despite the massive input of nutrients.

In enclosed or semi-enclosed coastal waters or over shallow continental shelves, however, impacts of nutrient addition may be more substantial. The estimated nitrogen input to the lower Hudson River estuary-New York Bay of 160 metric tons N day^{-1} dominates fluvial input (Garside et al., 1976). The estuary is able to assimilate only about 90 percent of this load and the remainder is exported to the New York Bight apex. An additional 5 percent of the inorganic nitrogen flux is added to the Bight apex with the direct disposal of sewage sludge (O'Conners and Duedall, 1975). Based on productivity rates measured in the Bight apex, an area of 257 km^2 is required for assimilation of sewage-derived nitrogen during the summer and 1,370 km^2 during most of the rest of the year. Within the estuary and adjacent apex of the Bight, nitrogen is present in excess of phytoplankton requirements and biostimulation is moderated principally by light and temperature limitation (Malone, 1976). Increased nutrient additions would not further stimulate productivity in these areas unless these other factors, e.g., turbidity, were eliminated or diminished. At present, the stimulated phytoplankton in the lower estuary and Bight apex contributes significantly to the organic load and thus to observed local oxygen depletion (Garside et al., 1976; Garside and Malone, 1977). Noxious blooms also occur and Yentsch (1977) concluded that the level of primary productivity in the New York Bight apex is approaching maximum yield. Managing such a situation entails considerable risk in that factors beyond direct control, such as turbidity, regulate the potential for intense stimulation.

An even more extreme case of stimulation by nutrient enrichment exists in the Potomac River estuary. In the lower Hudson River estuary, maximum monthly chlorophyll _a_ levels were about 10 μg Chl _a_ l^{-1} (Malone, 1976) while more than 150 μg Chl _a_ l^{-1} has been found in the summer in the Potomac 25 to 30 km below Washington (Di Toro et al., 1977). Furthermore, simulation models by Di Toro et al. (1977) estimate that, even with 90 percent removal of nitrogen and phosphorus from Washington sludge, chlorophyll _a_ levels would not begin to approach the 25 μg Chl _a_ l^{-1} water quality objective. Excessive nitrogen is present in the Potomac to the point where phosphorus has been limiting. Nitrogen discharges from the upper Potomac River to the estuary are such that planned sewage denitrification facilities may be only marginally effective in reducing phytoplankton growth.

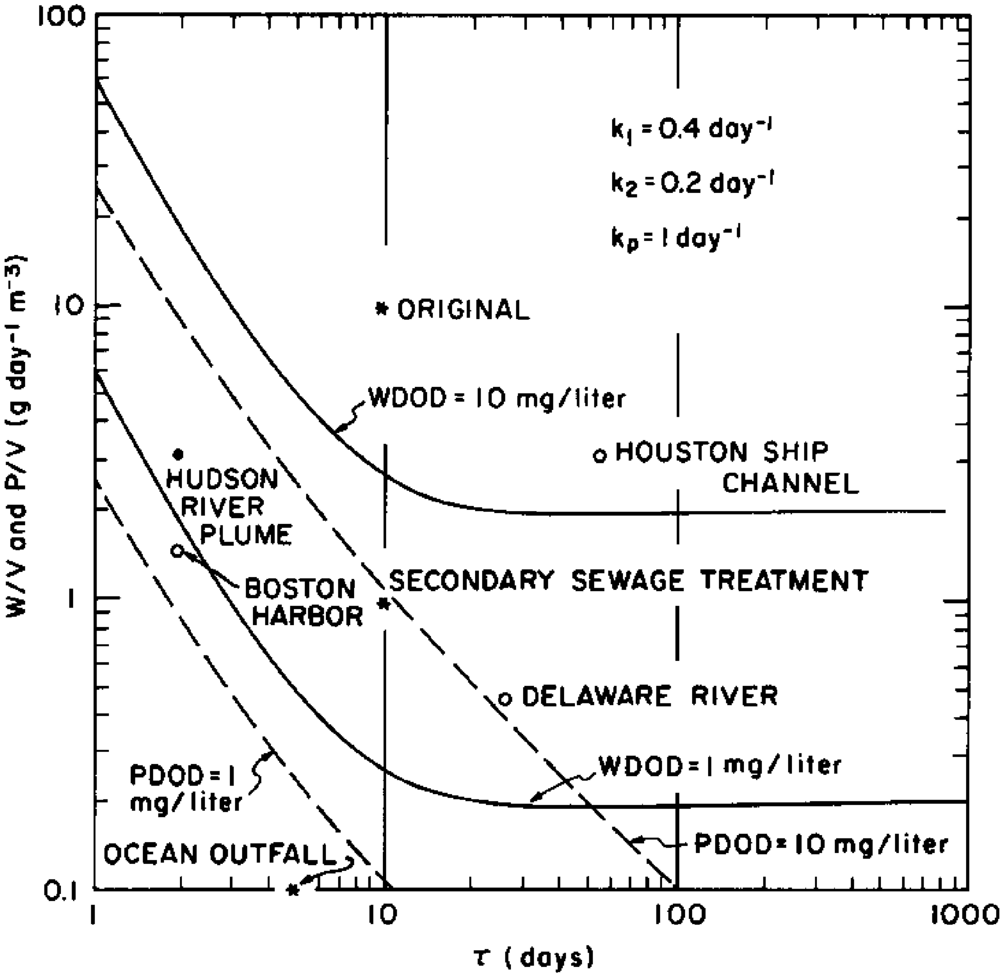
Eutrophication

Eutrophication involves the stimulation of primary producers to the point where there is excess oxygen utilization in phytoplankton respiration or decay. The effective oxygen demand of municipal wastes includes both that attributable to the oxidation of organic material in the waste (the waste biochemical oxygen demand, WBOD) and that required for the respiration and decay of phytoplankton produced because of nutrient additions (phytoplankton biochemical oxygen demand, PBOD). Typically, only WBOD is considered in water quality models of the effect of waste discharges on dissolved oxygen in the environment. The PBOD is much more difficult to predict because, as discussed above, many factors other than nutrient concentrations _per se_ serve to regulate primary productivity.

Officer and Ryther (1977) present compelling arguments to show that the effective PBOD is as important as WBOD in municipal effluent and that in the secondary treatment of wastes, reduction of WBOD may be offset by equal increase in PBOD. They estimate that WBOD is about 400 mg l^{-1} and that, assuming nitrogen limitation, a ratio of 20:1 by weight for the amount of oxygen required for the catabolic decay of organic nitrogen and 20 mg l^{-1} inorganic nitrogen, the PBOD of untreated wastewater will be in excess of 400 mg l^{-1}. The organic nitrogen content of untreated effluents is about 20 mg l^{-1} and, allowing for a loss of nitrogen to the atmosphere during secondary treatment, a typical secondary effluent has an inorganic nitrogen content of 20 mg l^{-1}. Officer and Ryther conclude that the PBOD of a secondary effluent is thus at least as great as the WBOD of raw sewage and may, if nitrogen is not lost in the treatment, be double that amount. This puts in question the efficacy of secondary treatment in reducing dissolved oxygen depletion.

Although the discharge of untreated sewage into confined coastal marine waters with restricted circulation is undesirable, the implication of Officer and Ryther's (1977) argument is that unless treatment of sewage effects significant nutrient (e.g., nitrogen (N)) removal, secondary treatment may have little impact on eutrophication of the receiving water. Rather, they suggest that diverting the untreated effluent to receiving waters with a greater flushing rate is more effective in reducing eutrophication. This may be illustrated in Figure 7.3 in which waste loadings attributable to WBOD and PBOD are compared to the flushing time yield estimates of waste oxidation potential (WDOD) and eutrophication oxidation potential (PDOD). For example, in an estuary with a waste loading of 400 x 10^6 g day^{-1}, a volume of 40 x 10^6 m^3 and a flushing time $\tau = 10$ days (labeled "original" in Figure 7.3), the dissolved oxygen deficit due to organic loading exceeds 10 mg l^{-1}. Secondary treatment of these wastes may effect a 90 percent reduction of organic loading, but because of PBOD the dissolved oxygen deficit would be reduced to slightly less than 10 mg l^{-1} (labeled "secondary sewage treatment"). Disposing the same untreated effluents via an ocean outfall into a coastal volume of 4,000 x 10^6 m^3 with a flushing time $\tau = 5$ days would reduce the oxygen deficit to less than 1 mg l^{-1} (labeled "ocean outfall").

Figure 7.3 Officer and Ryther's model of the relationship of waste oxidation potential (WDOD) and eutrophication oxidation potential (PDOD) to waste loadings (W/V and P/V) and flushing time (τ). Note the possible effects of secondary sewage treatment (WDOD only) and ocean outfall (WDOD and PDOD) on an original hypothetical pollution condition (Officer and Ryther, 1971).



Several caveats need to be mentioned in assessing the implications of Officer and Ryther's model. As they point out, the BOD potential for eutrophication is a potential regulated by other limiting factors such as solar insolation, water temperature, turbidity and mixing. Thus, the assumption regarding the complete utilization of dissolved inorganic nitrogen may not be met. Secondly, Officer and Ryther's arguments deal only with eutrophication potential and not with the relative impacts of particulates, toxicants and pathogens in comparing alternate treatment and disposal practices.

Density stratification in coastal marine waters increases the hazard of eutrophication by creating a sink for organic material. Phytoplankton sinking may be hastened by zooplankton grazing and the PBOD exported below the euphotic zone where oxygen cannot be replenished by photosynthetic oxygen production. A sharp thermocline or halocline inhibits vertical mixing, thus hindering replenishment of oxygen in bottom waters. In this manner, the usual effects of eutrophication are anoxia or severe hypoxia of waters below the pycnocline (typically a halocline in tidal estuaries and a thermocline in the coastal ocean).

Eutrophication in the New York Bight. Although usually thought of as a problem only in inland and confined coastal waters, symptoms of eutrophication in the New York Bight raise the specter of widespread eutrophication of the coastal ocean as a result of waste disposal. For this reason, the New York Bight situation will be reviewed in some detail.

Concern about the possibility of extensive eutrophication in the New York Bight was catalyzed by the widespread occurrence of oxygen deficient (hypoxic) and anoxic conditions in bottom waters over the inner half of the continental shelf off the New Jersey coast during the summer of 1976 (Sharp, 1976; Swanson and Sindermann, 1979). The effect of this severe oxygen depletion was extensive mortalities of benthic animals, including surf clams and scallops (Swanson and Sinderman, 1979). Of particular interest in this event was the role in the hypoxia of organic and nutrient additions to the Bight apex from sewage discharges in the New York Bay system and disposal of sewage sludge and dredged material at dumping grounds in the Bight apex.

Segar and Berberian (1976) and Garside and Malone (1977) used somewhat different approaches in estimating carbon and oxygen budgets for the New York Bight apex. The authors differed by a factor of more than two in the total carbon flux in the Bight apex. This was due to differences in the contribution by primary production because of the larger area considered by Segar and Berberian and disparate estimates of the importance of dissolved organic carbon input via estuarine discharge. Nonetheless, between 56 (Segar and Berberian, 1976) and 77 percent (Garside and Malone, 1977) of the organic matter is derived from in situ primary production and the difference in the relative importance is almost totally due to the larger role of dissolved organic inputs estimated by Segar and Berberian. Inputs of organic carbon in sewage sludge were considered to be less than 3 percent and 7 percent, respectively. Organic inputs from dredged materials were considered to be about equal to that of sewage sludge by Garside and Malone (1977) and almost five times greater by Segar and Berberian (1976). Both papers conclude that ocean dumping activities are not important in depletion of oxygen in the Bight apex but agree that in situ production dominates the oxygen loading of the system. Using the estimates of Garside et al. (1976) for nutrient flux from the estuarine system in the Bight apex, which Segar and Berberian (1976) criticize as too low, Malone (1978) estimated that 59 percent and 37 percent of the winter and summer phytoplankton nitrogen uptake, respectively, is supplied by sewage dominated estuarine inputs, the rest resulting from regeneration. Thus, inorganic nutrient inputs are of far greater importance in the carbon-oxygen budget than direct inputs of organic matter by sewage or sludge discharges.

Comparing the oxygen demand of the total organic carbon loading in the Bight apex with the oxygen available for its total oxidation, it is concluded that this source of eutrophication can only be responsible for localized depletion of dissolved oxygen below the seasonal thermocline and cannot account for the widespread hypoxia observed during 1976 (Garside and Malone, 1977). Still, Segar and Berberian (1976) conclude that the Bight apex is eutrophic, that periodic hypoxia observed for several years during summer in the Bight apex is the result of nutrient addition and that increases in nutrient loading are likely to increase oxygen depletion. The effects of growing eutrophication of another area of open coastal sea, the German Bight, have been demonstrated by Rachor (1977).

The widespread hypoxia in the Bight in the summer of 1976 was accompanied or preceded by several unusual conditions which have been linked with the event. These included strong and persistent vertical stratification and intense blooms of the dinoflagellate *Ceratium tripos* throughout the New York Bight between January and July 1976. The stratification was the result of unusual southwest winds during the spring and relative lack of intense winter storms which serve to vertically mix the shelf water (Sharp, 1976). The *Ceratium* bloom had complex causes which are not completely understood, nevertheless, Malone (1978) concluded that it is unlikely that the bloom occurred in response to local nutrient enrichment related to waste disposal in the Bight apex. This conclusion is based primarily on the fact that blooms did not begin, nor were they more intense, near the Bight apex. Malone (1978) was, however, able to demonstrate that once sinking below the thermocline, respiration and decay of the observed biomass of *Ceratium* were sufficient to account for the observed oxygen depletion. The cause of the proliferation of *Ceratium* remains unknown but may be related to complex species successional phenomena in the phytoplankton. This underlines the need to understand the effect of addition of nutrients and toxicants on phytoplankton structure and not simply on primary production.

Widespread Eutrophication of Coastal Waters. Eutrophication of enclosed coastal waters around the world is evident from such symptoms as altered planktonic communities and low dissolved oxygen conditions. Urban estuaries, including the Hudson River, Delaware Bay, Chesapeake Bay and San Francisco Bay, in particular are showing signs of degradation due to wastewater inputs as well as those from non-point sources (Neilson and Cronin, 1981). Even in some very large bodies of water, such as the Baltic Sea, there is evidence of disrupted oxygen balance because of nutrient enrichment (Gerlach, 1981). However, the Baltic is an enclosed basin and there should be little eutrophication experienced in open coastal waters because of the tremendous potential of dilution and oxygenation. However, the experience of the New York Bight and perhaps the North Sea, warns that anthropogenic inputs may play a significant role, acting in concert with natural processes, in eutrophication of open coastal waters.

Recently, Walsh et al. (1981) suggested that increased primary production as a result of anthropogenic nutrient inputs is mainly lost to the deep sea and constitutes an important sink in the global carbon dioxide cycle. They present data suggesting that the nitrate flux through rivers with densely populated drainage areas, such as the Mississippi, Rhine, Mekong and Yangtze, has increased by up to ten times prehabitation levels and has more than doubled in the last 25 years. This increase has of course resulted from extensive utilization of fertilizers as well as sewage discharges. Walsh et al. concluded that much of the resulting increase in organic carbon fixed on the shelf is not consumed but is deposited on the slope. Their analyses suggest that up to half of the presumed slope carbon sink could result from increased nutrient enrichment since the industrial revolution. This could mean that disposal of waste nutrients in well-flushed coastal waters could help avert increases in atmospheric CO_2 content. However, before this phenomenon should be included in a management strategy, many of the untested assumptions of the Walsh et al. model need to be rigorously evaluated.

Effects on Pelagic Food Chains

Municipal wastes discharged into the marine environment may affect pelagic biota directly by toxicity or stimulation or the effect may be indirect, operating through the food chain. Direct toxic effects on individaul species have been discussed above and will not be specifically addressed here. Rather, this discussion will focus on the effect of toxic and stimulatory materials on pelagic communities.

Effects of pollutants on pelagic communities are very difficult to assess in field studies involving surveys relating the biota to contaminant levels. The pelagic biota is highly variable temporally and is spatially heterogeneous. Concentrations of dissolved toxicants are usually very low and difficult to measure reliably. Experimental studies in which pelagic biota, particularly plankton, are exposed to controlled concentrations of the material in question are generally more rewarding but are difficult to accomplish at the community level. Laboratory microcosms and controlled field experiments involving enclosures deployed in the water column have provided the best understanding to date of the effects of substances on planktonic communities. Similar experiments involving large volume, transparent cylinders have been conducted as part of the

Controlled Ecosystem Pollution Experiments (CEPEX) in Saanich Inlet, British Columbia (Menzel and Case, 1977; Grice et al., 1977) and in Loch Ewe, Scotland (Gamble et al., 1977).

In these experiments, pollutants are added to some enclosures and others are maintained as controls. Experiments involving the addition of copper, mercury and petroleum hydrocarbons at Saanich Inlet and copper at Loch Ewe have been conducted. Although the concept of field experimentation is to simulate natural conditions as much as possible, water mass enclosures produce some associated artificial effects which influence interpretation of results of the experiments. These include shading by the surface float and enclosure, adsorption and fouling of the walls of the enclosure, severe reduction of vertical water movements in the enclosures resulting in faster sinking of plankton and particulate matter and depletion of surface water nutrients.

The general trends found in these experiments are often similar despite the pollutant added and serve to underscore the importance of indirect effects of the pollutants through food chain interactions as opposed to direct toxic effects. Bacterioplankton seem to respond most quickly to the pollutants. Addition of copper (10 and 50 $\mu g\ l^{-1}$) initially resulted in an increase of heterotrophic bacterial activity which was stimulated by a release of organic material by copper sensitive phytoplankton (Vaccaro et al., 1977), but the mercury (1 and 5 $\mu g\ l^{-1}$) (Azam et al., 1977) and petroleum (Hodson et al., 1977) additions resulted in initial inhibition of heterotrophic activity. With both copper and mercury, however, tolerant populations soon developed and heterotrophic activity was similar to that in controls. The populations were cross-tolerant in that those which developed in the copper treated enclosures were also tolerant of mercury and vice-versa.

Both metals resulted in a rapid decline in centric diatoms which dominate the phytoplankton at both Saanich Inlet and Loch Ewe (Thomas and Seibert, 1977; Thomas et al., 1977b; Gamble et al., 1977) and the eventual dominance by a phytoplanktonic community substantially different from that found initially and in the experimental controls. In the copper experiments, microflagellates, dinoflagellates and pennate diatoms become important, while in the mercury experiments, dinoflagellates, centric diatoms and microflagellates were the eventual dominants. Measures of standing stock (chlorophyll a, particulate

C, ATP) and productivity (^{14}C fixation and N uptake) showed initial depression (Thomas et al., 1977a,b; Harrison et al., 1977), but rebounded quickly in that they were not different from the controls after several days. Thus, the structure of phytoplankton communities and their resultant trophic availability, may be altered substantially by a pollutant without rate processes being affected.

Effects of copper (>5 $\mu g\ l^{-1}$) and mercury (5 $\mu g\ l^{-1}$) additions in the zooplankton community resulted both because of direct toxicity and because of alterations in intensity of predation or abundance of phytoplanktonic food. Smaller zooplankters appeared to be more sensitive (Beers et al., 1977a, b), but some important larger predators, e.g. ctenophores, were also relatively sensitive (Reeve et al., 1977). Sublethal effects in copepods were observed in terms of reduction in the rates of egg production and ingestion (Reeve et al., 1977). In the Saanich Inlet and Loch Ewe copper experiments the inclusion of predaceous ctenophores (Pleurobranchia bachei and Bolinopsis infundibulum, respectively) resulted in reductions in the populations of zooplankters (Gibson and Grice, 1977; Gamble et al., 1977), whereas in the Saanich Inlet mercury experiment, herbivorous zooplankton increased after an initial reduction in response to fertilized phytoplankton blooms and a lack of predators (Beers et al., 1977b). Differential sensitivity of zooplankters can thus cause changes in plankton community structure. For example, if levels of a pollutant are toxic to ctenophores but not the zooplanktonic grazers, the grazers might proliferate and exert effective grazing pressures on phytoplankton (Thomas et al., 1977b).

Large consumers such as juvenile salmonid fishes may be affected more by resultant decreases or compositional alterations in lower trophic levels than by toxicity (Koeller and Parson, 1977; Koeller and Wallace, 1977). If toxic effects shift the phytoplankton community to smaller flagellates, adjustment in the zooplankton community may favor the smaller grazers. Reduction in the populations of grazing crustaceans which constitute the prey of juvenile fishes will affect growth and survival of the fish (Parsons and Le Brasseur, 1970; Koeller and Parsons, 1977). Similarly, O'Conners et al. (1978) found that PCBs at concentrations of 1 to 10 $\mu g\ l^{-1}$ reduced phytoplankton biomass and size and hypthesized that reduced phytoplankton size could increase the number of trophic levels and divert the flow of energy from harvestable fish, which rely on short food chains, to jellyfish and other gelatinous predators which are favored by long food chains (Greve and Parsons, 1977).

Biostimulation through the addition of inorganic nutrients and organic matter may also result in food chain modifications. Although stimulation of primary production through nutrient enrichment could result in stimulation of secondary production and higher ultimate food chain yeilds, the stimulation may often result in modification of the structure of pelagic communities. Heinle et al. (1979) were able to demonstrate effects in the primary consumer populations in plankton microcosms enriched by sewage addition. Often nutrient enrichment, especially at higher temperatures, results in phytoplankton shifts toward predominance by nanoplankton and phytoflagellates (Malone, 1977a), but there are exceptions (Eppley and Weiler, 1979). If the above hypotheses relating phytoplankton size to food chain structure (Greve and Parsons, 1977) are true, such enrichment effects may result in suppression rather than stimulation of fisheries production despite the overall stimulation of secondary production.

EFFECTS ON BENTHIC SYSTEMS

Contamination of Bottom Sediments

Pollutants emanating from the discharge of municipal waste to the marine environment may contaminate bottom sediments through one of three general pathways: 1. the direct disposal of particulates removed from the waste, i.e., sludge, 2. the sedimentation of suspended particulates present in effluents and 3. the adsorption of dissolved pollutants on natural particulate matter or absorption by organisms and subsequent sedimentation. Partitioning of pollutants between dissolved and particulate phases will tend to favor sorption and sedimentation of many inorganic and organic compounds (Chapter 6). This is particularly so in the case of fine sediments (silts and clays) which, because of their greater surface area per unit volume and their larger cationic exchange capacity, tend to scour and bind dissolved constituents. As a result, high concentrations of organic matter and potential toxicants may develop in depositional environments affected by waste discharges. Benthic organisms may thus be exposed to concentrations of pollutants very much higher than those dissolved in the water column.

Among pollutants, the geochemical fate and bioavailability of trace metals are best known and have been reviewed by Bryan (1976). Trace metals in sediments include those incorportated in the structural lattice of sediment minerals, those adsorbed on the surface of sediment particles and those dissolved in interstitial waters. Structural metals are essentially unavailable to organisms and because of complex geochemical processes; much of the adsorbed and interstitial metals are also unavailable. An important factor is the complexing and reaction of metals as a result of reducing conditions which develop in sediments following the exhaustion of dissolved oxygen through the anaerobic metabolism of microorganisms. Surface sediments are usually oxidized and appear brown or yellow, but below a few millimeters to centimeters reducing conditions develop sharply, causing black coloration below the redox potential discontinuity (RPD). Under reduced conditions, metals may exist largely as insoluble metal sulfides (Chapter 6), although the presence of certain organic or inorganic compounds may enhance their solubility (Bryan, 1976). Although sediments generally serve as a sink for trace metals, remobilization and diffusion of metals to the water column may take place if the concentration gradients favor it. Thus, sediments may serve as a reservoir of pollutant trace metals which can then continue to supply contaminants to the water column long after the introduction of the pollutant has been curtailed. Benthic organisms, through their metabolic, bioturbating and burrow ventilating activities, may assist in the release of metals from sediments (Bryan and Hummerston, 1973). For example, Jernelöv (1970) found that in freshwater sediments, tubificid worms could release mercury from contaminated sediments buried under uncontaminated sediment to a depth of 2 cm and bivalves from a depth of 9 cm.

Benthic organisms may also be responsible for localized concentrations of trace metals in sediments. For example, Aller and Yingst (1978) found that metals concentrated near the wall of the burrow of the polychaete Amphitrite ornata, where they were mobilized and deposited because of the intensified sediment-water exchange in the burrow due to respiratory ventilation by the polychaete.

Often the concentrations of toxicants measured in interstitial waters are greater than those reported to be toxic, suggesting that the material must not be bioavailable. However, there is little direct information on the availability and toxicity of sediment accommodated toxicants to the benthic organisms which live in this sediment medium and, in may cases, even ingest it.

Organic material directly discharged with municipal wastes or produced as a result of nutrient stimulation of phytoplankton activity also concentrates on the seabed. McIntyre (1977) estimated that in an area of the Firth of Clyde, where sewage sludge from Glasgow is dumped, organic carbon input to the seabed is about 55 times the natural rate. In another portion of the Clyde, Irvine Bay, river discharge enriched with sewage causes roughly six times the normal background rate for deposition of organic carbon.

The impact of organic loading and sediment-associated toxicants depends greatly on the environment of deposition. In areas with little turbulent mixing, sheltered from waves and strong currents, or relatively deep with little water movement and resusupension of bottom sediments, deposited material will tend to accumulate in relatively small areas and oxygen demand of the organic material and concentration of the pollutants will be great. On the other hand, in turbulent areas, in shallow water or exposed to strong currents, deposited material will be more rapidly dispersed. McIntyre and Johnson (1975) refer to these "accumulating" and "dispersing" grounds. This concept is fundamental to understanding the effects of municipal waste additions on the benthos and is used in managing sewage sludge disposal in the United Kingdom (Standing Committee on the Disposal of Sewage Sludge, 1978).

Benthic Communities

The effects of organic enrichment and pollution on the macroorganisms inhabiting marine sediments have been extensively studied, particularly in Europe (O'Sullivan, 1971; Pearson and Rosenberg, 1978). Results of these studies typically show that as organic loading of the seabed increases or as toxicants become more concentrated, many species in the natural community will decline while other species, relatively uncommon in the natural community, will become more abundant. This phenomenon is the basis of the indicator species concept, long applied in the study of freshwater stream pollution and first applied to marine benthos by Reish (1959, 1960, 1972) in his studies of pollution in Los Angeles and Long

Beach Harbors. The presence of certain sensitive species was used to indicate healthy conditions and the presence of certain species favored by perturbations was used to indicate polluted conditions. Strikingly similar patterns of response of macrobenthos to organic pollution have been widely witnessed, for example, in Japan (Kitamori and Kobe, 1959), the Mediterranean Sea (Bellan, 1967; Stirn et al., 1975), the Baltic (Bagge, 1969; Leppäkowski, 1975; Anger, 1975) and off southern California (Smith and Greene, 1976). The species of macrobenthos characteristically widely favored by organic pollution were summarized by Pearson and Rosenberg (1978).

Based on extensive studies of the response of a wide range of benthic communities in the Baltic and on the west coast of Sweden to organic pollution (sewage and pulp mill effluents), Bagge (1969) developed a scheme to show the change of community dominants under varying intensities of pollution for the major salinity regimes represented (Table 7.5). The dominant species in unaffected habitats of all salinity regimes were subject to elimination under heavy pollution. Furthermore, species favored by pollution (pollution indicators), such as the polychaetes Capitella capitata, Scolelepis fuliginosa and Polydora ciliata (= P. ligni) occurred in a wide variety of sediment types under heavy pollution. Leppäkowski (1975) classified species on the basis of their characteristic response to environmental change due to organic pollution as:

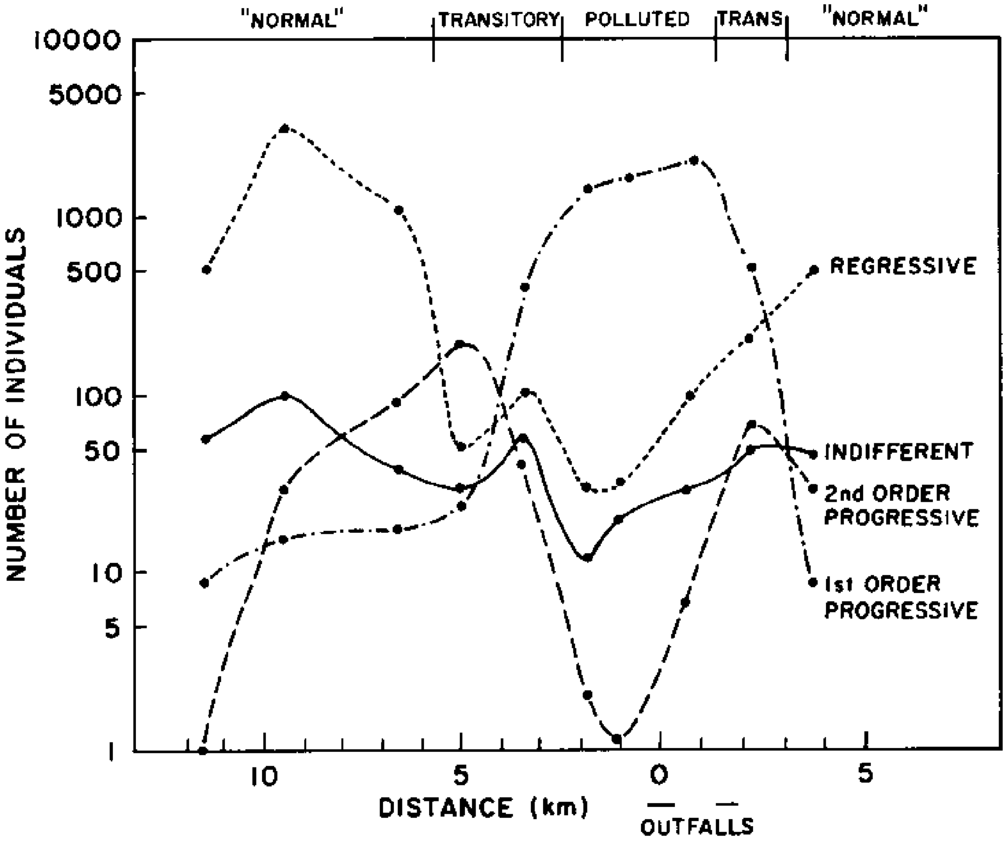
1. progressive species of the first order, which are scarce or uncommon in unpolluted areas but occur in great numbers in polluted areas;
2. progressive species of the second order, which tolerate less pollution but are found in increased abundance under slight pollution;
3. regressive species of the second order, which occur in slightly polluted areas but in reduced abundance than in unpolluted areas;
4. regressive species of the first order, which are excluded by pollution; and
5. indifferent species, which are broadly found in all but azoic habitats.

Table 7.5 Characteristic Dominant Macrobenthos Under Various Levels of Pollution in the Salinity Regimes of the Baltic Sea (Based on Bagge (1969) and Rosenberg (1976)).

Salinity Regime	Normal	Slight Pollution (Transitory)	Heavy Pollution
Oligohaline (0-5 ppt)	*Pontoporeia*	*Corophium* *Euilyodrilus*	*Chironomus*
Mesohaline (5-18 ppt)	*Macoma*	*Macoma* *Corophium* *Polydora*	*Chironomus*
Polyhaline (18-30 ppt)	*Amphiura*	*Abra* *Thyasira* *Heteromastus*	*Capitella* *Scolelepis*
	Nephtys *Nucula*	*Mya* *Cardium* *Corophium*	*Capitella* *Polydora*

This scheme may be related to the results of Greene and Smith (1975) who applied numerical classification procedures to group species of benthos based on their patterns of occurrence in an area off the Palos Verdes Peninsula, southern California, which receives sewage and sludge discharges from two outfalls (Figure 7.4). Regressive species (e.g., the bivalve *Axinopsida* sp. and the polychaete *Mediomastus ambiseta* and the ophuiroid *Amphiodia urtica*) which dominate the benthos of the 60 m habitat off southern California were reduced in combined abundance by more than an order of magnitude in polluted habitats. At the other extreme, first order progressive species (e.g., the polychaetes *Capitella capitata*, *Schistomeringos longicornis* and an unidentified dorvilleid and the bivalve *Solemya panamensis*) were present in combined densities more than two orders of magnitude higher in the polluted habitat than in unaffected bottoms. Species which may be termed second order progressives (e.g., the bivalve *Parvilucina tenuisculpta*) were very uncommon both in polluted and normal habitats, but peaked in abundance in the transitional zones. More recent investigations of the composition of benthic communities along the length of the southern California shelf at 60 m (the depth of many outfalls) have shown similar patterns

Figure 7.4 The combined abundance of species classified on the basis of their response to sewage inputs along the 60 m isobath off the Palos Verdes Peninsula, southern California (modified from Greene and Smith, 1975).



associated with major waste discharges based on an index reflective of the response of the benthos to organic pollution and predominant feeding strategies (Word, 1979).

Under relatively slight organic pollution, as in the transitional zones between heavily polluted and natural habitats, standing crop and productivity may be enhanced and species present in generally low abundance in the natural communities may increase greatly in abundance (Anger, 1975; Greene and Smith, 1975; Pearson and Rosenberg, 1978). As in the case of nutrient enrichment of phytoplankton, organic enrichment of the benthos usually results in altered community structure as well as enhanced productivity. Such alterations may be very subtle but ecologically important. For example, McIntyre (1977) found that macrobenthic communities in nearshore areas of the Firth of Clyde enriched by sewage inputs had a similar composition but higher biomass than in unaffected zones of the Clyde, suggesting a potentially beneficial enhancement in secondary production without altering community structure. However, investigations of the meiobenthos showed that sewage-affected habitats supported far fewer harpacticoid copepods which are important food of larval and juvenile fishes which use these habitats as a nursery ground.

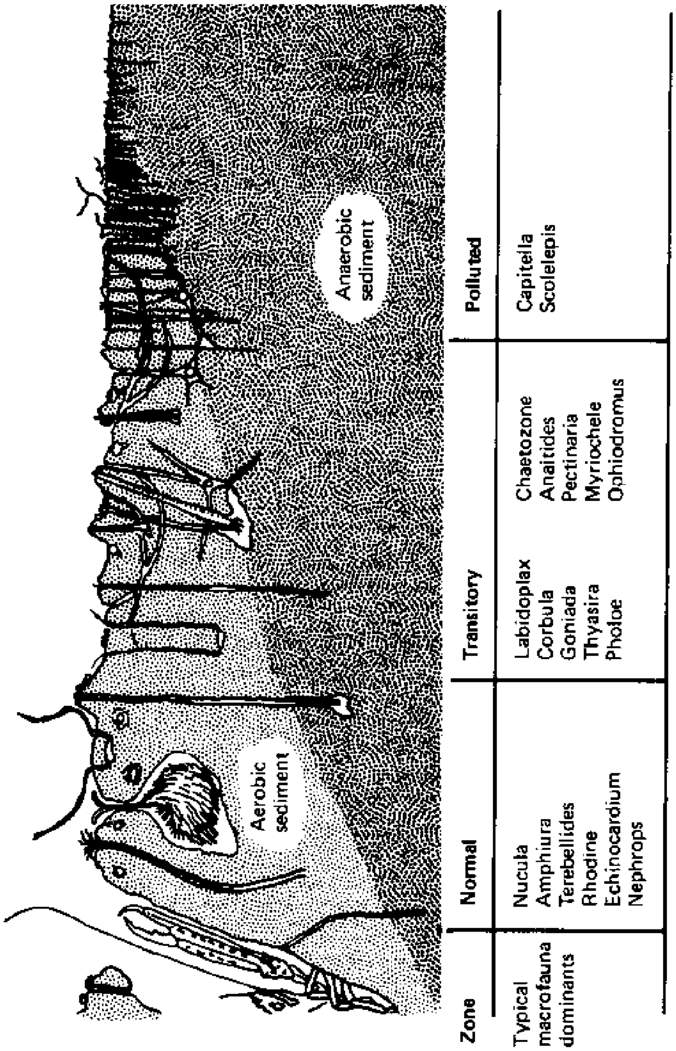
As a result of the elimination of the less resistant, regressive species, species diversity is often reduced in the impacted zone (Boesch, 1972; Anger, 1975; Leppakowski, 1975; Pearson and Rosenberg, 1978). However, the relationship of indices of species diversity to pollution stress is not unequivocal because of great natural variation in patterns of diversity (Gray, 1976); because the stress may act to reduce the abundance of dominant species, thereby raising the evenness component of diversity indices such as the Shannon index (Logan and Maurer, 1975; Boesch, 1977; Swartz, 1981); or because slight disturbances may actually increase species diversity (Connell, 1978).

Similarities in the response of benthic communities to organic pollution are indeed striking. A most amazing example of parallel response is given in Pearson and Rosenberg's (1976, 1978) comparisons of succession of benthos in response to abatement of pulp mill pollution in a Swedish fjord and the concomitant commencement of similar pollution in a Scottish sea loch. In the Swedish fjord, three years after the closure of a sulfite pulp mill in 1966, recovery of the benthic fauna began and the heavily polluted bottom which supported almost no macroscopic animals was colonized first by the progressive species *Capitella capitata* and *Scolelepis fuliginosa*. By 1974, 60 species were present, comparable to normal species richness in both Swedish and Scottish habitats. The Scottish pulp mill began operation in 1966, effects on the benthos were soon felt and by 1972-73 diversity was reduced to levels comparable with those during the early recovery in the Swedish fjord, with *Capitella capitata* and *Scolelepis fuliginosa* again dominating. In 1969 during the transitory period between polluted and normal conditions, the species diversity of the communities in both locations crossed, increasing in Sweden and declining in Scotland. Remarkably, the dominant species in the two communities at this time were largely the same. The juxtaposed successional sequences are schematically depicted in Figure 7.5. Note the opposite effects that organic loading and development of a mature benthic community have on the depth of the redox potential discontinuity, with important implications in geochemical exchange between the sediment and water.

The pattern of recovery of the benthos following pollution abatement in the Swedish fjord provides perhaps the best evidence of the systematic reversibility of the effects of excessive organic enrichment in which persistent toxicants are not a serious problem. In deeper bottoms of the fjord where organic matter had built up, recovery took at least 8 years, but the community returned to a state similar to that recorded 50 years earlier (Rosenberg, 1976).

Progressive species favored by pollution stress are very similar in widely distributed geographic areas (Pearson and Rosenberg, 1978). Annelid taxa such as *Capitella capitata*, *Polydora ciliata* (=*ligni*), *Scolelepis fulginosa*, *Streblospio* sp., *Heteromastus filiformis*, *Nereis* sp. and *Peloscolex* sp. frequently are found in polluted benthic habitats. These species are usually characterized as opportunistic in that they have life history characteristics which allow them to rapidly increase in unexploited habitats but cannot normally maintain high populations in the face of inter- or intraspecific competition or predation. Opportunistic species are characterized by their ability to find new habitats, to rapidly increase in population size and to mature and reproduce rapidly, but they exhibit high mortality rates (Grassle and Grassle, 1974). Gray (1979) has hypothesized that plastic reproductive strategies with both direct

Figure 7.5 Diagramatic representation of changes in the macrobenthos under increasing organic loading, exemplified by pulp mill discharges in Sweden and Scotland (Pearson and Rosenberg, 1976). Burrows of polychaetes, bivalves, brittle stars, a sea urchin and a Norway lobster are represented.



larval development and short-term larval dispersal in the plankton is the most adaptive for opportunistic benthic species.

In addition to their resilience, the progressive species also have to be fairly resistant to stress (hypoxia and toxicants), otherwise, together with the regressive species, they too would be eliminated by pollution. Gray (1979) argued that opportunism (adaptation for resilience) and stress tolerance (adaptation for resistance) may be independent and that progressive species such as Capitella capitata are not necessarily the least sensitive to pollutants. However, Boesch and Rosenberg (1981) note a correlation between resistance and resilience, at least at the community level. Communities which naturally experience great stress or are frequently disturbed, such as estuarine benthos, will be composed of more or less opportunistic species. Thus, the impacts of pollution will generally result in less alteration in the composition and structure of these communities. The great natural spatial and temporal variation of the benthos of inconstant environments (estuaries, intertidal habitats, etc.), coupled with their adaptive resistance and resilience, makes the assessment of all but catastrophic impacts of pollutants in these habitats extremely difficult (Eagle and Rees, 1973; Gray, 1976; Pearson and Rosenberg, 1978; Boesch and Rosenberg, 1981).

Sewage discharges may also exert effects on epibenthic communities of hard substrates, which are not natural sites of sediment accumulation. These effects may be attributable to increased turbidity and sedimentation, nutrient enrichment of epiphytic growth, or toxicants. Littler and Murray (1975) described very localized changes in intertidal algae near a small discharge of domestic effluents on San Clemente Island off southern California. On a larger scale, Wilson et al. (1980) reported the virtual elimination of kelp beds off Palos Verdes by the 1960s as a result of the massive discharge of particulates from the White's Point outfall. As particulates were reduced in the discharge, an extensive restoration program has allowed substantial recovery of the beds by the late 1970s. Gerlach (1981) noted the widespread impoverishment of intertidal and shallow water algal communities in the vicinity of coastal cities around the world. Moore (1973) found an altered animal community inhabiting kelp holdfasts near sources of municipal and industrial wastes on the northeast coast of England and suggested that this may be due to the toxicity of particulate matter trapped by the holdfast community. Johannes (1975) described the destruction of coral reef communities in the vicinity of sewage discharges as a result of proliferation of algae which overgrow the coral due to nutrient enrichment.

Sludge Disposal.

The major environmental concern regarding ocean disposal of sewage sludge is focused on the benthos, as it is generally thought that effects on pelagic organisms are insignificant or transient (McIntyre and Johnson, 1975; National Academy of Sciences, 1978). As mentioned earlier, a key in determining the impacts of sludge disposal on benthos is the degree to which sedimented material is dispersed in the receiving environments. McIntyre and Johnson (1975), McIntyre (1977) and Standing Committee on the Disposal of Sewage Sludge (1978) showed that on non-accumulating ground, the effects are negligible or will be difficult to detect. For example, the dumping of large quantities of sewage sludge from London in tidally scoured bottoms at the mouth of the Thames River causes little buildup of organic deposits and few demonstrable effects on the benthos (Skelton, 1973). However, disposal of one-fifth as much sewage sludge from the city of Glasgow onto accumulating grounds in the Firth of Clyde has caused reduction in the diversity of macrobenthos by elimination of regressive species and has caused overwhelming dominance by progressive species (McIntyre, 1977). The heavily polluted area is 10 km^2 and is characterized by sediment organic carbon concentration of 3 to 8 percent. The benthos is more dense and has a higher biomass in this region than on unaffected bottoms, but is dominated by capitellid polychaetes and the oligochaete *Peloscolex* sp. Norway lobsters, *Nephrops norvegicus*, typically found in the mud bottoms of the Clyde in densities of 1 to 2 individuals m^{-2}, are excluded from the impacted 10 km^2 area.

Similar comparisons may be drawn on the major sites of ocean disposal of sewage sludge in the United States. The present Philadelphia dump site is located over a sandy bottom on the outer continental shelf off Maryland. Higher concentrations of trace metals and organic carbon were found in sediments near the dump site (Lear et al., 1977), but sediment carbon concentrations which are generally less than 1 percent suggest that sediments are not heavily enriched. The local distribution of organic matter, trace metals and macrobenthic organisms at the Philadelphia dump site seem to be largely related to the ridge and swale topography (Swift et al., 1972) characteristic of the Middle Atlantic shelf. Organic carbon and trace metal concentrations are higher in topographic depressions where fine sands containing small quantities of silt and clay are deposited. The seabed in the region is, however, basically non-accumulating and the sludge is probably widely dispersed by bottom currents. This appears also to have been the case at the previously used dump site for Philadelphia sludge off the mouth of the Delaware Bay. Little accumulation of pollutants has been observed at the site itself, although there has been possibly some accumulation in the deeper channel to the southwest (Watling et al., 1974).

In the New York Bight apex, sewage sludge is dumped on relatively shoal banks where it does not accumulate. Rather the sludge is dispersed by bottom currents and a significant portion of it is deposited in the adjacent Christiaensen Basin at the head of the Hudson Shelf Valley (Hatcher and Keister, 1976), where it does accumulate as evidenced by sediment organic carbon concentrations of more than 2 percent (Hatcher and Keister, 1976) to as high as 20 percent (Pearce, 1972) and high trace metal concentrations (>100 mg kg^{-1} each of copper, chromium, zinc and lead and >25 mg kg^{-1} of nickel (Carmody et al., 1973). The benthos of the Christiaensen Basin is not dominated by the first order progressive species, although _Capitella capitata_ is present in a portion of the Basin near the sludge dump site (Pearce, 1972; Pearce et al., 1976; Boesch, 1982). Although certain regressive species appear to be lacking, the macrobenthos present in the Basin could be characterized as indifferent or second order progressive species (Leppäkowski, 1975). The chief difficulty in assessing the impact of the dumped wastes on the benthos is that there are no comparable habitats which could reasonably be used as a control for the Christiaensen Basin, which is surrounded by shallower, sandy bottoms which support considerably different communities.

The disposal of sewage sludge in the southern California Bight is by deep ocean outfalls because of the narrowness of the continental shelf. These discharge mostly at depths of 60 m or more. The enhanced flushing time achieved by such outfalls causes very rapid dilution and dispersion of dissolved or suspended pollutants. However, particulate matter which settles out near the outfall is deposited in an accumulating environment. In addition to local accumulation around the outfall, many of the sewage particulates may eventually be transported to deep sea basins offshore. The Hyperion outfall in Los Angeles discharges at the head of the Santa Monica submarine canyon resulting in the transport of most of the sludge to a deep hypoxic basin, which has a depauperate macrobenthos (Garber et al., 1975). Because of the long residence time of water in the basin, the lack of bioturbation or physical disruption of sediments and the diminished mobilization of toxicants from the sediments because of reducing conditions, it has been suggested that most of the pollutants reaching the basin are permanently buried. The most significant biological effects of the southern California ocean outfalls have been shown to be effects on the benthos caused by the deposition of particulate material (Bascom, 1977). Moderately large areas of the sea bed (73 km^2 for the major southern California outfalls combined) have been affected (Mearns and Young, Appendix A in this volume).

The exact mode of impact of particulate pollution by municipal wastes on the benthos is not well known. In most cases, it has been suggested or presumed that effects were caused either by smothering or by stresses resulting from an oversupply of organic material. If the oxygen demand of decomposing of organic deposits exceeds the rate of resupply of dissolved oxygen to the sediment, severely hypoxic conditions may prevail in interstitial waters of surface sediments and in the overlying water column. Furthermore, toxic hydrogen sulfide produced by anaerobic microbes may build up in or over the sediments. Observed effects on the macrobenthos near southern California outfalls were shown to be more closely correlated with the sulfide potential of sediments than any other sediment quality parameter measured (Smith and Greene, 1976). The effects of toxicants which generally accompany organic enrichment of sediments are almost completely unknown. Although organic loading exerts the predominant effects, toxicants may act to reduce an organism's resistance to hypoxia or sulfide toxicity. Furthermore, in the case of pollution abatement, the process of detoxification of sediments contaminated with a persistent organic or inorganic toxicant is presumed to be much more lengthy than the process of reduction of excess organic material in the sediments.

Benthic Food Chains.

As with the plankton, the implications of changes in community structure of the benthos with respect to higher trophic levels are poorly understood. If sewage additions increase the standing stock of the benthos, as has often been shown, they then have the potential for increasing the yield of fisheries dependent on the benthic food chain. Therefore, organic waste additions may serve a beneficial function or organic loading may select for benthic species which are of less value to predaceaous fish and crabs.

McIntyre and Johnson (1975) state that fishes do not seem to favor as food the invertebrate benthos which dominate heavily polluted environments (i.e., the first order progressive species, mainly small annelids). On the other hand, some of the more recessive species (e.g., amphipod crustaceans) are very important prey of bottom-feeding fishes. In those areas on the periphery of sludge dump sites or around sewage outfalls where production of benthos is enhanced by organic inputs, but community structure is not greatly altered, fishes may be attracted and foraging might be more intense than in unaffected habitats (McIntyre and Johnson, 1975; Allen and Voglin, 1976; Standing Committee on the Disposal of Sewage Sludge, 1978). However, Boesch (1982) concluded that the trophic value to bottom-feeding fishes of such enriched habitats in the New York Bight apex is reduced despite generally more plentiful standing crops. Benthic crustaceans which are important prey for demersal fishes elsewhere in the Middle Atlantic Bight are excluded from contaminated sediments in the apex and upper Hudson Shelf Valley.

Benthic food chains are harder to study experimentally than those in the plankton because of the greater longevity and complicated life cycles of the benthos. McIntyre (1977) reviews results of experiments on the effect of copper and mercury on a simple food chain including phytoplankton, a bivalve _Tellina tenuis_ and newly settled plaice, _Pleuronectes platessa_, held in large fiberglass tanks. The plaice graze the siphons of _Tellina_ which are therefore regenerated. Sublethal concentrations of copper and mercury had effects throughout this food chain. For example, copper reduced the standing crop and photosynthetic efficiency of phytoplankton which in turn resulted in diminished condition and smaller siphon weight of the _Tellina_. This had the effect of reducing the growth rate and condition of the plaice, despite the fact that growth and condition of plaice was not directly affected by the concentration of copper used in the experiments.

EFFECTS ON FISHERIES RESOURCES

Pollutants emanating from discharge of municipal wastes into the ocean may affect fisheries resources by directly altering population densities or suitable habitats of fishery species or may affect the availability of the resource to humans without affecting the population itself. The availability may be reduced by contamination of the organisms with materials which are distasteful (tainting) or are potentially toxic to humans or by precautions taken to reduce the likelihood of ingestion of human pathogens of sewage origin. The latter human health effects are the subject of detailed considerations in Chapter 9 and this discussion will focus mainly on effects on the fishery species themselves.

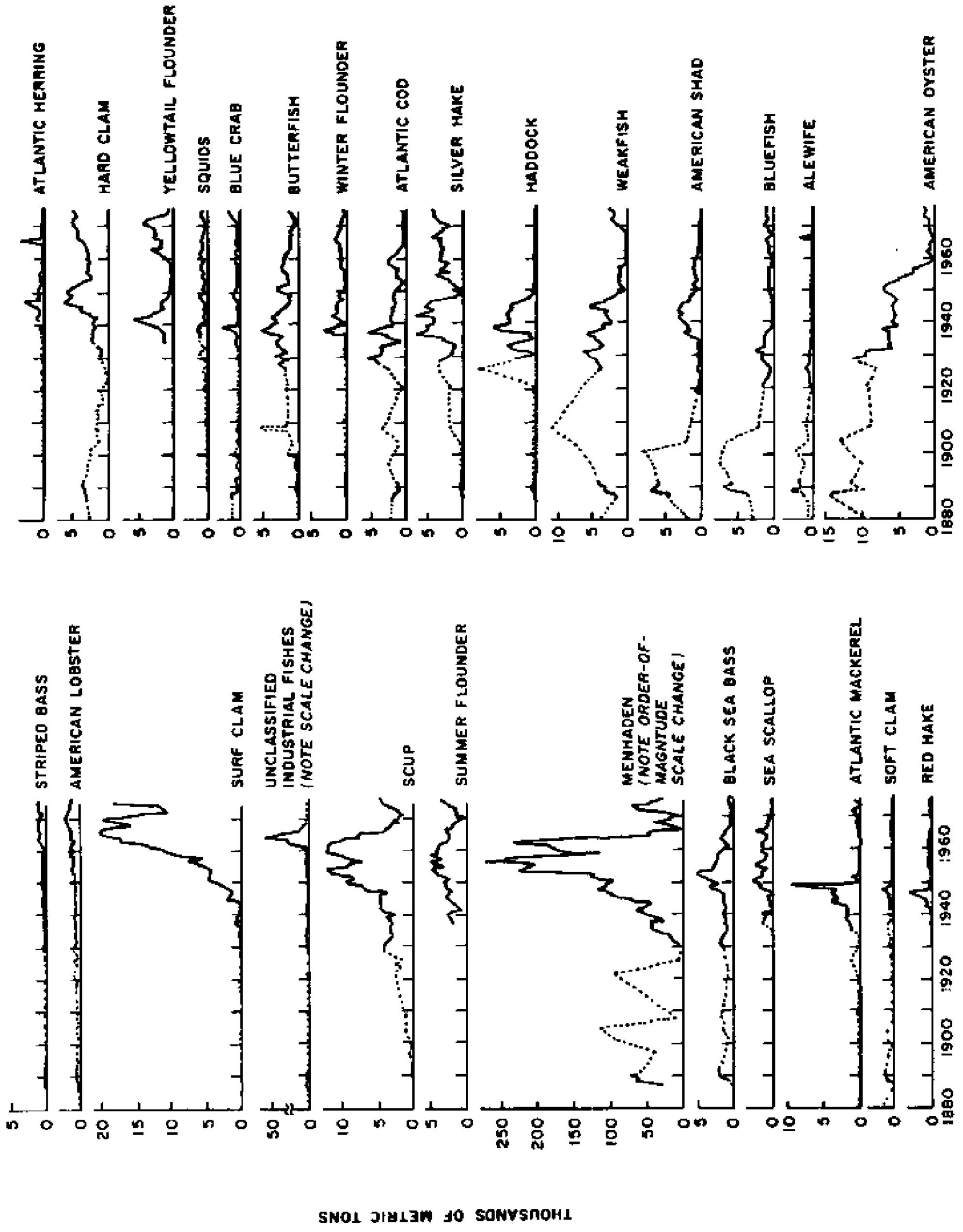
There are surprisingly few documented cases of serious diminution (or increases) of fisheries stocks caused by municipal waste additions to the sea. However, the assessment of such effects is made extremely difficult by: 1. changes induced by overfishing, 2. the large natural variations in populations, 3. the overwhelming effects of some of other human activities, including dredging and other habitat modifications, 4. the motility of many species, 5. problems in relating demonstrated effects on plankton and benthos to higher trophic levels and 6. the previously discussed limitations in translating experimentally determined effects to natural populations. Nonetheless, it is inconceivable that the lethal and sublethal effects of toxic materials and the effects on the planktonic or benthic food of fishery species, as reviewed above, do not exert some, albeit slight, impact on fish populations.

In estuaries, the effects on fishery species which have been best documented are principally related to the effects of eutrophication due to organic and nutrient additions. The demise of fishes in the lower Thames estuary due to severe oxygen stress and their partial recovery following curtailment of waste discharges is a classic story (Johnston, 1976). Similar effects of oxygen depletion on fish species in the upper reaches of estuaries have been demonstrated in the Delaware River, for example (Chittenden, 1971). In addition to the effects of hypoxia, alterations in the phytoplankton composition due to nutrient additions is thought to have caused demise in shellfish populations; for example in Moriches Bay (Ryther, 1954) and in Dutch estuaries (Korringa, 1968). Effects on estuarine fishery populations due to toxic components of municipal wastes are little documented. The over-chlorination of sewage discharges in the James River estuary, Virginia, is thought to have affected the successful recruitment success of oysters to the important seed beds nearby (Bellanca and Bailey, 1977). Bechtel and Copeland (1970) related the composition and diversity of fish communities in Galveston Bay to the concentration of outflow from the Houston ship channel which presumably exerted toxic effects. The Houston ship channel receives large amounts of both municipal and industrial wastes.

The effects of discharges of municipal wastes in the coastal ocean in the New York and southern California bights have been a matter of concern and speculation. Sindermann (1976) reviewed the effect of coastal pollution on the fisheries of the Middle Atlantic Bight (including New York Bight) and found localized effects on small segments of fish and shellfish populations, but no evidence of widespread damage which could be specifically attributed to pollution. McHugh (1977) reviewed trends in landings of some 48 species of fishes in the New York Bight which showed a general downward trend for many species during the last 25 years (Figure 7.6). A number of factors other than pollution were implicated for these reductions: lack of effective management, overfishing, economics (low prices and high costs) and natural fluctuations.

Detailed investigations of the fishes in the dumping grounds in the New York Bight are lacking, but extensive investigations have been carried out around ocean outfalls as part of the southern California Coastal Water Research Project (Allen and Voglin, 1976). Areas of depressed fish abundance and diversity were noted around several major outfalls off Palos Verdes and on the Santa Monica shelf. These areas were bounded by areas of higher abundance and biomass than background. Populations of certain species were more concentrated near the outfalls (e.g., calico rockfish, Dover sole and California scorpionfish), while those of others were depressed (e.g., Pacific sanddab, pink seapearch, yellowchin sculpin). In San Pedro Bay, movement of one ocean outfall to deeper water resulted in a decrease in fish abundance at the abandoned outfall and an increase around the new outfall. Apparently, waste discharges

Figure 7.6 Historic landings of major species of fish and shellfish in the New York Bight area (McHugh, 1977).



which are not highly toxic or do not impose severe oxygen stress are attractive to fish, either because of increased food resources or protective cover provided by pipe structures or sedimented deposits.

Pathological effects have been found in marine fishes associated with waste discharges off Southern California, in the New York Bight apex and in the Duwamish River estuary in Seattle, Washington (Sinderman, 1976; Murchelano and Ziskowski, 1976; Mearns and Sherwood, 1976; Sherwood, 1977). The most common pathological effects are lesions which cause erosion of fins, primarily in flatfishes, but other disorders are also known (Sinderman, 1976), notably histopathologic anomalies in the liver (Pierce et al., 1977). Based on correlative incidence in field studies and on experimental laboratory and field exposure, fin rot has been linked both with high concentrations of toxicants in sediments and with indicators of human fecal pathogens. Although pathogenic microorganisms are associated with the lesions, the specific etiology of the disease (even whether it is chemically or pathogenically induced) is not known. Ongoing work by Southern California Coastal Water Research Project staff suggests that toxicants (perhaps organic) may be the primary cause (A. Mearns, personal communication).

SUMMARY AND CONCLUSIONS

This review has emphasized the great complexity of biological responses to constituents potentially introduced with municipal wastes into the marine environment. Because of the complicated and usually poorly understood nature of biological effects, summarization is difficult and definitive conclusions are virtually impossible. Our conclusions are addressed to the key technical issues identified in Chapter 1: 1. the fate and effects of toxicants and the effectiveness of source control of toxic substances; 2. the role of particulate materials; 3. the predictability of effects and the reliability of models on which they are based; 4. the bases for regional differentiation of discharge policies; 5. the reversibility of effects and 6. the effects of sludge versus effluent discharges.

Fate, Effects and Effectiveness of Control of Toxicants

Biological processes are quantitatively important in affecting the fate of some toxic substances released in municipal wastes. Food chain transfer may be an important source of contamination of higher trophic levels, particularly with regard to persistent organic compounds such as chlorinated hydrocarbons and polynuclear aromatic hydrocarbons. Benthic organisms, both macroscopic animals and microorganisms, may affect the mobilization of sedimented toxicants and thus regulate their bioavailability. Although trace metals may accumulate to very high concentrations in bottom sediments in the vicinity of sewage discharges or sludge dump sites, these metals are probably largely not bioavailable, although some bioaccumulation may occur in particle-feeding invertebrates. Persistent organic toxicants accumulated in bottom sediments may be of greater concern and deserve more research emphasis. Source controls for such persistent compounds should be more practical than controls for inorganic and biodegradable toxicants of diffuse sources. However, the association of many toxicants with particulate material and their accumulation in sediments of depositional environments, may make source controls ineffective in the short term since sediment-accomodated toxicants may be remobilized due to physical or biogenic processes.

Much information is available on the effects of various toxicants on marine organisms based on laboratory studies. While there are serious limitations to such approaches, effluent control requirements can be based on the best available biological criteria from sublethal tests, with a safety factor (e.g., 0.2 of the effective concentration) applied to compensate for insensitivity of laboratory tests to determine maximum acceptable toxicant concentrations. These results can be used in conjunction with physical-chemical models of the fate of the subject toxicant to assess probable impact and required dilution. However, the effects on benthos must also be taken into account if toxicants accumulate in bottom sediments. The effectiveness of source controls for major discharges should be monitored through field studies to insure the desired effect is achieved, given enough time for elimination, by whatever mechanism of toxicants residing in local sinks. Refinement of control requirements should be made as appropriate.

Role of Particulate Materials

Many toxic, biostimulatory or oxygen demanding constituents of municipal wastes are particulate or have a tendency to associate with particles in the marine environment. The deposition of such particulate material produces the most frequently observed and best documented biological effects of waste discharges--alteration of benthic communities in the vicinity of the discharges. The fate, bioavailability and mode of biological effects of such particle-associated substances are very poorly known compared to that of dissolved constituents.

Assessment of the biological effects of particular discharges needs to be based on a sounder understanding of the fate of contaminated particles. Depositional environments which may serve as sinks for toxic constitutents deserve particular attention. Further research is needed on the biogeochemical effects of deposited contaminants, including the effects of interstitial conditions on their bioavailability (e.g., complex redox reactions affecting metals speciation), biodegradation and biomodification and mobilization and release due to biological processes. Experimental research on the effects of specific toxicants in sediments on benthic organisms is needed to identify toxicants of specific concern.

Predictability of Effects and Reliability of Models

Models which have been developed to describe uptake, depuration and bioconcentration of toxicants seem adequate in some situations, but not in all cases. Most of these models do not consider effects of temperature and other significant environmental factors on the rates described. Variance in sublethal effects is not well documented, largely because different experimental procedures have been used by various researchers, and time and expense do not usually allow repetition of sublethal bioassays. Results of acute bioassays in tests repeated over seasonal cycles or with different populations may vary by over an order of magnitude. It seems likely that concentrations producing sublethal effects may also vary by such a factor.

In terms of community or ecosystem response to wastewater constituents, models of nutrient biostimultory effects on phytoplankton are best developed. Although complex interactive models incorporating nutrient form, temperature, light and grazing pressures have been developed to explain and predict responses to coastal upwelling, such detailed models have not been applied to waste nutrient additions. Simplified phytoplankton response models have proven realistic for eutrophic, estuarine systems such as the Potomac River and the upper San Francisco Bay area. Comparable models for open coastal ecosystems have not yet been developed. Other models describing community responses to waste additions are mainly empiricial and conceptual rather than quantitative, e.g., that for the responses of the benthos to organic enrichment.

The predictability of long-term biological effects axiomatically is less certain than that of shorter term responses. This is due to characteristic long-term biological variability, which is very poorly understood for virtually all marine ecosystems and uncertainties about the processes affecting accumulation and remobilization of toxicants from sediments.

Regional Differentiation of Policies

There is little basis, considering the biota exclusively, for regional differentiation of discharge policies. Although there are some theoretical reasons to expect that organisms in more variable environments (e.g., estuarine and coastal environments of the US East Coast compared to the West Coast) may be more resistant to a variety of stresses, this relationship is not well enough understood as to constitute a basis of policy. The maximum acceptable toxicant concentrations for the most sensitive species, the best basis for a rational policy to protect the biota, are not likely to vary widely. From a strictly biological standpoint, a rational policy would seem to be to set effluent standards in such a manner that biological effects are negligible.

Regional differences are more important with regard to physical, geological and chemical environmental conditions which interact to affect the fate of pollutants and thus their concentrations and availability to the biota.

Reversibility of Effects

In those cases where discharges of municipal wastes or other organic wastes (e.g., pulp mill discharges) have been reduced or terminated, a general return to presumably pre-existing conditions has been noted. The best documented cases concern the response of benthos to cessation of pulp mill discharges in Sweden and sewage discharges off southern California. Thus, the most commonly observed biological effects mainly attributable to organic over-enrichment are reversible and communities appear to return along a reversed, but similar successional sequence as followed during degradation. The time period for recovery may range from a few months to nearly a decade if organic enrichment of sediments is heavy. Based solely on biological considerations, recovery should proceed more rapidly in more variable environments than those characterized by a high degree of environmental constancy (e.g., estuaries versus the deep sea). In reality, the nature and persistence of pollutants may be more important than biological response in determining ecosystem recovery. Relatively little is known about the long-term fate of persistent organic toxicants in the marine environment and the subtle biological effects they may cause may far outlast the eutrophication effects of waste discharges. Although extinction of species due to municipal waste discharges has never been documented, recovery of damaged habitats which are highly structured biologically, such as coral reefs, oyster reefs and kelp beds, may be so uncertain or interminable that habitat losses may be considered permanent.

Effects of Sludge Versus Effluent Discharges

The environmental trade-offs of sludge versus effluent discharges are problematic and highly dependent on the location and nature of these discharges, i.e., they depend largely on factors affecting dispersal of contaminants. Effluents discharged into deep ocean waters in which dilution and dispersion are rapid may have little biological effect but sludge disposed under the same conditions may cause unacceptable effects if the depositional regime favors accumulation of particulate pollutants. Often effluents and sludge may be discharged in different areas, which requires comparison of biological effects in quite different ecosystems. For example, improvement in effluent quality of discharges in New York Harbor increases the volume of sludge disposed on the continental shelf. Given these possibilities, it is inadvisable to make generic conclusions regarding the preferability from an ecological viewpoint of effluent versus sludge wastes.

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