EVALUATION OF SAFETY FACTORS WITH RESPECT TO OCEAN DISPOSAL OF WASTE MATERIALS

by

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ABSTRACT

In the past, waste materials too toxic or hazardous for disposal on land or in estuaries have customarily been disposed of at sea. Assessment of the risk and consequent environmental harm to the oceans is essential if ocean dumping is to be continued.

The author has surveyed the available literature, bioassay studies, and pertinent research concerning chronic effects and the risk they impose on the marine ecosystem. The main purpose of this study was to investigate and define the correlations between acute and chronic toxicities for known hazardous materials. This relationship is vital for the determination of an appropriate safety factor to be used in evaluating allowable discharges or concentrations in the marine environment.

The variables that the author defines to be of most importance are: stage of development, concentration of toxicant, time of exposure, specific or non-specific reactions, lifetime of the compound, reactions with other chemicals, and bioaccumulation. The author has determined the ranges of ratios for different conditions and situations or at least the ratios of acute to chronic toxicities for various classes of materials. This will permit the proper scientific thought to be given for the safety factors needed to protect our marine environment.

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CHAPTER I

INTRODUCTION

In the past, waste materials too toxic or hazardous for disposal on land or into our rivers and estuaries have customarily been disposed of at sea. With the advent of a permitting system and stringent laws to protect the marine environment from harm, the transport and disposal of wastes into deep ocean waters is being more thoroughly and critically examined. Assessment of the risk and consequent environmental harm to the oceans is essential if ocean dumping is to be continued. The degree of risk is dependent upon numerous variables such as the type and characteristics of waste, the disposal site and, most importantly, the organisms that will be affected by the waste.

It is presently acknowledged that the disposal of waste material into the oceans presents a risk to the marine environment. The risk of harm to the oceans by transport of hazardous materials is a function of three probabilities:

$$\text{Risk} = P_1 * P_2 * P_3$$

where P_1 is the probability of an accident; P_2 is the probability of a spill if there is an accident; and P_3 is the probability of environmental damage if there is a spill. The risk associated with ocean dumping is a function of only one probability:

$$\text{Risk} = 1 * 1 * P_3$$

where P_3 is the probability of environmental harm since by deliberate spillage P_1 and P_2 become unity. By this representation, it is shown that a risk to the marine environment always exists with ocean disposal at the spill site.

The concept of risk as it is conceived by the public carries the meaning that an endeavor or action poses a possibility of a negative return. From an optimist's point of view, the benefits outweigh the costs. In our society monetary values are placed upon systems for relative comparisons. It is very easy to distinguish between two alternatives. When the risk involves human health, it is very difficult to place a monetary value on it. The ultimate cost in this case is death. It is equally as difficult to place a price on the environment. However, our technological society sometimes does this.

Ocean dumping is a risk that we accept everyday. We also accept risks by discharging wastes to rivers, bays, and estuaries as well as by direct dumping in the ocean. This is a prime example of a technological tradeoff involving environmental pollution. The processes that produce the wastes yield a greater return than does the measurable economic damage done by ocean disposal. Our society may depend heavily on these technological processes and the products that they produce. Therefore, man is willing to accept the risk presented by ocean disposal. Chauncey Starr (1971) examined risk and benefit cost studies in great detail. He stated that the public acceptance of a risk can be influenced greatly by authorities and dogma. Many people are willing to accept what other people of higher stature, so called "experts", tell them since they are knowledgeable in that field. One must keep in mind that sometimes authorities, whether they are private or governmental, tell only what they want others to know. The general public is usually willing to accept this.

Mr. Starr also pointed out the fact that historical trends are indicators of social acceptability. For example, national accident records contain consistent patterns that enable one to predict or determine the social benefits arising from these activities. Historical data on ocean disposal are not sufficient to make the same analysis. There have been very few, if any, instances where fatalities have resulted directly from effects of ocean disposal. Chronic effects such as food poisoning from contaminated marine life, however, are documented. But this low frequency of fatalities significantly reduces the significance of ocean disposal. Since there exists such a low frequency of health accidents associated with ocean disposal, people do not take an interest in it other than a dogmatic preservationist attitude. Other activities that also have a low-frequency, but a catastrophic effect, pose a greater risk. Hurricanes, tornadoes, and earthquakes present this type of risk. Tornadoes occur only under specific meteorological conditions and usually during certain times of the year. Their frequency is low, but the damage they cause is very great, not only physical damage, but of human life also.

The ultimate or extreme risk posed by ocean disposal is death or irreversible contamination of the marine environment. What may be happening with ocean dumping is that these infrequent accidents are just indications of things to come. There is normally a series of steps or events that lead to a major event. Man may just now be seeing the steps to a larger and more dramatic effect.

Objective

The author has surveyed the available literature, bioassay studies, and pertinent research concerning chronic effects and the risk they impose on the marine ecosystem. The main purpose was to investigate and define the correlations between acute and chronic toxicities for known hazardous materials. This relationship is vital for the determination of an appropriate safety factor to be used in evaluating allowable discharges on concentrations in the marine environment. An attempt was also made to identify and correlate, as best as possible, the various factors that influence the toxicity of a compound. With these goals in mind, it is hoped that a better understanding of the risks involved with ocean disposal can be reached.

Procedure

Chapter I discusses the limiting permissible concentration of a waste material in the environment. A brief definition of acute and chronic toxicity is given, along with a list of terms most commonly used in expressing toxicities.

Chapter II presents a short summary of ocean disposal over the past few decades. The probable origins of ocean disposal, the types of waste dumped, and the present status of this practice are reported in this chapter.

A description of the ocean environment is discussed in Chapter III. The geomorphology is examined first and then followed by the significant environmental factors that make the marine environment unique. Concluding this chapter is information on the various types of marine life present in the oceans which would be impacted by ocean dumping.

Chapter IV comprises examples of chronic toxicities. Covered are the most common effects of chronic concentrations in the marine environment. The following chapter, Chapter V, identifies the many variables and factors affecting the ultimate toxicity of compounds.

Chapter VI discusses the acute/chronic toxicity ratios and stress-strain relationships developed by the author. The steps that should be taken to arrive at a safety factor are also presented.

Limiting Permissible Concentration

Discharges from ocean dumping barges are controlled by law, whereas barges transporting materials are not controlled with reference to discharge concentrations. The Environmental Protection Agency has set a limiting permissible concentration for ocean discharges in their final regulations and criteria for ocean dumping (Federal Register, 1973). They state that the limiting permissible concentration is one that will not exceed 0.01 of a concentration shown to be toxic to appropriate sensitive organisms or 0.01 of a concentration of a waste material or chemical shown to be detrimental to the marine environment. One point of the controversy surrounding this value is that no time period is specified concerning when this 0.01 value is to be achieved.

This 100/1 ratio consists of both the acute/chronic ratio plus the addition of a safety factor. Figure 1.1 illustrates this clearly.

Acute Toxicity

The risk to the marine environment is normally perceived in terms of lethal and sublethal effects on organisms that inhabit the marine environment. The acute or lethal toxicity of a compound is defined as that concentration which results in death to a significant number of a given species within a specified exposure period. Acute levels are usually reported as that concentration which results in death to a significant number of a given species within a specified exposure period. Acute levels are usually reported at those levels that result in greater than 50 percent mortality to a selected species. The most common terms employed in expressing acute toxicities are presented in Table 1.1

Chronic Toxicity

Sublethal or chronic effects produce changes or disruptions in an organism's body functions, which initially are not severe enough to result in death, but may after an extended period of time. A certain percentage of mortality may occur in a short period of time, but this might not be statistically significant. The author has classified chronic toxicities into three subheadings: behavioral, physiological, and bioaccumulation and biomagnification.

The cause of a behavioral change can normally be attributed to an effect on a body process. However, the response shows up in the

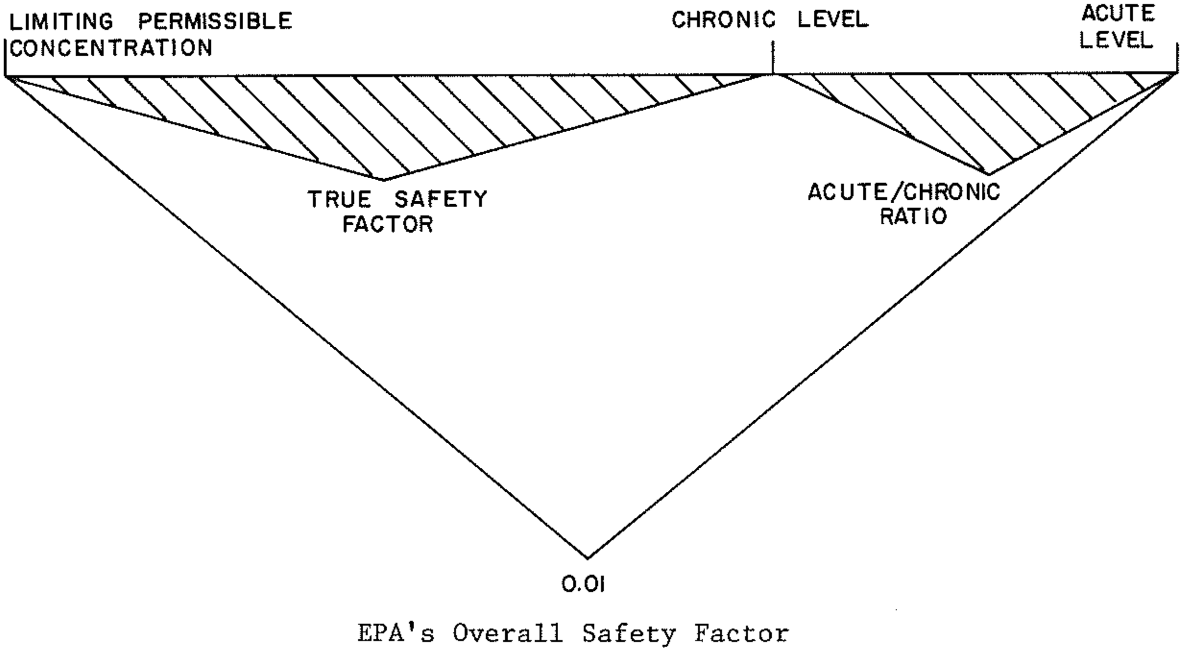

FIGURE I.I. ALLOWABLE DISCHARGE CONCENTRATION FOR OCEAN DISPOSAL.

TABLE 1.1. Acute Toxicity Terms

Term	Meaning
LD_{50}	lethal dose fifty. weight of toxicant per body weight of organism that produces 50% mortality (mg/kg). statistically determined.
LC_{50}	lethal concentration fifty. concentration of toxicant in water which results in 50% mortality (ppm).
EC_{50}	median effective concentration. concentration which produces a designated effect to 50% of test organism (ppm).
ED_{50}	therapeutically effective dose. produces a designated effect in 50% of organisms and effect is reversible (ppm).
TLm-24,48,96	median lethal concentration. concentration that produces 50% mortality to exposed organisms in 24,48,96 hours respectively (ppm).

behavior of the organism. Hansen, et al. (1971) examined the chronic effects of polychlorinated biphenyls on grass shrimp, and the results showed that the shrimp avoided water contaminated with 10 ppm of the chemical. Petrocelli, et al. (1973) presented another example of a behavioral effect; sublethal concentrations of dieldrin in water caused reduced siphoning in clams.

Physiological changes include any changes in the organism's metabolic processes. Since most processes are controlled by enzymes and enzymatic systems, an effect on processes can be related back to the inhibition of an enzyme. Janicki and Kinter (1971) presented evidence that DDT at 1-10 ppm inhibits the sodium transport enzyme in some marine teleosts. This enzyme commonly referred to as Na^+, K^+, Mg^{+2} - ATPase, maintains an osmotic balance between the organism and its surroundings. Inhibition of growth, reproduction, and productivity are also classified under physiological effects.

Many compounds are readily absorbed or taken up by organisms and accumulated in their body tissues or organs. This is referred to as bioaccumulation. If these absorbed compounds are passed on from one level of the food chain to the next, this is known as biomagnification. Oysters and other shellfish are known to accumulate compounds in their fat tissues. Keil, et al. (1971) presented data showing that a marine diatom can concentrate Aroclor 1242 in its cells to a concentration greater than 1,000 times the ambient concentration.

CHAPTER II

STATUS OF CURRENT OCEAN DISPOSAL OPERATIONS

History of Ocean Dumping

An increase in population followed by economic and industrial growth brought about the utilization of our oceans for waste disposal. In 1800, the population of the United States was 5,305,937 and only four cities could boast of a population in excess of 10,000 inhabitants. At this time, removal of wastes by large sewers to rivers and the use of cesspools were common and acceptable methods of waste disposal. As the population increased with the growth in industry, these methods became obsolete. The utilization of rivers and inland waterways as receiving bodies for wastes grew rapidly. In addition, many industries discharged directly into municipal sewer lines. This practice introduced toxic chemicals into the treatment plants, thus, more often than not, compounding the problem.

When the first attempts were made to improve municipal disposal practices, the manurial value of the wastes was examined. The fertilizer value was investigated and large profits were envisioned. However, while debate ensued regarding the aesthetic and public health ramifications of this practice, U.S. coastal cities considered the fact that the public economy and interests could best be served by direct discharge into the water bodies of sufficient size which would prevent waste oxidation from becoming offensive (Waring, 1903). Those arguing for land disposal brought out the point that the nutrients present in the sludges would be lost to the sea and would not be returned to land (Rafter and Baker, 1893). This objection was later dismissed as scientific investigations revealed the presence of a rudimentary marine food web.

Some major cities took advantage of the fertilizer potential of sludge and put it to use. Sludge contains a spectrum of micro-nutrients that are not normally found in chemical fertilizers. Chicago, Schenectady, Houston, and Milwaukee were just a few of the cities that processed and sold dry digested sludge as a soil conditioner. In Melbourne, Australia, raw sewage was used for over 50 years to irrigate pasture lands. Miami, Florida, in 1956 started using sewage sludge to fertilize the 30 acres of land surrounding the plant site (Adler, 1971).

For many inland cities the practice of land disposal was the only disposal method available. Economically, ocean disposal was not reasonable. Coastal cities had both options available for their use initially. However, the large influx of people and growth into these coastal cities put a higher price and demand on the land. Industrial growth occurred more rapidly on the coastal areas than in the inland cities. Their wastes contained constituents that could be potentially harmful in a health-related sense. Therefore, alternatives to land disposal had to be considered. In 1902 the Encyclopedia Brittanica announced ocean disposal as a "cleanly method" because man's activities were not unduly affected by this disposal method and because the waste constituents were assumed to return to man in the form of fish, shellfish, and seaweed.

Adopting this philosophy, many cities and industries started barging their wastes out into the oceans. By the 1940's this practice was very widespread and rarely questioned. Pollution of inland waters, estuaries, and coastal areas became a more pressing problem. This was more of a reality and posed a greater impact on the health of the people. Ocean pollution was intangible to the public and presented no immediate effect. The public instead focused its attention on industries discharging wastes into rivers and estuaries. During the 1950's, industry, after numerous fish kills had already taken place, realized that their wastes contained too many toxic constituents to be discharged into inland waters. With this realization, they began to barge certain wastes to deep ocean sites for disposal.

Corps of Engineers' Letters of No Objection

Not until April 23, 1973, when permits were available from the regional EPA offices were permits required for ocean dumping. Prior to this date, the U.S. Army Corps of Engineers had jurisdiction over ocean disposal. Under the Refuse Act of 1899, the Corps governed the disposal of waste materials in navigable waters.

Industry would first contact the appropriate regional Corps Headquarters to obtain permission to discharge their wastes. The Corps required that data concerning the characteristics and quantity of the waste be submitted to them. Expert opinions had to be included testifying to the appropriateness of the practice. The Corps then submitted the proposals to various state and federal agencies for review. If the reviews were favorable the Corps of Engineers would grant letters of no objection. This would allow the person to dispose of waste material in the oceans. Disposal sites were designated by the Corps when these letters were issued. During this period, the disposal activities were not strictly monitored.

Types of Material Dumped

Categorically the materials dumped or being disposed of in the marine environment can be broken down into five types: municipal wastes, such as sewage sludge; industrial wastes; dredge spoils; military wastes and explosives; radioactive wastes; solid wastes; and construction debris. The first three wastes constitute the bulk of the materials presently being dumped in waters off the United States. Cox (1975) reported a comparison of the amounts of waste disposed in 1968 to 1973 in the United States. Her results are shown in Table 2.1. Cox also reported that in 1973, 44,208,000 tons of dredged material were dumped into the oceans.

Dredge spoils. Dredge spoils constitute the largest category of ocean-dumped waste. The spoil consists of any material that has been dredged from rivers or navigation channels. Dredge materials contain sand, silt, clay, detritus, rocks and municipal or industrial waste sludges (U.S. Department of Commerce, 1974). These materials are normally disposed of in waters less than 100 feet deep. Over a period of time the dredged material in an area builds up and spoil islands are formed. This is the case along the Texas coast where dredging of the Intracoastal Canal has produced small spoil islands in the bays. Spoils have also been utilized to purposely build up or extend land.

TABLE 2.1. Ocean Disposal in 1968 Versus 1973
(in tons)

Waste Type	Atlantic		Gulf		Pacific		TOTAL	
	1968[a]	1973[b]	1968	1973	1968	1973	1968	1973
Industrial waste	3,013,200	3,997,100	696,000	1,408,000	981,300	0	4,690,500	5,405,100
Sewage sludge	4,477,000	5,429,400	0	0	0	0	4,477,000	5,429,400
Construction and Demolition debris	574,000	1,161,000	0	0	0	0	574,000	1,161,000
Solid waste	0	0	0	0	26,000	240	26,000	240
Explosives	15,200	0	0	0	0	0	15,200	0
TOTAL	8,079,400	10,587,500	696,000	1,408,000	1,007,300	240	9,782,700	11,955,740

[a] Source: CEQ, Ocean Dumping--A National Policy, October 1970

[b] Source: EPA Regional Offices, Unpublished Reports, 1973 (8 months of dumping activity--May to December 1973--under permits issued by Ocean Disposal Program extrapolated for 12 months to provide an annual rate).

The Corps of Engineers has estimated that one-third of all dredge materials are polluted, which caused them to research and evaluate the present spoil disposal practice. The trend the past few years has been an increase in dredging so the problem of pollution from spoils is not diminishing any, but growing.

Industrial wastes. Industrial wastes include a very wide range of compounds. Generally, they consist of any waste material, liquid or semi-liquid, that is produced from an industrial process. The wastes often contain organic, inorganic, and synthetic chemicals as well as small amounts of metals. Normally industrial wastes are broken down into various categories: waste acids, refinery wastes, pesticides, paper mill wastes, oil drilling wastes, pharmaceutical wastes, and others. Many of the wastes are toxic which is why they are disposed of at sea. The liquid wastes are normally barged out to sea and dispersed through a jet nozzle into the sea. Another method is to pack the wastes in 55-gallon drums and drop them overboard. As a result of new technology, recycling and reuse, the quantity or volume of industrial wastes is decreasing. However, as technology has found ways to remove and reuse selected waste constituents, it has resulted in producing a more concentrated and a more toxic waste.

Municipal wastes. Domestic sewage sludge is the second largest category of waste dumped into the oceans. It is only exceeded by dredge spoils. Sewage sludge is a by-product of wastewater treatment plants. Two types of sludges are produced depending upon the type of facility. Primary treatment plants produce undigested sewage sludge which contains only 2.0 to 7.0 percent solid matter. Secondary treatment plants produce a totally different type of sludge. A comparison of the two is made by Metcalf and Eddy (1972) in Table 2.2. The majority of the domestic sewage sludge being dumped is of the digested type. It is transported to dump sites either by barge or through long pipelines referred to as marine outfalls.

Besides the constituents of sludge shown in Table 2.2, there are also present minute traces of other materials. Heavy metals, pesticides and toxic chemicals have been found in some sludges.

Radioactive wastes. Disposal of radioactive wastes has ceased since 1962 (Council on Environmental Quality, 1970). Most of the wastes are now buried on land. Before this the radioactive wastes were packaged in containers and dumped in waters remote from all land and in very deep waters. This practice was followed by the United States and foreign countries. The United States disposed of radioactive wastes in waters normally deeper than 6,000 feet. The distance from land varied anywhere from 12 to 150 miles offshore. For added protection the wastes or drums were encased in concrete.

Solid wastes. The dumping of solid wastes in the oceans has been reduced very significantly the past few years. Solid waste consisted primarily of paper, metals, plastics, foodstuffs, and all other types of trash. Disposal was accomplished by baling it and sinking the bale in the sea. With the passing of the Resources Recovery Act in 1970 the focus of attention was shifted from simple disposal techniques to the development of technology to recover and utilize the waste

TABLE 2.2. Typical Chemical Composition of Raw and Digested Sludge (Metcalf and Eddy, 1972).

	Raw Primary Sludge		Digested Sludge	
Item	Range	Typical	Range	Typical
Total dry solids (TS), %	2.0-7.0	4.0	6.0-12.0	10.0
Volatile solids (T of TS)	60-80	65	30-60	40.0
Grease and fats (ether soluble, % of TS)	6.0-30.0	...	5.0-20.0	
Protein (% of TS)	20-30	25	15-20	18
Nitrogen (N, % of TS)	1.5-4.0	2.5	1.6-6.0	3.0
Phosphorus (P_2O_5, % of TS)	0.8-2.8	1.6	1.5-4.0	2.5
Potash (K_2O, % of TS)	0-1.0	0.4	0.0-3.0	1.0
Cellulose (% of TS)	8.0-15.0	10.0	8.0-15.0	10.0
Iron (not as sulfide)	2.0-4.0	2.5	3.0-8.0	4.0
Silica (SiO_2, % of TS)	15.0-20.0	...	10.0-20.0	
pH	5.0-8.0	6.0	6.5-7.5	7.0
Alkalinity (mg/liter as $CaCO_3$)	500-1,500	600	2,500-3,500	3,000
Organic acids (mg/liter as HAc)	200-2,000	500	100-600	200
Thermal content (Btu/lb)	6,800-10,000	7,600*	2,700-6,800	4,000†

* Based on 65 percent volatile matter.

† Based on 40 percent volatile matter.

constituents (Pavoni, et al., 1975). The majority of the solid waste is still dealt with by incineration, sanitary landfill, and composting.

Military wastes. Included in this class of materials are surplus or obsolete explosives and ammunition such as shells, mines, solid rocket fuels, propellants, and chemical and biological warfare agents. Materials of this nature were loaded onto old World War II Liberty ships which were then scuttled in waters greater than 4,000 feet deep. This practice was halted in 1970 pending an investigation into the environmental effects of war materials on the marine system (U.S. Department of Commerce, 1974).

Construction debris. This type of waste consists of masonry, tile, stone, plastic, wiring, piping, wood and excavation dirt. Only New York City has been carrying out this type of dumping because they have limited available landfill areas. The U.S. Department of Congress reported that in 1968, 574,000 tons of debris were disposed of in New York Bight. The amount varies from one year to the next depending on the construction activity at that time.

Environmental Protection Agency Permits

The act that has really revolutionized the practice of Ocean dumping is the Marine Protection, Research, and Sanctuaries Act of 1972 (P.L. 92-532). It was passed on October 23, 1972. Under this law, no person may transport, by barge or other types of vessel, any material destined for ocean disposal without a permit from the regional EPA office. This stipulation was put into effect on April 23, 1973.

The EPA can issue five types of permits: general, emergency, interim, special, and research. A general permit allows the dumping of galley wastes, burials at sea, sinking of target ships, and non-toxic materials produced in small quantities. An emergency permit is issued for the disposal of prohibited wastes, if it is shown or proven that these wastes pose an unacceptable risk to human health and there is no feasible solution but to dump the wastes in the oceans. An interim permit is issued to an applicant if the materials desired to be dumped are in excess of the limiting permissible concentrations or when the constituents, that have been identified as trace elements, are in excess of the levels at which they may be dumped under a special permit. Special permits are issued only when the constituents in the waste are properly identified and meet certain criteria. A research permit is issued for the disposal of wastes so that the effects of these wastes on the environment can be studied.

Each permit contains a set of general and specific conditions. They define the dump sites, discharge rates, allowable dumping load, and expiration date. Also written into the permits are implementation schedules for phasing out ocean dumping.

CHAPTER III

PHYSICAL, CHEMICAL, AND BIOLOGICAL MAKEUP OF THE OCEANS

Geomorphology

Seventy-one percent of the surface of the earth is covered by the ocean. This represents an approximate total volume of 328,750,000 cubic miles or 36 X 10^{19} gallons. The average depth of the oceans is 2.35 miles. Eighty-five percent of the oceans area lies between 500 and 3,500 fathoms while only 0.1 percent lies below 3,500 fathoms (Chow, 1964). The oceans are continuous with each other and are also connected to adjacent seas by straits. Adjacent seas such as the Mediterranean, North Sea and the Caribbean are separated from the Atlantic Ocean by either islands, submarine ridges, or both. The Gulf of Mexico for example, is separated from the Atlantic as illustrated in Figure 3.1. Atlantic waters enter into the Gulf through the Yucatan Peninsula and the island of Cuba.

The Mediterranean Sea is an indentation of the Eastern Atlantic. In contrast to the Gulf of Mexico, the Mediterranean has only one opening to the Atlantic Ocean, this being the Straits of Gibralter. The circulation pattern of the Mediterranean is shown in Figure 3.2. The highly saline Mediterranean water, due to its high specific gravity, settles to the bottom and flows out of the Straits of Gibralter underneath the incoming Atlantic water. The high salinity of the Mediterranean water is a result of the very high evaporation rate that occurs in that area. It has been estimated that the complete flushing time of

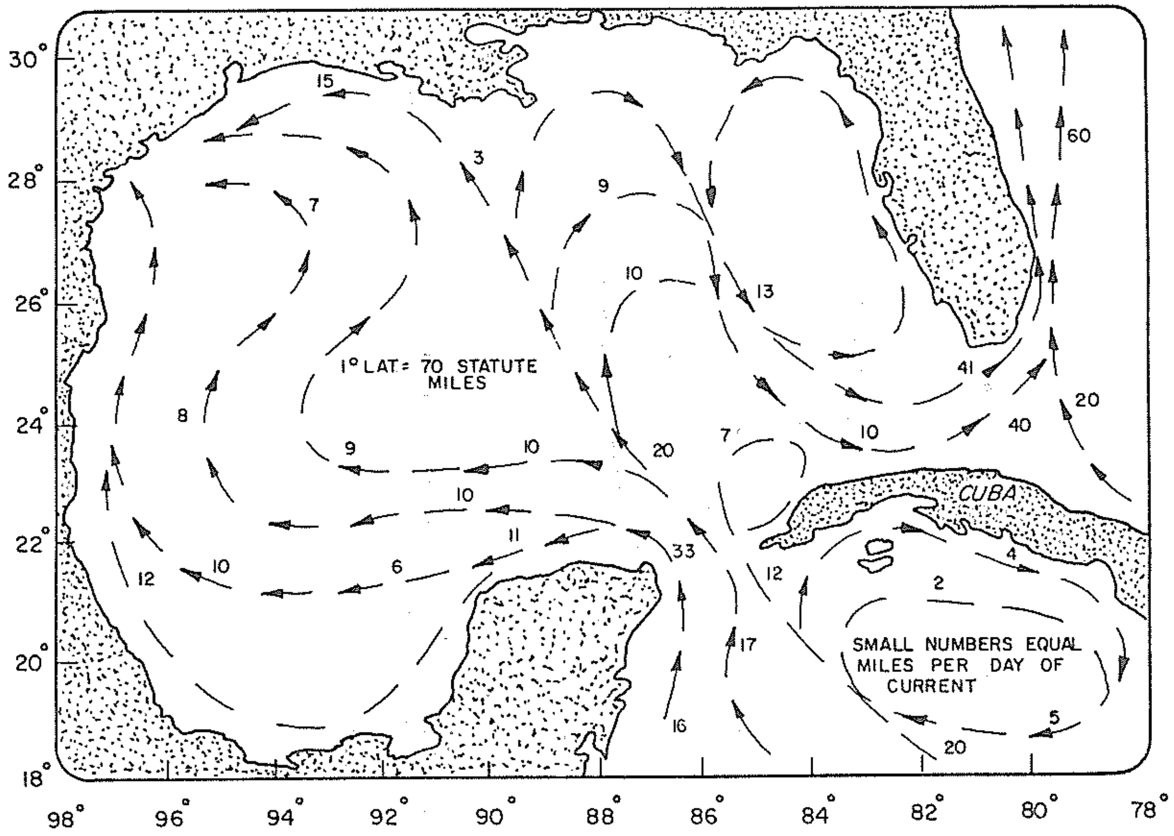

FIGURE 3.1. SURFACE OCEAN CURRENTS IN JUNE,
GULF OF MEXICO
(LEIPPER, 1954)

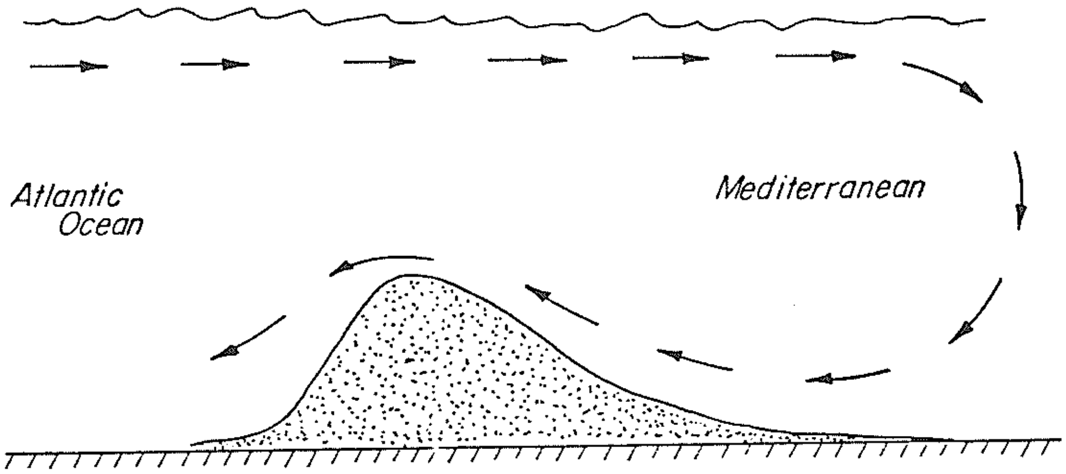

FIGURE 3.2 CIRCULATION PATTERN IN THE MEDITERRANEAN SEA

(FRIEDRICH, 1969)

the Mediterranean, the length of time required for all of its water to be replaced by the Atlantic's water, is around 80 years (Miller, 1970).

The shapes that characterize the oceans' bottom are varied and are a major factor of importance concerning the ecology of the marine, benthic environment. One can make two divisions between the types of formations commonly encountered. The major forms are represented by those characteristic on the Eastern Coast of the United States. These include the continental shelf, the continental slope, the deep sea basins, ridges and sills, and the deep sea troughs (Figure 3.3). The shelf is present along the continents and it slopes seaward at a gradual rate to varying depths. In general, at a depth of 200 meters, the gradient of the slope increases and the shelf at this point is referred to as the continental slope. The distance from this transition to the shoreline is non-uniform from one region to another.

The most productive regions of the oceans are in that area above the continental shelf. Therefore, the formation of the shelf warrants more description. Emery (1969) has shown that many of the shelves are formed by deposits behind underwater dams. He identifies three types of dams; tectonic dams, reef dams, and diapir dams. Tectonic dams are formed by geological uplifting or upwelling of lava. Such a structure exists off of the Western Coast of the United States. Reef dams, as the name implies, are formed biologically by marine organisms. The shelf around the coast of Florida is an example of this. Diapir dams are formed by the pushing upward of salt domes. The continental shelf bordering the Northern Gulf of Mexico from Alabama to southern Mexico

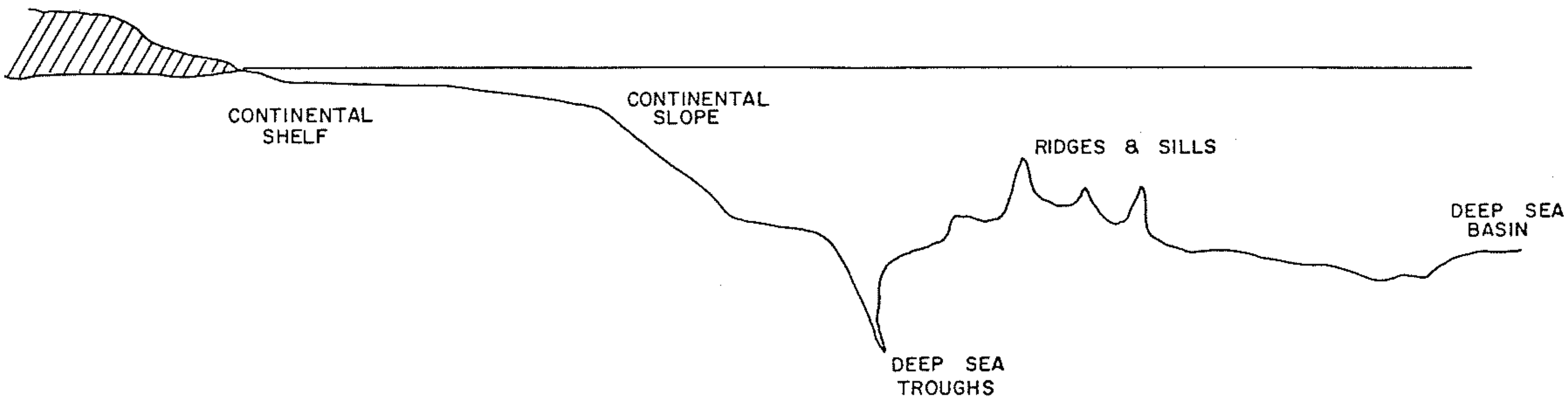

FIGURE 3.3. TYPICAL BOTTOM TOPOGRAPHY OF THE OCEANS.

is of this type. Finally, there are shelves termed damless shelves. These are characteristic off of the eastern coast of the United States. Examples of each dam are shown in Figure 3.4.

The minor types of sea bottoms encountered are the isolated rises with steep slopes, such as sea-mounts, banks and shoals, and submarine canyons. Submarine canyons cut into the continental slope as furrows leading down into deeper water (Friedrich, 1969).

Associated with the diverse bottom topography and makeup are unique marine communities. Due to the differences in sediment constituents, there will be different environments for organisms to inhabit. Therefore, analysis of the oceans benthic community relies greatly upon the bottom topography. Friedrich describes three different types of bottom sediments; soft bottoms, sandy bottoms, and hard bottoms. Soft bottoms are primarily terrigenous in origin and consist of mud and decomposed organic matter. The organic matter is derived predominately from the remains of planktonic organisms. Sandy bottoms are located close to the coastline where water movements prevent the deposition of very fine particles but allow for the settling of granular material. Hard or rocky bottoms are associated with the slopes of undersea ridges, sea-mounts, and sills. Rocky bottoms are also found near coastlines where the currents are too strong to allow for granular settling.

Environmental Factors

Light. Light has to be considered, from a biological standpoint, as one of the most vital of the physical parameters. Primary productivity, the production of organic matter for food, relies heavily upon

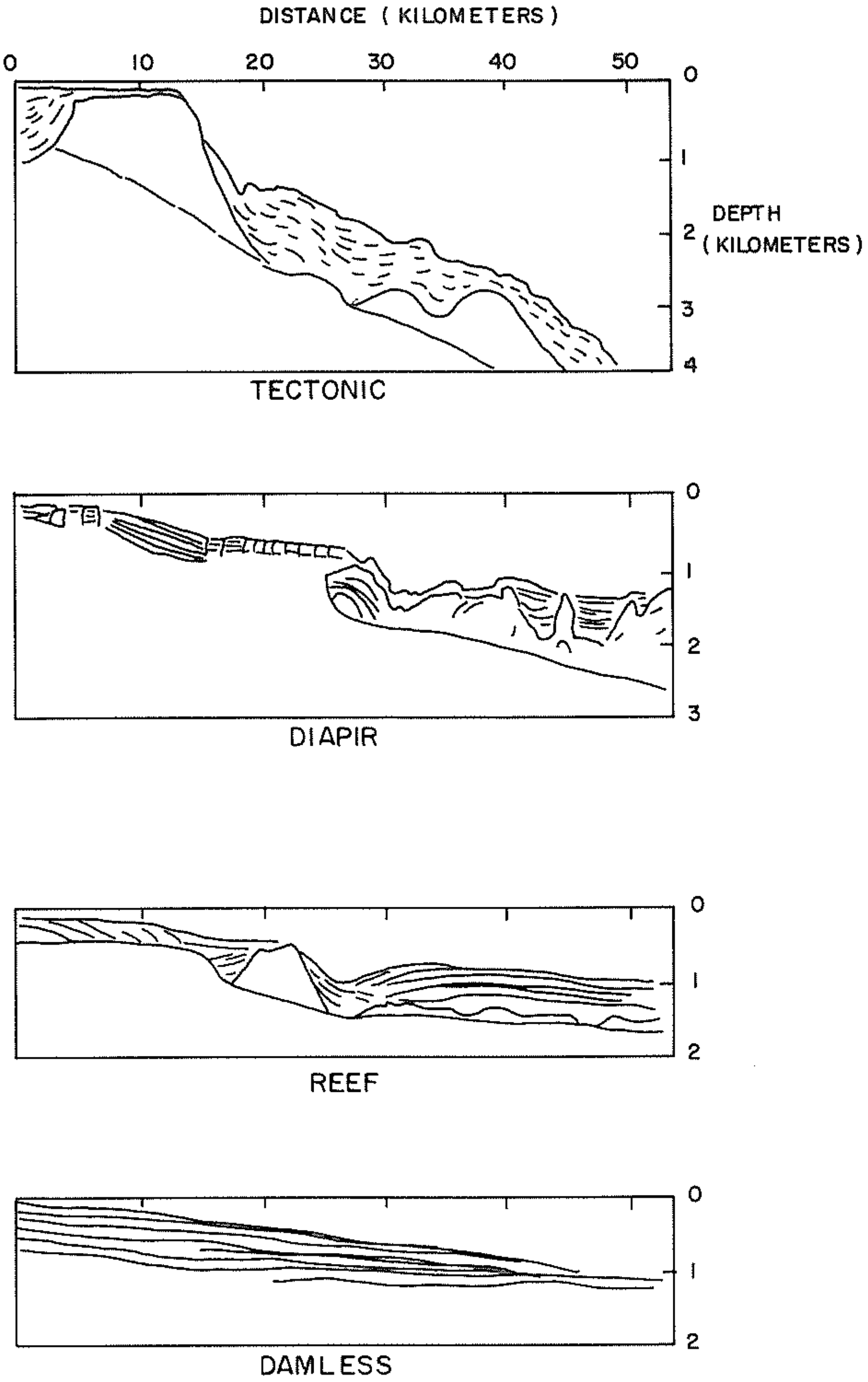

FIGURE 3.4. TYPES OF UNDERWATER DAMS THAT FORM THE CONTINENTAL SHELVES.
(EMERY , 1969)

the quantity of radiant light energy hitting the surface of the oceans. Light energy is utilized by the phytoplankton in the upper waters to produce food for marine organisms. The degree of primary productivity occurring is proportional to the amount of light available. It subsequently follows that the majority of productivity takes place in the upper zones of the water column where light is readily available.

Vertically, the ocean can be divided into an euphotic zone and an aphotic zone (Figure 3.5). The depth of the euphotic zone varies from region to region. Along the coastal areas, light penetration may only reach 30 meters. This is correlated with the turbidity of the area. Wave action, tides, and sediment inflow from rivers result in high turbidity levels. In the open oceans, the waters are normally clear and light penetration can exceed 100 meters. Any factors, whether they be physical or chemical that prevent light penetration can be detrimental to the productivity in that area.

Temperature. Temperature is defined as the condition caused by heat or as the thermal state of a material. Kinne (1970) states that in oceans and coastal waters solar radiation is absorbed and converted into heat at the water surface. This heat is transferred through the water column by both convection and conduction. The average temperature of the waters in all of the oceans is about 3.8°C. At the equator, the average temperature in the total water column is still surprisingly low, 4.9°C. The total heat budget is presented in Table 3.1.

In many regions, the temperature follows an orderly decrease with respect to depth. Factors that disturb this are currents and the bottom morphology. It has been shown that the Gibralter Sill prevents colder

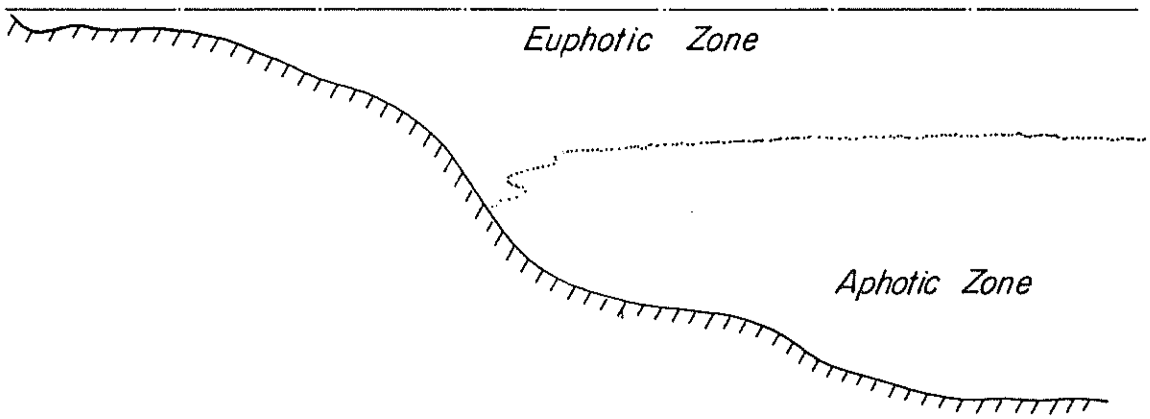

FIGURE 3.5. EUPHOTIC AND APHOTIC ZONES IN THE OCEANS

TABLE 3.1. Heat Budget of the Oceans
(Sverdrup, et al.,1963)

Processes heating the ocean water:	Processes cooling the ocean water:
(1) Absorption of radiation from sun and sky	(1) Back radiation from the sea surface
(2) Conduction of heat through the ocean bottom from the earth interior	(2) Convection of sensible heat to the atmosphere
(3) Transformation of kinetic energy into heat	(3) Evaporation
(4) Heating due to chemical processes	
(5) Convection of sensible heat from the atmosphere	
(6) Condensation of water vapor	

Atlantic waters from infiltrating the deeper Mediterranean Sea thereby allowing the deeper Mediterranean waters to be uncharacteristically warm. Surface and subsurface temperatures normally change seasonally and to a lesser extent diurnally. As one can expect, the bottom and deeper regions are less susceptible to changes in temperature.

Temperature is also a very important ecological factor because many marine organisms rely upon it for their life processes. All organisms possess a temperature range which they are restricted to. Outside of their range most organisms undergo some form of stress. Kinne points out that temperature affects marine organisms principally in three ways; it determines the rate and mode of chemical reactions and hence biological processes; it affects the state of the water, the basic life-supporting medium; and it modifies basic properties of living matter.

Salinity and chemical constituents. Salinity, which is a measure of the total amount of dissolved salts, varies in the world's oceans from 32 parts per thousand (ppt) to 38 ppt. One kilogram in weight of seawater contains 19 grams of chlorine as chloride ion, 11 grams of sodium ion, 1.3 grams of magnesium, and 0.9 grams of sulfur as some form of sulfate ion. Seawater can be looked upon as being a 0.5 M NaCl solution, 0.05 M in $MgSo_4$, with traces of all other compounds (Horne, 1969). Table 3.2 illustrates the major constituents of seawater with a salinity of 35 ppt. These constituents make up 99 percent of the seas' salinity. Trace elements account for 0.02-0.03 percent of the remaining one percent (Friedrich, 1969). These trace elements are very important for the biochemical processes which take place in the sea. Some of the most common

TABLE 3.2. Major Constituents of Sea Water.
(Martin, 1970)

Constituent	Concentration[a]		
	g/kg sea	C moles/liter	logC
Water		54.90	1.74
Chloride	19.353	0.5483	-0.26
Sodium	10.76	0.47015	-0.33
Sulfate	2.712	0.02824	-1.55
Magnesium	1.294	0.05357	-1.27
Calcium	0.413	0.01024	-1.99
Potassium	0.387	0.00996	-2.00
Bicarbonate	0.142	0.00234	-2.63
Bromide	0.067	0.00083	-3.08
Strontium	0.0080	0.0015	-3.82
Boron	0.0045	0.00043	-3.37
Fluoride	0.001	0.00007	-4.15

or required trace elements are: nickel, zinc, molybdenum, vanadium, chromium, iron, iodine, aluminum, and lithium. In essence the list would include all of the known elements.

A value of 35 ppt is used to express the mean salinity of all the oceans. This value holds true mainly for the open oceans. Adjacent seas vary more, either higher or lower, depending upon the evaporation, rainfall, and river inflow. In the tropic zones where the evaporation rates are high, the surface salinities are noticeably higher than normal. Vertically, the ocean's salinity does not change very significantly.

Turbidity. Turbidity is a measure of the light penetration through a medium such as seawater and it is a function of the particle size, shape, and its concentration. The presence of particulate matter results in a reduction of light intensity through the water column. Measurement of this reduction yields the turbidity of that medium. C.G. Wilber (1971) found that suspended particles modify light penetration in numerous ways. Large and dark-colored particles absorb large amounts of light of all wavelengths. If the particles have a bright surface, it exhibits two properties, absorption and diffusion. Small transparent particles present a complex situation which permits no clear-cut summary. Particle size produces other scattering effects as well. Small suspended particles tend to scatter the shorter wavelengths of light whereas the large particles scatter light of all frequencies.

LeGrande (1939) presented what is now considered a classical view of light penetration in the oceans. He defined the extinction coefficient by the following equation:

$$F - F_o e^{-cx}$$

where F_o and F are the light intensities before and after passing through an "epaisseur" of water (x), e is the base of Naperian logarithms, and c is the extinction coefficient. The relation is only valid for monochromatic light. The extinction coefficient of seawater is the summation of the true coefficient of absorption and the apparent coefficient of absorption resulting from the diffusion of light. Because the oceans vary infinitely in the number and size of particles they contain the extinction coefficient is not very easy to determine.

Jerlov (1951), from a study he undertook, came to the conclusion that the turbidity of all the oceans is rather constant. This study was made from 1947 to 1948 as a part of the Swedish Deep Sea Expedition. Coastal zones are more turbid than the deeper waters due to the greater concentration of suspended matter produced by the wave action and inland sediment flow into that area.

Specific gravity. The specific gravity of seawater depends upon the salinity, temperature and the pressure. The specific gravity or density of the oceans is greater than that of freshwater. Specific gravity is inversely proportional to the temperature and in the ocean it attains its highest value at temperatures below 0°C. Conversely, specific gravity is proportional to salinity. The average density of surface seawater varies between 1.022 and 1.028 g/cm^3 (Chow, 1964). Its main importance in the marine environment is that when differences in density exist between adjacent water masses with unstable stratification, currents may be formed (Friedrich, 1969). Horizontal density layers can be formed which prevent vertical movement of water, nutrients, gases and heat between the two layers. Migration of organisms can also be hindered by these discontinuity layers.

Viscosity. Viscosity of a liquid is that liquid's resistance to change of its form or to movement. It is a function of the molecular and chemical structure of the liquid in question. Seawater, due in part to the salinity and greater adhesion properties between the water particles, has a greater viscosity than freshwater. The viscosity increases with increasing salinity and with decreasing temperature. As a result of this relationship between viscosity and temperature objects sink at a faster rate nearer the surface than in the colder, deeper regions. Seawater retards the sinking velocity of organic matter, but there are other factors which also affect this rate. Particle size and shape are two important variables of sinking velocity (Coker, 1962). The viscosity of seawater fluctuates between seasons corresponding with the seasonal changes in temperature. The viscosity of seawater with 35 ppt salinity and 0°C is 0.01877 g/cm/sec and 0.01075 at 20°C.

Water movement. The ocean is in a state of constant motion which can be attributed to two forces: internal and external forces. The internal forces are those produced by the density differences or stratification caused by salinity and temperature. The forces produced by the earth's rotation, winds, and celestial forces make up the external forces. The three forms of motion the oceans experience are currents, tides and waves. Koh and Chang (1973) state that ocean currents are generated by a combination of the following forces: geostrophic forces associated with the steady state density field in the ocean; surface tidal forces; internal tidal forces; local wind-induced forces (Ekman wind drift) which are restricted to relatively shallow depths; and wave-induced forces. There exist many types of currents (Chow 1964). Drift, or wind, currents are developed from friction exerted on the sea surface by a steadily blowing wind. Slope currents are caused by inclination of the water surface developed by wind, barometric differentials, or inflow from rivers. Density currents are caused by the differences in density of the water. Tidal currents are caused by tidal actions.

The force produced by the wind blowing across the surface of the water causes the top layer of the water to move in the direction of the wind. The assumption is made that the term layer refers to a slab of water a few inches thick. As this slab is pushed by the force of the wind, frictional forces act on it from the slab below. This resistance reduces the effect of the wind force on that upper slab. If the top slab overcomes the frictional forces, it will be set in motion and it in turn will set the slab below it into motion. This effect proceeds down the water column and as it does, the surface wind force is subsequently dissipated. The rotation of the earth, however, determines the actual direction of flow in the water column. The rotation subjects the moving water to a "coriolis acceleration" which is directed at a right angle to the direction of the moving water. Stewart (1969) goes on to say that an acceleration at right angles to the velocity of an object causes circular motion of that object. The term applied to this circular motion is "inertial oscillation." It is based upon this phenomenon that the currents flow clockwise in the Northern Hemisphere and counterclockwise in the Southern Hemisphere.

The other form of motion is that produced by tides. The effects of this movement are experienced mainly along the coasts where they are most noticeable. Tides are generated from the gravitational forces between the earth, moon, and to a lesser degree the sun. Vector addition of the forces produced by the earth and moon yields a tidal force. The gravitational forces between the earth and moon are in the same plane, but in opposite directions. The resultant force is directed toward the moon. A centripetal force is present due to the motion of the earth around the moon. It is directed outward from the earth's surface. Addition of the resultant gravitational force and the centripetal force will yield the tidal force. Only the horizontal component of the tidal force is of consequence in creating the tides (Clancy, 1969). By horizontal he means the component parallel to the surface of the earth. It is this horizontal water displacement which produces tidal action. The range of tides is not constant worldwide and varies from between one to thirty feet.

Dissolved gases. The oceans absorb a wide variety of gases from the atmosphere, but one plays a major role in the life processes of organisms in the sea. Oxygen is required by most organisms, with the exception of anaerobic organisms, to carry out the metabolic processes within their system. Oxygen is used to create energy for these processes by oxidation of organic matter. The concentration and distribution of oxygen in the water column does dictate to which regions organisms can be located. Those organisms which require oxygen will inhabit areas only where a sufficient or adequate amount of dissolved oxygen is present. Oxygen is taken up at the interface between the sea and the atmosphere. Oxygen will continue to be absorbed by seawater until the saturation point is reached. Then, no more oxygen can cross this interface boundary unless a pressure differential exists between the atmosphere and the ocean which forces more oxygen into the seawater. However, the oxygen content is governed by two other factors, temperature and salinity. Higher temperatures and salinities cause a reduction in the capacity of oxygen that water can absorb. For example, the saturation value for oxygen at 0°C and 0 ppt is 12-13 mg/l O_2, and at 15°C and 30 ppt, it is reduced to 6 mg/l (Friedrich, 1969).

Movement of oxygen to deeper waters depends primarily upon the water circulation in the water column. Vertical diffusion of oxygen is a very slow and inefficient process. In very deep reaches of the oceans where no oxygen exists anaerobic organisms predominate and produce hydrogen sulfide. This gas poisons the water.

Carbon dioxide is a second gas relationship abundant in seawater. Carbon dioxide is present in a variety of forms; CO_2, carbonic acid H_2CO_3, carbonate $CO_3^{=}$, and bicarbonate HCO_3^{-}. The form it assumes dissolved in the water is a function of salinity, temperature, pH, and pressure. Its saturation value decreases with salinity and temperature, also.

Nitrogen and other rare gases sum up the other gases found in seawater. Gases representative of the noble gases, He, Ne, Ar, Kr, and

Xe, are present in very small concentrations and are chemically very inert (Horne, 1969).

Marine Life

Ecologically the oceans are divided into two distinct divisions, the pelagic and the benthic zones. The open waters are referred to as the pelagial division and the sea floor is the benthal division. These two areas are not only physically distinct, but also biologically distinct. Each division is discussed as it generally applies to most of the oceans.

Pelagic organisms. The organisms which inhabit the pelagic zone are commonly classified into two groups; nekton and plankton. Nekton are those organisms which are able to move or swim independently of the waves and currents. Fish and marine mammals are explicit examples of nektonic organisms. From observations of some organisms the line between these two divisions is a rather fine one. Shrimp are one set of organisms that are on the borderline. They are able to maneuver when the currents are not very strong, but helpless in strong currents.

Plankton by definition means 'that which drifts'. This then includes all marine organisms whose movement is controlled and guided by the currents, tides and waves. Plankton themselves are further divided into two subdivisions to distinguish between plants and animals. Phytoplankton refers to the plant life and zooplankton to the animals. Phytoplankton refer to diatoms, dinoflagellates, coccolithophores, coccoliths, and different classes of algae. The most common zooplankton encountered in the open oceans are protozoans, copepods, and foraminifera. Eggs or larvae of nektonic organisms also fall into this category.

The plants of the sea are by far the most numerous and the most important form of marine life. They constitute the base of the marine food web from which all other life in the sea is dependent. The basic food production and nutrient source is accomplished by these marine plants (Issacs, 1969). Like their counterparts on land, the phytoplankton are very dependent upon abiotic factors. Without enough light the productivity process will not be carried out or will be hindered. Therefore, the euphotic zone is the most heavily populated with respect to phytoplankton. Temperature, salinity and nutrients are limiting factors. During early spring, the conditions are optimum for maximum growth whereas in the winter it tapers off quite drastically.

Although their movement is controlled by the currents, zooplankton do possess mobility and are able to move up and down in the water column. These organisms are grazers and feed primarily on the phytoplankton. They represent the next stage of the marine food web. Zooplankton are similar to phytoplankton in that they are a very diverse group and dependent on abiotic factors although not to as great an extent as the marine plants. Their abundance or composition varies seasonally and geographically with respect to water temperatures. The distribution of zooplankton throughout the water column varies within a 24-hour day. At night, greater numbers migrate into the upper layers where they feed on the phytoplankton. During the day they retreat into the deeper or aphotic zone for protection against predators. Not all zooplankton exhibit this mode of behavior. All are not herbivores either. The larger species are carnivores and feed on eggs, larvae, and other zooplankton.

Benthic Organisms. The sea floor provides a firm and stable substrate for benthic organisms. The types of bottom-dwelling organisms encountered are dependent upon the form and composition of the bottom. This governs whether organisms can live within or below the bottom as well as on top of it. Soft bottoms can more easily support plant life or burrowers than can a hard rocky bottom. Sand, which could be classified as a soft bottom, would not be that readily adaptable to plant life due to the constant shifting it undergoes. A definite distinction is made between those animals living on the substrate and those below it, epifauna and infauna respectively. The epifauna can again be subdivided further into edriobenthos, the fixed organisms, and herpetobenthos, those that move by crawling.

The benthos can be divided into a littoral zone and an abyssal zone. The littoral zone extends from the upper tide line to a depth of 100 to 200 fathoms. This region contains the greatest number and diversity of organisms. There is light present in this region and vertical mixing by waves and tides maintains an abundance of nutrients for growth. In some areas the waves and tides cause turbulent conditions which require the benthic flora and fauna to be able to cope with this action. Oysters, mussels, and barnacles are adapted by attaching themselves to rocks or to a hard substrate. Clams and worms are able to burrow into the sand to avoid the turbulent conditions. Many plants in the littoral zone have developed hold fasts by which they attach themselves to the bottom. Also, as a result of turbulence and mixing in the littoral zone the organisms experience changes in their environment, either periodically or irregularly. These are changes in salinity, temperature, turbidity and chemical composition. The benthic organisms are adaptable to these wide fluctuations in the environment, more so than other marine life since they are restricted to the bottom and cannot swim away.

The abyssal zone is actually preceded by the sublittoral and archibenthic zones which in essence are just transition zones between the littoral and abyssal. The abyssal region is the true deep-sea area. It is well below one mile in depth and beyond light penetration. Without sunlight there are no green plants and therefore, no photosynthesis or food production. The bottom-dwelling organisms depend upon falling matter from above regions for nutrition. The abundance and diversity of species is small compared to that in the littoral zone. The abyssal is characterized by a stillness not found in shallower regions. There is no movement due to tides or waves and only a little movement caused by currents or internal waves. Wide fluctuations in environmental parameters do not exist in these deep regions. Besides the absence of light and motion, the benthic fauna have to cope with the great pressure exerted by the water column above them.

It should be noted that not all organisms are totally restricted to either the littoral or abyssal zone. It has already been pointed out that a transition zone does exist which contains representative species of the two major zones. However, there do exist some organisms which can cross from one zone to the other with no adverse effects. These organisms are termed eurybathic.

CHAPTER IV

RISK TO THE MARINE ENVIRONMENT

Chronic Effects

Before a safety factor can be applied, the chronic levels and their effects must be recognized. In Chapter I a brief definition of chronic toxicities was given. This chapter will examine chronic toxicities in greater detail.

The chronic toxicities discussed here include the long-term effects on juvenile organisms, effects on adult growth and reproduction, effects on enzyme activity, effects on productivity, and bioaccumulation and biomagnification. These examples were chosen because most of the research on chronic toxicities involved these effects. These examples are also easily identifiable and frequently found in the marine environment.

The level or concentration of the toxicant that will produce these effects depends not only upon the type of chemical, but heavily upon the species of organism. One may assume that all organisms of the same species are predominately homogeneous in their response to a dose of a selected chemical. That level of dosage should indeed produce the same effect whether it be LD_{50} or ED_{50}, on the majority of that given species, all environmental factors being equal. Variations between the organism's natural environmental factors and testing conditions can cause deviations in the dosage required to produce that effect. Changes in physical or chemical parameters may induce stress conditions upon the organism, making it more susceptible to foreign chemicals in its environment. When conditions are optimum for a given organism it stands a better chance of resistance toward foreign materials. V. E. Shelford defined this in 1913 by his now classic "Law of Tolerance."

With respect to the marine environment, the organisms inhabiting this vast domain are subjected to constant and sometimes drastic changes in their environmental factors. Because the seas are dynamic, there are introduced into the areas, by currents and tides, compounds of a varied nature. Since this is an act of nature that has taken place as long as the oceans and marine organisms have existed, the oceanic flora and fauna have developed, through evolution, a wide range of tolerances toward these changes. Compared to their counterparts in freshwater, marine organisms, especially estuarine and marine organisms, are more adaptable to variations in the environment. When attempting to relate toxicity studies on freshwater animals to marine animals, this greater tolerance needs to be taken into account.

Effects on life stages. Biological alterations in the organism itself produce varied responses. Specifically speaking, stages in the growth or life cycle of an individual place that individual in a different environment each step of the life stages. The response to a concentration of compound at one stage may in fact be totally opposite the response produced at another stage. Odum (1971) stated that limits of tolerance for reproductive individuals are usually narrower than for non-reproductive individuals. He applied this to limits of temperature, salinity, water, and other environmental factors. Odum laid the basis for an investigation into all life stages of an organism to clearly understand how it will react to different changes in its surroundings.

In dealing with acute and chronic toxicities and trying to formulate a safety factor which would be conservative a majority of the time for an organism, all of that individual's life stages should be considered during toxicity studies. A safety factor of 10 might be applicable for the adult, but 100 may be needed for the juvenile stage. A question that must be answered is where and when in the water column will the concentration defined by that safety factor be attained. Also, what areas of the oceans, both vertically and horizontally, do the juvenile stages inhabit. These two questions are very important in many respects. The highest concentration of a waste dispersed from a barge will be in that area directly behind the barge and a few feet deep. Consequent dilution of the waste will depend on the nature of the chemical and the mixing caused by currents. Therefore, there is a higher probability that any juvenile organisms closer to the surface in waters subjected to ocean disposal will be affected to a greater extent than the adult organisms of the same species. However, one might expect the greatest responses to occur in the upper pelagic layers, specifically the euphotic zone, where life is most abundant and pollutants are in higher concentrations than at deeper depths. Therefore, the site of disposal is of prime importance. What is present at the site will determine the exact effects of the compound. This is the primary reason dump sites for industrial wastes are located far offshore and at least off the continental shelf. The closer one gets to shore and to the coastal zone, the more numerous and varied is the marine life.

The fact that younger organisms are more vulnerable can be related to the biochemical and enzymatic processes within the organism. Loomis (1974) explains the biological and chemical factors that influence toxicity. A reaction must occur, either chemical or physiochemical, between the compound and an organism for an effect to be registered. Organisms are equipped with natural coverings which protect them from physical changes in the environment. These membranes or protective layers block the free transfer of chemicals into the internal organs. Adequate development of these membranous barriers is essential for protection against foreign compounds. Larval or juvenile organisms may not have developed these coatings to their full extent.

During growth and development, very important and precise biochemical and physiological metabolic processes take place. A minor upset in the balance of these processes produced by introduction of foreign compounds can cause either death or incomplete growth to the organism.

Epifanio (1970) examined the effects of dieldrin in seawater on the various stages of development of two crab larvae, *Leptodius floridanus* and *Panopeus herbstii*. For his purposes, Epifanio defined acute concentrations as those in which less than 10% of the crabs complete larval development and chronic as the concentration where more than

10% completed development. Five and ten parts per billion were found to be lethal to *L. floridanus*. The larvae of this species were reared in a concentration of 1 ppb dieldrin which produced significant results. The development of the crab larvae was divided into five stages; zoea stages I, II, III, IV, and megalopa stage. The first and second zoea stages were found to be the most sensitive to 1 ppb dieldrin. Exposure of dieldrin to larvae in these first two stages prevented molting to the next stage. These larvae remained in this unmolted state for ten to twelve days before they died. Larvae first exposed to the toxicant when in stages III or IV were not affected, and they completed their development. The study concluded that the toxicity of dieldrin to this specie of crab larvae is dependent on the stage of development at exposure rather than the time of exposure. The other species of crab larvae, *P. herbstii*, was not affected at all by exposure to 1 ppb dieldrin.

Similar work was done by Buchanan, et al. (1970) on larvae of the Dungeness crab, *Cancer magister*. They carried out their experiments with carbaryl, an insecticide commonly called Sevin. The TLm 96 for first stage zoeae was estimated to be 10 ppb. The survival of zoeae after twenty-five days exposure to concentrations of 0.1, 0.32, 1.0, 3.2 and 10 ppb was 83, 60, 69, 21 and 0% respectively. Interestingly, it was found that 1 ppm concentration of carbaryl did not affect egg hatching but did prevent all molting of prezoeae to zoeae. A finding similar to this, where eggs are more tolerant to a compound than the larvae, was presented in other works (Davis and Hidu, 1969). Davis and Hidu studied the effects of numerous pesticides on oyster and clam eggs and larvae. Embryos of the hard clam exhibited normal development when exposed to concentrations of Amitrol as high as 500 ppm. However, the larvae showed good growth only up to concentrations of 100 ppm. Concentrations above 100 ppm approach the acute level for the larvae. In another case, using the same organism but a different compound, Endothal, the results are reversed. The larvae can survive and grow in a concentration of 50 ppm Endothal, but the eggs can only do so in a 10 ppm concentration.

Emery (1970) conducted experiments to determine the comparative acute toxicity of cresol (phenol with a single methyl group) to two benthic crustaceans. In his findings Emery noted that the immatures of both species, *Gammarus fasciatus* and *Asellus militaris*, were more susceptible to cresols than the adults. Adult asellids were two times more tolerant than asellid immatures and adult gammarids 3.6 times more tolerant than their immatures. The different life stages of the two crustaceans were tested with respect to susceptibility. The molting first instar life stage of each organism was the least resistant stage. For gammarid immatures in the molting first instar state, the TLm 48 was 7 mg/1 and for asellid immatures, the TLm 48 was 21.6 mg/1 in the molting first instar stage. Emery postulated that the physiological processes in casting an exoskeleton reduced the tolerance to cresol.

These examples illustrate the difficulty in trying to assess the effects that a certain class of compounds will have on an organism's growth and development. If an organism's response to a compound is stage-dependent rather than time-dependent, this situation makes time of exposure an insignificant variable. Only the stage of development and the concentration of toxicant present need be considered. It has already been shown by Epifanio (1970) that chronic doses will prevent molting of crab larvae and subsequently lead to death of the larvae within twelve days. In this instance death is an ultimate result of a chronic dose. This is not always so for chronic doses. Whether the dose results in lethality or just impairs functions for the rest of the lifetime of the individual is a function of the compound and the organism. Chronic doses can be seen to produce three distinct effects; impairment of a function which leads to death ultimately, impairment of a function which does not lead to death but affects normal biological mechanisms, and bioaccumulation of the toxicant which does not produce an effect until the organ in which it is accumulated is utilized.

Enzyme activity. Many of the effects exerted by a compound on an individual are commonly caused by some type of reaction with cell components, specifically speaking, enzymes. These protein molecules are responsible for all metabolic processes. They are an integral part of all biochemical reactions and insure that the completion of a reaction will occur. An effect on an enzyme system may be evident by external changes or alterations. These external changes are sometimes easy to see such as in the form of growth, reproduction, sense, etc. Until recently it was very difficult to examine the exact and precise mechanism by which a compound reacts with an enzyme system. Research is now able to define what enzymes are affected by certain chemicals. All systems are affected differently and to varying degrees. The reaction that takes place between a chemical and an enzyme might not always produce a direct change. It may not produce any change at all. In the realm of pharmacology, if the enzyme with which the foreign chemical reacts alters the function of the cell, such enzymes are assigned the term of "specific receptors." Non-specific receptors are defined as those enzymes whose reaction with a foreign chemical does not alter the function of the cell (Loomis, 1974).

Enzyme activity is the basic level of all biochemical life processes. The products or reactants that are formed at this level are essential for other levels. Biochemistry within a cell should be considered as a very basic level and should be related whenever possible to a higher level of organization such as the efficiency of a tissue or an organ (Sprague, 1971). Any disruption or alteration at the enzyme level could possibly be transmitted to a higher level. This would depend primarily upon the mode of action of the toxicant. To understand the mode of action, a great deal of information must be known about the physiological makeup of organisms. This would be very difficult for environmental toxicologists to accomplish. However, knowledge in this area is essential to give a complete picture of how toxicants cause the changes that one can measure or observe. Some areas that can give an insight to these mechanisms are histopathology, histochemistry, haematology, biochemistry and physiology.

Acetylcholinesterase(ACHE),an enzyme responsible for the breakdown of the neurotransmitter acetylcholine, possesses a specific receptor or active site for organophosphates and carbamates (Coppage and Matthews, 1974). These two compounds bind the active site of the enzyme and prevent breakdown of acetycholine. This causes a disruption of nerve impulse transfers which can lead to death, but this has not been confirmed for fish. Coppage and Matthews exposed different organisms to several compounds at varying concentrations. Results of their experiments are reported in Table 4.1. All of the organophosphates produced significant acetylcholinesterase inhibition. Only the survivors were assayed for enzyme inhibition. The shrimp that survived lost their equilibrium and were in a dying state. Previous to this work, Holland and Lowe (1966) carried out similar experiments with almost matching results. They exposed juvenile spot fish to 10 ppb malathion for 26 weeks. At the end of this period the fish examined had lower than normal acetylcholinesterase levels in the brain, about 70 percent of normal. The fish, however, showed no adverse effects from this long-term exposure.

Several other authors have shown another enzyme system to be disrupted by toxic compounds. Janicki and Kinter (1971) showed that DDT inhibited (Na^+, K^+, Mg^{++}) - dependent ATPase. This enzyme plays a major role in the transport of sodium across epithelial membranes to control osmolarity. DDT at concentrations as low as 1-10 ppm produced 40% inhibition of this enzyme in selected marine teleosts. The enzyme activity in the intestinal mucosae and in the gills was affected the most. This enzyme functions to secrete sodium from the gills of these teleosts to maintain tissue osmolarity below that of seawater. Inhibition of this enzyme system may cause tissue damage. They also found that cyclohexanone completely inhibited (Na^+, K^+, Mg^{++}) - dependent ATPase. Wells, et al. (1974) showed that aldrin at sublethal concentrations inhibited the enzymes' activity in all tissues of the map

TABLE 4.1. AChE Inhibition in Fish and Shrimp by LC 40-60 of Organophosphates. (Coppage and Matthews, 1974)

Animal	Pesticide	Theoretical Conc. (ppb)	Hours Exposed	AChE Reduced (%)		Inhibition Significant at $t_{0.001}$
				Mean	Range	
Spot	Malathion	1250	24	70	65-82	Yes
	Naled	75	24	85	82-89	Yes
	Guthion	20	24	96	93-98	Yes
	Parathion	10	24	88	87-89	Yes
Pinfish	Malathion	1000	24	88	87-89	Yes
	Naled	75	24	88	88-88	Yes
	Guthion	10	24	80	77-84	Yes
	Parathion	10	24	90	88-92	Yes
Croaker	Malathion	1000	24	86	79-90	Yes
Sheepshead Minnow	Malathion	200	24	96	90-99	Yes
Pink Shrimp (moribund)	Malathion	1000	48	75	72-82	Yes

turtle but to the greatest extent in the intestinal mucosa. Campbell, et al. (1974) concluded that DDT has the same effect on rainbow trout. Davis, et al. (1972) examined the effects of fourteen polychlorinated insecticides, two PCB's and two herbicides on ATPase activity in rainbow trout.

Engel, Neat and Hillman (1970) showed that enzyme levels in the quahog *Mercenaria mercenaria* were significantly affected by sublethal exposure to DDT and lindane. The results of the experiment found that quahogs exposed to 0.002 ppm DDT showed a 40% reduction in foot fructose diphosphatase and 100% reduction in gill glucose-6-phosphate dehydrogenase and an increase in gill phosphofructokinase. Lindane exposure at 0.002 ppm showed a similar reduction in foot fructose diphosphatase. They concluded that these alterations in enzyme levels could result in an increase in rate of glycolytic degradation of glucose and suppression of gluconeogenesis. The time of exposure in these experiments was 30 weeks.

Effects on productivity. Primary productivity is defined, by most researchers, as the rate at which radiant energy is stored by photosynthetic and chemosynthetic activity, primarily by green plants, in the form of organic substances which can be used for food. Gross primary productivity is the total rate of photosynthesis including the uptake of inorganic carbon. Most investigators measure this uptake of carbon to monitor the productivity. Carbon-14 is supplied for a carbon source and its uptake rate is an indication of the productivity. The greater the uptake rate the more productivity taking place.

Keil, et al. (1971) experimented with polychlorinated biphenyls and the effect they have on a marine diatom, *Cylindrotheca closterium*. The specific mixture of PCB used was Aroclor 1242. At levels of 0.1 ppm growth of the diatom was significantly inhibited. Keil measured the inhibition by recording harvest weights and cell counts. Associated with growth reduction was a reduction of RNA synthesis and the chlorophyll index. This may account for the decrease in the growth rate. At one-tenth of this concentration, 0.01 ppm there was no effect on the growth, RNA synthesis, and chlorophyll index. Examination of the diatoms found that they concentrated Aroclor 1242, 900 to 1000 times the exposure level, 0.1 ppm.

Butler (1963) conducted experiments with pesticides on the productivity of natural phytoplankton communities in an estuarine system. A list of his results is shown in Table 4.2. He used a 1 ppm exposure level for four hours in all instances. From the data in Table 4.2 certain conclusions can be drawn. Chlorinated hydrocarbons have a greater effect on productivity than do the organophosphates. The average percent decrease for the chlorinated hydrocarbons is 75.3%, whereas for organophosphates it is 23.6%. Menzel, et al. (1970) did similar work with four species of marine phytoplankton. He exposed them to varying concentrations of DDT, dieldrin and endrin to determine the effects on photosynthesis and growth of the organisms. Measurements of ^{14}C uptake and cell division were made at the end of seven days. Listed in Table 4.3 are the results from DDT exposure of the marine phytoplankton. Of the four species it is evident that *Dunaliella tertiolecta* is most resistant. This may be explained by

TABLE 4.2. Percentage Decrease in Productivity of Natural Phytoplankton Communities During a 4-hour Exposure to a Concentration of 1.0 ppm of the Indicated Pesticide (Butler, 1963)

Pesticide	Percent Decrease
<u>Chlorinated hydrocarbons</u>	
Aldrin	84.6
Chlordane	94.0
DDT	77.2
Dieldrin	84.8
Endrin	46.0
Heptachlor	94.4
Kepone	94.7
Lindane	28.5
Methoxychlor	80.6
Mirex	41.6
Thiodan	86.6
Toxaphene	90.8
<u>Organophosphorus insecticides</u>	
ASP-51	29.5
Bayer 29493 (Baytex)	7.2
Bayer 25141	0
Diazinon	6.8
Dibrom	55.6
Di-Syston	55.2
Dylox	0
Ethion	69.0
Guthion	0
Imidan	7.7
Malathion	7.0
Meta-Systox R	0
Methyl trithion	85.9
Systox	7.11
<u>Carbamates</u>	
Bayer 37344	38.7
Bayer 39007	0
Bayer 44646	0
Sevin	16.8

TABLE 4.3. Chronic Effects of DDT on Phytoplankton
(Menzel, et al., 1970)

Skeletonema costatum (coastal centric diatom)

@ 100 ppb cell division blocked after 2-3 divisions

@ >10 ppb C^{14} uptake reduced significantly

Coccolithus huxely (coccolithophorid)

@ 100 ppb no effect on cell division

@ >10 ppb C^{14} uptake reduced

Cyclotella nana (centric diatom)

@ 100 ppb cells divide more slowly

@ > 1 ppb C^{14} uptake inhibited

Dunaliella tertiolecta (naked green flagellate)

@ 1000 ppb no effect on cell division

@ 1000 ppb no effect on C^{14} uptake

the fact *D. tertiolecta* is an estuarine species and naturally more resistant. The other three species inhabit the waters outside of an estuarine system. This brings out a very important point in assessing the impact of ocean dumping on an area. The organisms in the immediate area should be examined first for their reactions to the waste compounds since the effect is immediate. Hopefully, by the time a waste reaches another distinct region, such as an estuary, the level of the compound is diluted well below the chronic level.

Effects on adult growth and reproduction. Discussed in a previous subheading was the fact that chemicals can alter or inhibit development of larvae or eggs. Adult growth can also be affected by sublethal doses of a compound. Larval growth is commonly determined by defining the different growth stages. Adult species normally do not go through distinct stages after maturity, therefore, another means of growth detection is employed. Increases in length and weight are the parameters measured most often. With algae and phytoplankton, it is difficult to measure the length or weight of individual organisms so another method is utilized. Growth is measured in terms of total weight or total number of individuals. Proliferation is synonomous with growth and productivity for these organisms. This is not so with organisms other than algae.

Marine organisms spawn or reproduce in very great numbers to insure proliferation of the species. This is primarily due to the high risk of predation on the eggs or juveniles and to offset great losses from adverse environment conditions. Any effect on reproduction by toxicants can make itself evident in the number or abundance of organisms in the area affected by the waste discharge. However, one must keep in mind that there are other factors which could cause a decrease in the numbers of organisms in a species. This section deals with those effects that directly affect the actual reproductive processes, including fertilization, and development of the egg itself, not egg development to larval stages.

Davis (1970) presented findings concerning the relationship between pollutants and reproduction. Chronic doses of sulphates tended to reduce the percent of successful fertilization in herring eggs and increased structural abnormalities in hatched fry. He further reported that sulphate pulp mill wastes reduced reproduction and settling of oysters but on the other hand, kraft-mill wastes stimulated spawning by mussels. Phenols and metal ions in small concentrations produced abnormal development in sea urchins and pelecypod eggs.

In experiments conducted by Boyd (1964) using nine insecticides, he showed that at sublethal concentrations these insecticides caused pregnant female mosquitofish (*Gambusia affinis)* to abort. Boyd states that a pregnant female at almost any stage of pregnancy may abort when exposed to an insecticide solution even though the female survives. At chronic concentrations of methoxychlor and lindane approximately 15 percent of the pregnant females aborted. The other insecticides used were aldrin, dieldrin, DDT, DDD, endrin, heptachlor, and toxaphene.

The results of Rosenberg, Grahn, and Johansson (1975) on reproductivity of *Ophryotrocha labronica,* a polychaete, are presented in Table 4.4. For 1,2-dichloroethane an increase in concentration from

TABLE 4.4. Number of Eggs, Egg Masses and Percentage of Hatching of the *Ophryotrocha labronica* in Different Concentrations of some Chlorinated Aliphatic Hydrocarbons. Temperature: 21-25°C. Salinity 35°/₀₀ (Rosenberg, Grahn, and Johansson, 1975)

Compound	Conc. ppm	No. of egg masses	Tot. no. of eggs	Average no. of eggs per egg mass	Hatching %
1,2-dichloroethane	50	8	325	41	100
	100	7	230	33	100
	200	8	560	70	100
	400	8	290	36	10
	600	3	75	25	0
1,1,2-trichloroethane	25	6	270	45	87
	50	8	380	48	93
	75	6	400	67	61
	100	6	365	61	70
	150	5	275	56	0
	200	7	395	56	0
1,1,2-trichloro ethene	25	8	495	62	98
	50	10	525	53	81
	75	9	505	56	66
	100	8	440	55	82
	150	6	360	60	44
	200	5	190	38	29
Controls	0	9	500	56	95

200 to 400 ppm produces a 90% reduction in eggs hatching. Exposure time was four weeks. For trichloroethane and trichloroethene, the increase in concentration from 100 to 150 ppm was significant. This was the break between acute and chronic levels. It is easily seen that the acute/chronic ratios are very small.

Bioaccumulation and biomagnification. Bioaccumulation and biomagnification are a very important aspect of chronic toxicities. The literature cites many examples of bioaccumulation. Wilson (1965) conducted many experiments using oysters, fish and a variety of pesticides. He found that oysters exposed to endrin at a concentration of 0.001 ppm for ten days accumulated 1 ppm in their tissues. Another group of researchers examined accumulation of polychlorinated biphenyls in grass shrimp (Nimmo, et al., 1974). Grass shrimp exposed to 2.3 ppb concentrated PCB's up to 11,000 times in their tissues. In a similar study by Hansen, et al. (1971), they stated that Archlor 1254, a PCB, can be stored in pinfish and spot for three months with no change. At chronic exposures of 1 ppb pinfish are more susceptible to disease. Accumulation was found to be proportional to the degree of chlorination in tests using PCB's and oysters (Vreeland, 1974).

Once the toxicant is accumulated in an organism's tissues the danger is two-fold. Harm can be done to either the organism itself or to others. It has been proven that these accumulated toxicants can be passed from one generation to the next. If the biological half-life of the compound is small it will persist in the organism's tissues and be transferred to the next generation virtually unchanged. Another method by which biomagnification can occur is by progressing up the food chain. As one organism feeds upon another from a lower level, any accumulated residues are also moved up and possibly magnified. However, all of this depends upon how long the toxicant remains in the body tissues.

After exposing spot fish to a concentration of 0.05 ppb endrin for five months, 78 ppb had accumulated in their tissues (Lowe, 1965). When these fish were moved to clean water no endrin could be detected in their tissues. The toxicant was flushed out of their system. Wilson (1965) did the same experiment with brook trout. The trout lost 41.3% of the accumulated toxicant, methoxychlor, when placed in fresh, clean water for seven days. The fish may have either metabolized or flushed out the residues. Gunner (1970) has found that fish liver microsomes can metabolize diazinon. Methoxychlor can also be metabolized by bluegills (Kennedy, et al., 1970). Therefore, most organisms have some type of safeguard against harmful buildup of toxicants in their tissues. But if the concentration in the water gets too great these built-in safeguards could fail.

CHAPTER V

SELECTED VARIABLES AFFECTING THE TOXICITY OF A COMPOUND

In a report published by the National Academy of Sciences entitled "Assessing Potential Ocean Pollutants" (1975), four charactertistics that are essential for the evaluation of a material's importance were defined as:

1. rates of release into the environment;
2. lifetimes in the environment (or residence times in regions where accessible to biological systems);
3. concentration factors in parts of the system (e.g., surface films or estuaries) or into organisms (bioaccumulation); and,
4. levels of toxicity.

In addition to these four characteristics, the author has identified others. They are specific or non-specific reactions, stage of development, shock effect, and modifying factors. The modifying factors are abiotic conditions and consist of the following; water temperature, dissolved oxygen content, pH, bicarbonate alkalinity, hardness, and CO_2 concentration.

Rates of Release

The rates at which materials are released or dumped into the ocean can be examined in two ways. First, there is the periodicity of release. Most materials are dumped on a fairly regular schedule. For some industries it may be a matter of days; for others it might be weeks between trips. However, the number of trips and quantity of material for each trip are supposed to be known and regulated for each industry.

This is written into the ocean dumping permits by the Environmental Protection Agency. The GAF Corporation in Texas City, Texas, was allowed not more than four trips a month, with each trip not exceeding more than 4,800 tons of waste. E.I. DuPont De Nemours and Company at La Porte, Texas, was allowed up to eight trips a month, each trip not exceeding 4,800 tons of waste. In a third instance, the Ethyl Corporation in Baton Rouge, Louisiana disposes of its wastes in 55-gallon steel drums. Its permits set the limit at 700 barrels per month and trip. The corporation may dump all 700 barrels either at once, or divide the quantity into as many trips as desired. Therefore, from these figures the quantity dumped can be estimated rather accurately.

Secondly, there is the matter of the actual release into the water column. This differs from the total quantity dumped because it is dispersed over a wide area and not all dumped in one spot. This rate of release is also written into the permit. GAF, in Texas City, was allowed a maximum release of 7,000 pounds per minute while moving at a speed of not less than 5 knots. The DuPont permit had the same rate of release. Because of the nature of Ethyl's method their rate was different. Ethyl has to space at least 500 feet between barrels dumped overboard. The barrels contain a sodium-calcium sludge and are punctured with at least six holes before discharge into the sea. As the drums sink the water reacts with the waste and causes an explosion which ruptures the drums and releases the waste to the marine environment. Theoretically, the drums are supposed to explode a few feet below the surface. There is always the chance that the drums will not explode at all. An incomplete explosion may not rupture the drums and consequently not release the waste evenly.

Lifetimes in the Environment

The lifetime of a chemical is a very complex function and dependent upon many variables. The actual lifetimes of many chemicals in the marine environment are not known. The seas are very reactive both chemically and biochemically. Two things can happen to chemicals in the marine environment, they remain unchanged, or transformed and degraded. Transformation and degradation can occur by microbial processes or by naturally occurring processes. The type of chemical governs which one of these pathways it will follow.

A majority of industrial wastes dumped in the oceans consist of synthetic compounds not naturally found in nature. The problem encountered with this type of waste is that there may be no metabolic pathways present in nature to degrade, synthesize, or detoxify these compounds. This could result in a harmful buildup of this chemical in the sediments or in organisms. Naturally occurring compounds disposed of in an area foreign to their occurrence may possibly accumulate. There may not be present any enzyme reactions in that area able to degrade these compounds.

Another possibility is that the chemical will be degraded to its constituents. Dieldrin for example is metabolically degraded to photodieldrin and other metabolites by algae (Patil, et al., 1972). What has to be examined in these cases is the relative toxicity of the metabolites with respect to the original chemical. DDT is metabolized by organisms and broken down into five metabolites. They are: DDE, DDA, kelthane, dichlorobenzophenone, and DDD. DDD and DDE are the most commonly encountered metabolites and are relatively non-toxic compared to DDT. Malathion on the other hand breaks down into diethyl fumarate which turns out to be more toxic than malathion. These two examples exemplify the fact that degradation does not always mean detoxification.

Rice and Sikka (1973) report that certain chlorinated pesticides are known for their low biodegradability and high accumulation in living organisms. Batterton, et al. (1971) found that photodieldrin and metabolites G and F were as toxic to *Anacystis nidulans*, a marine phytoplankton, as was dieldrin itself. Aldrin is degradable under most environmental conditions as well as by organisms. It has been shown that marine microorganisms metabolize aldrin to dieldrin and trans-aldrindiol (Patil, et al., 1972). A marine phytoplankton, *Dunaliella sp.*, transforms aldrin to 23.2% dieldrin after thirty days. Carlson (1974) has also documented this transformation by showing that the American lobster (*Homarus americanus*) is capable of metabolizing aldrin to dieldrin.

Jensen and Rosenberg (1975) conducted experiments to investigate the degradability or disappearance of four chlorinated aliphatic hydrocarbons in seawater. The substances they utilized were chloroform 1, 1,2-trichloroethane, 1,1,2-trichloroethene, and 1,2,2,2-tetrachloroethene. These substances are waste by-products from a vinyl chloride production and they were commonly dumped in the North Sea. From their studies, it was determined that the concentration of these chlorinated hydrocarbons decreased the greatest in an aquarium kept in the light and partly open. After eight days only 20% of the trichloroethene was present in the seawater and between 40-50% of the other substances were found. The fast decrease in trichloroethene was attributed partly to biological degradation, but also to evaporation. The investigators concluded that the disappearance would be slower in the ocean. Evaporation only occurs at the surface and the substances would not always be located on the surface.

Compounds that do occur in nature are present at concentrations termed background levels. Addition of these compounds to an ecosystem will cause an increase in the level of concentration. Too much of an increase may result in toxic levels. To safeguard against this, nature is provided with metabolic pathways which degrade or decompose this excess to safe levels. However, if too great a load is dumped in an area, either by a single dump or repeated dumps, which cannot be handled by the microbes, a buildup of compounds may occur. Some metabolic processes may not be able to handle large concentrations at a time.

Shock Effect

Organisms are not always able to avoid harmful or toxic concentrations of chemicals in the environment. They may not always encounter a chemical after it has been diluted or dispersed. Sudden or immediate exposure can produce a shock effect.

Rosenberg, Grahn, and Johansson (1975) attempted to examine the shock effect of dichloroethane, trichloroethene, and trichloroethane on a polychaete (*Ophyryotrocha labronica*). In one experimental series, the test organism was suddenly exposed to the test solutions and in the other test series, the organism was gradually exposed to increasing concentrations over a one-hour time span. These authors found that the estimated 96-hour LC_{50} values for the test with successive increases were 1.8-3.1 times higher than those found for the test with sudden exposure (Table 5.1). In the experiments with trichloroethane for example, at greater than or equal to 200 ppm almost all of the test population was killed within 24 hours. However, a gradual increase killed all test organisms in 600 ppm within 4 days, and at concentrations less than 400 ppm no mortality was recorded. These differences are very significant. A shock loading to an ecosystem could totally destroy the whole community.

This leads to a very important point. In bioassay or toxicity experiments, the test organism should be slowly acclimated to the toxic compound. A shock effect can produce a greater initial mortality thereby altering the final estimated LC_{50}. All values would be erroneously lower. However, it would appear to be that in the ocean environment some organisms would encounter the shock effect more often than others. Organisms in the upper layers of the water column would experience a shock effect more so than bottom-dwelling organisms as a whole. Therefore, <u>in situ</u> experiments should take this into account, otherwise, two different LC_{50} values could be attainable. This would just complicate the determination of a safety factor even more. To offset this shock effect, the concentration of the compound discharged into the marine environment needs to be well below the LC_{50} value before discharge. If the concentration of the material aboard the

TABLE 5.1. Estimated 96-Hour LC_{50} for *Ophyryotrocha labronica* (Rosenberg, et al., 1975)

Component	A Shock (ppm)	B Successive Exposure (ppm)	$\frac{B}{A}$
1,2-dichloroethane	400	900	2.3
1,1,2-trichloroethane	160	500	3.1
1,1,2-trichloroethene	225	400	1.8

barge is sublethal, dispersion of the concentration into the water will greatly decrease its concentration. This alone may be a sufficient safety factor in itself. However, other variables such as bioaccumulation, degradation, and chemical reactivity influence the final concentration.

Concentration Factors and Bioaccumulation

The factors that lead to concentration levels in parts of the ocean are not very well understood. Much of this depends upon the physical and chemical makeup of the compound and of the receiving water.

[Many organic compounds, especially pesticides, are hydrophobic. They have water solubilities in either the parts per million or parts per billion range.] Compounds possessing low solubilities can be readily taken up and accumulated by organisms. In contrast to their low water solubilities, many compounds are lipid-soluble.

Parke (1968) states that the transfer of compounds across membranes follows one of these four mechanisms:

1. simple diffusion;
2. filtration;
3. pinocytosis; and
4. active transport.

Of these four mechanisms simple diffusion is thought to be the principal method. The rate of diffusion is a function of four variables and expressed by Fick's Law:

$$\text{rate} = \frac{kA(c_1 - c_2)}{d}$$

C_1-C_2 is the concentration gradient across the membrane, A is the surface area available for transfer, d is the thickness of the membrane, and k is the diffusion coefficient. Only lipid-soluble, un-ionized molecules readily pass through membranes.

Bioaccumulation has been studied extensively by many researchers (Schoor, 1974; Petrocelli, et al., 1973; Hansen, et al., 1971; Keil, et al., 1971; Nimmo, et al., 1974). A detailed discussion of bioaccumulation and another phenomenon, biomagnification, is presented in the following chapter.

Levels of Toxicity

Four kinds of information are needed to estimate the level of toxicity or exposure levels of a compound, to target systems. These are:

1. data on the quantities of the chemical released into the environment;
2. data on physical and chemical properties;
3. the expected environmental transformations of the chemical; and
4. the likelihood of bioaccumulation (NAS, 1975).

The first, third, and fourth point have already been discussed in the previous subheadings.

Estimation of exposure levels involves knowledge of the physical and chemical properties and the behavior of the toxicant. A chemical's behavior is largely influenced by its water solubility and the latent heat of solution. Many organic compounds, including pesticides, are hydrophobic having solubilities in either the parts per million range or parts per billion range (NAS, 1975). Chemicals possessing low solubilities may be more readily taken up and accumulated by organisms. Aldrin and dieldrin are readily accumulated in living tissues because they are more soluble in tissues than in water (Wurster, 1971). Solubility is influenced by temperature. It normally increases with temperature.

The level of toxicity also depends upon the compounds' interactions with other chemicals in the environment. The action of a toxic agent can be modified by exposure to other agents. If the action produced by the combination of two agents resulted in a higher mortality than the two of their effects added separately, this would be termed synergistic. For example, if one-half the LD_{50} of compound A is added to one-half the LD_{50} of compound B and the resultant mortality is greater than 50%, synergism has occurred (O'Brien, 1967). However, if less than 50% mortality is produced this is termed antagonism. Synergism can take place even if only one of the compounds is toxic. When this occurs, the non-toxic compound is referred to as a synergist.

Repeated exposures may not allow the organism to recover. In some instances removal of the toxicant will allow the affected organism to flush the toxicant out of its system and resume normal life patterns. Petrocelli and co-authors (1973) showed that after clams were removed from an environment of sublethal dieldrin which suppressed their rate of siphoning their siphoning returned to normal after 24 hours. What is important here is the interval of repeated exposures. If the intervals are spread far between the organisms may be able to recover without any bad side effects.

Non-Specific and Selective Chemical Action

Non-specific chemical actions are characterized by general destruction of cells (Loomis, 1974). Burns originating from highly acidic or basic compounds are examples of this type of action. There is no specific or selective receptor for the compound that produces the effect. This action is primarily concentration-dependent. The degree of destruction is directly related to the concentration of toxicant.

A majority of the chemicals are more selective in their action. Chemicals as well as enzymes possess specific active sites on the molecule. A reaction will occur when these sites come in contact with receptors which molecularly complement the active site. The reaction that does take place is termed a specific chemical action, if the function of the cell component is altered by the product of the reaction. A chemical that selectively alters biochemical processes need only be present in small concentrations, unless it is actively competing with another compound for the same site. Then, it would have to be in greater concentrations.

Stage of Development and Time of Exposure

In dealing with acute and chronic toxicities and trying to formulate a safety factor which would be conservative, all of an organism's life stages should be examined. A safety factor of 10 might be applicable for the adult stage, but 100 might be required for the juvenile stage. During growth and development very important and precise biochemical and physiological metabolic processes take place. A minor upset in the balance of these processes can cause either death or incomplete growth to the organism. Epifanio (1970) examined the effects of dieldrin in seawater on the various development stages of two crab larvae. His study concluded that the toxicity of dieldrin to one of these species, *Leptodius floridanus*, is dependent upon the stage of development rather than time of exposure. A concentration of 1 ppb dieldrin was used in these experiments.

Similar work was done by Buchanan, et al. (1970) on larvae on the Dungeness crab, *Cancer magister*. They carried out their experiments with carbaryl, an insecticide commonly referred to as Sevin. It was found that a 1 ppm concentration of carbaryl did not affect egg hatching, but did prevent all molting of prezoeae to zoeae.

These examples illustrate the difficulty in trying to assess the effects that a certain class of compounds will have on an organism's growth and development. If the response of an organism to a toxicant is stage-dependent rather than time-dependent, then this almost makes time of exposure an insignificant variable.

Modifying Factors

Many researchers have identified numerous abiotic conditions that directly affect the toxicity of a compound or the susceptibility of an organism to that compound. They have termed these modifying factors. Those factors that are most commonly recognized to cause variations in toxicity are: water temperature, dissolved oxygen content, pH, bicarbonate alkalinity, hardness, and CO_2 content of the water. Much of the research done in this area was summarized by Sprague (1970).

In his literature review, Sprague cites many examples of how these factors modify toxicity. Brown, et al. (1967) reported that the sensitivity of rainbow trout to phenol in saline waters increased linearly as salinity increased. If this is the case, it would appear that fish inhabiting estuaries would be most affected by this relationship. This would be due to the fluctuations in salinity characteristic of these regions. The degree of ammonia toxicity is dependent upon numerous variables (Lloyd and Orr, 1969). Natarajan (1970) has stated that the toxicity depends upon the concentration of either molecular non-ionized ammonia or ammonium hydroxide. Wuhrmann (1952) and Lloyd (1961) have also shown this to be true, especially the effect pH has on ammonia toxicity. The ammonium ion is relatively non-toxic. The influence of salinity and temperature on the toxicity of undissociated ammonia was shown to be less for striped bass than for sticklebacks (Hazel, et al., 1971).

There are many cases where the modifying factors produce opposite effects on classes of chemicals or on organisms. Pickering and Henderson (1966) found that two carbonates are affected in totally opposite directions with respect to water hardness. There are only a few cases where pesticide toxicity is affected by water hardness (Johnson, 1968). The effects that temperature has on toxicity are so varied that it is difficult to state a general assumption. Each case has to be reviewed individually. In the past, higher temperatures were thought to increase the toxicity of compounds. A correlation was also made with the fact that warmer water also held less dissolved oxygen. This reduced concentration could place the organism in a stressed condition which would result in respiratory malfunctions. Therefore, whether the temperature change affects the compound or organism directly is still a debated issue. As for the case where lower temperatures may increase the toxicity of compounds Sprague (1970) presents the notion that the lower temperatures slow down metabolic processes. Normally these processes might metabolize or detoxify the toxicant.

It is generally accepted by most researchers that these modifying factors do exist. But, the actual mechanism of their action is varied and not very well understood. Whether these factors affect the compound or the organism directly is still a major controversy. An example is that of a pollutant reducing the amount of oxygen in the water. The lack of oxygen is the actual or direct cause of lethality. A further understanding of these mechanisms is required and can only be obtained by more research. Modifying factors are far too complex at this point to make any conclusions regarding their modes of action.

CHAPTER VI

ASSESSMENT OF A SAFETY FACTOR

Summary

The foundation for the determination of a safety factor has been presented in the preceding chapters. With this knowledge in hand, the logical sequence of steps needed to arrive at an adequate safety factor can be made. The type of waste to be disposed of warrants first consideration. It is the waste material that poses the initial hazard. Therefore, complete identification of the waste into its constituents is required. The reactive properties of the waste as a whole and individually should be thoroughly examined. This will give some insight as to how long the material will remain in the marine ecosystem and in what chemical form. A step further should be taken with compounds known to be very toxic. The breakdown of their reactions should be identified. For example, it has been exhibited that diethyl fumarate, a breakdown product of malathion, is more toxic than malathion itself.

The types of materials disposed of in the oceans are carefully controlled by federal regulations. Dredge material, municipal wastes, and industrial wastes are the three categories of waste material most frequently disposed of. Of the total volume of waste dumped each year dredge material by far constitutes the largest volume. It is reasonable to assume that this volume will increase in the future as more and more navigable waterways are being dredged. On the other hand, the volume of industrial wastes being disposed of in coastal waters can be forecasted to decline. Increased pressure on industries by federal, state, and local agencies is forcing many industries to abandon ocean disposal for other land-based disposal operations. The status of municipal wastes is still very much in question. There are numerous conflicting reports about the effects domestic sewage sludge has on the marine environment. The main controversy centers around the philosophy of "fertilization or pollution."

Secondly, the marine organisms that will be directly affected by the waste have to be identified. A survey of the pelagic and benthic organisms in the dump area is necessary. The biological relationships between species and how each contributes to the system as a whole is vital information. It may be found that some species play a very intricate and integral role in the ecosystem. It is these organisms that should be protected from harm. One such group of organisms are the phytoplankton. They are the basic level of life forms in the sea from which all others build.

The life stages or cycles of vital marine flora and fauna should be investigated. A safety factor selected should be sufficient for the weakest link in an organism's life stages and development.

A delicate balance also exists between marine organisms and their physical and chemical environment. Any disruption of this balance can also be detrimental to the well-being of organisms. Any effects that ocean disposal has on the physical and chemical make-up of the marine environment will indirectly affect the biological organisms. For instance, a waste such as sewage sludge could increase the turbidity in an area. Organisms which depend on light, phytoplankton in particular, would suffer due to the decrease in light available to them. Dredged material and sludges that settle to the bottom will affect the substrate organisms present on the bottom. The waste sludges may alter the substrate to a point where it would be unsuitable for marine life. An industrial waste, either too acidic or basic, could conceivably cause a pH change in the receiving water. Although a change of this nature may only be short-term because of the dilution factor in the oceans. But even a short-term pH change could adversely affect organisms in the dump area. The biochemical oxygen demand (BOD) of some wastes could lower the dissolved oxygen content in the disposal site thus resulting in dead areas. However, it is assumed that the oceans have a great oxidizing ability which would prevent a hazardous reduction in dissolved oxygen. The factors that affect the oxygen content are temperature and salinity. If disposed materials affect these two factors it is certain to affect the capacity of the water to hold oxygen in a dissolved state. These examples illustrate how wastes can cause harm or damage to marine organisms without directly affecting them.

The limiting permissible concentration proposed by the Environmental Protection Agency includes the acute/chronic ratio in addition to the true factor of safety. The acute/chronic ratios have to be determined. Table 6.1 compares these ratios for different compounds and organisms. All but one of these compounds are pesticides. These data were obtained from the research of numerous people. The column titled "Factor" is the magnitude of the difference between the acute and the chronic concentration. A factor of 10 means the acute

TABLE 6.1. Comparison of Acute/Chronic Toxicity Ratios of Different Substances

Compound	Organism	Acute/Chronic (ppm)	Factor
Aldrin	clam eggs	10/1.0	10
PCB	pin fish	0.005/0.001	5
Carbaryl	clam larvae	72.5/1.6	45
	clam eggs	3.8/0.02	190
	oyster eggs	3/0.02	150
2,4-D	oyster	2/0.1	20
Diuron	clam eggs	2.53/1.0	2.5
Endrin	oyster eggs	0.79/0.05	16
	oyster larvae	10/0.05	200
Lindane	oyster eggs	9.1/1.0	9
Malathion	oyster eggs	9.07/5.0	2
	oyster larvae	2.66/0.5	5
	carp	6.59/5.0	1.3
	bluegills	0.11/0.0055	20
	fatheads	10.45/0.58	18
Methoxychlor	bluegills	0.062/0.04	1.6
Toxaphene	clam eggs	1.12/0.5	2.2

concentration is 10 times greater than the chronic concentration. According to the Environmental Protection Agency's criteria a factor of 100 is required between the acute level and the limiting permissible concentration. Therefore, any factor in the table greater than 100 means that the compound requires a larger overall EPA factor of 100. The EPA's factor of safety in these cases is not large enough to cover even the acute/chronic ratio and thus there is no true safety factor. The acute/chronic ratio for oyster larvae exposed to endrin is 200 (see Table 6.1). A true safety factor would have to be applied to this number to obtain an overall safety factor that would adequately protect the larvae from harm. If this true safety factor was determined to be equal to 10, the overall safety factor would equal 2000. Therefore, the limiting permissible concentration of endrin in an environment with oyster larvae present would be 0.005 ppm.

Another method of representing the factor of safety and a safe concentration is by using stress-strain diagrams. In structural theory, five different types of strain are recognized. They are linear-elastic, nonlinear elastic, viscoelastic, plastic, and anelastic.

Correlations can be made between these five types of strain and the effects of toxicants on organisms. In structural design, loads are applied to members producing effects. This same concept can be applied to the marine environment. Loads or concentrations of chemicals produce strains or effects on organisms. The stress-strain relationships vary according to the class of compound and the organism. However, these five relationships generally take into account all of these variations. Figure 6.1 illustrates the linear-elastic relationship.

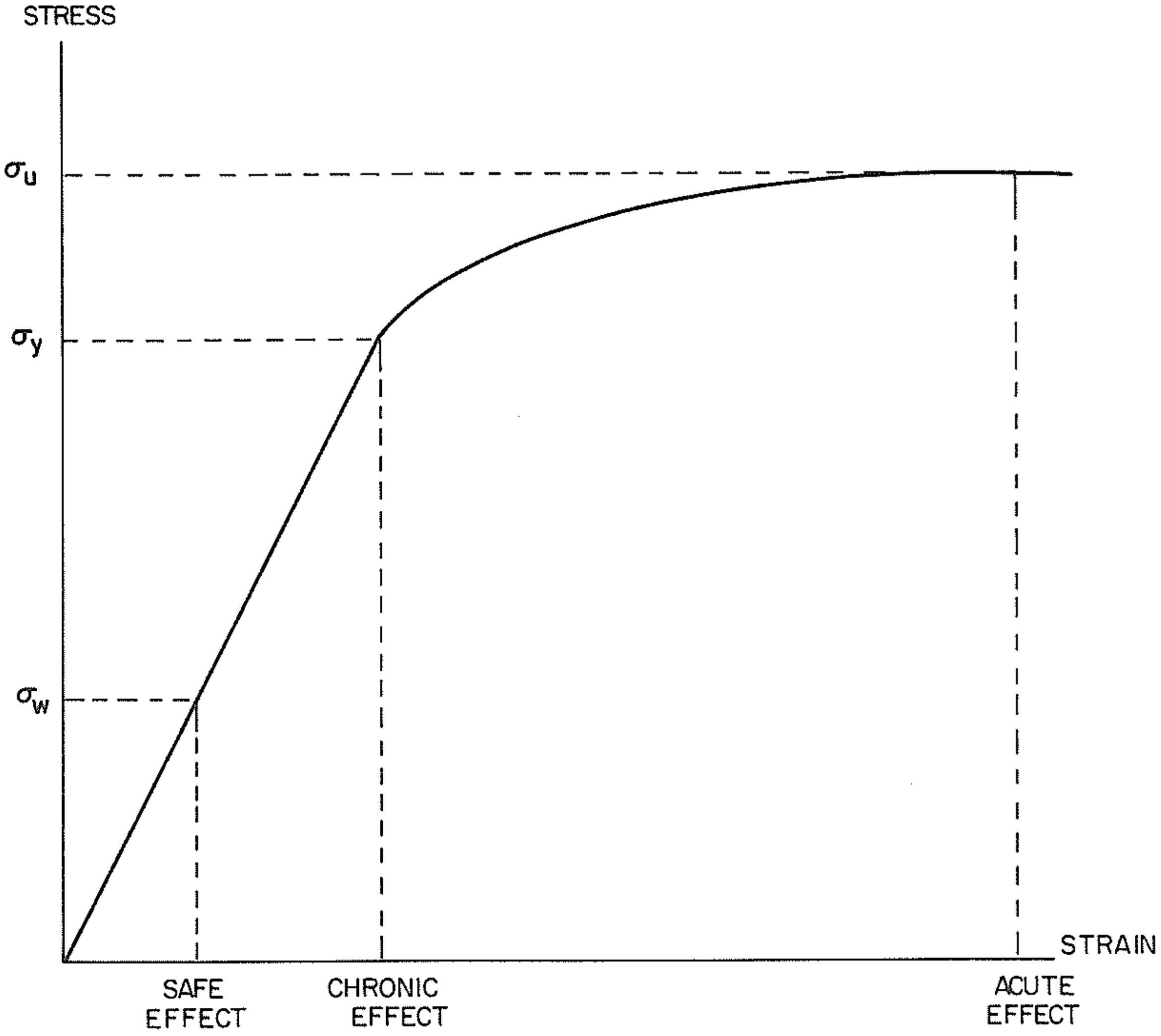

FIGURE 6.1. LINEAR—ELASTIC RELATIONSHIP

On the y-axis is plotted the stress and on the x-axis is the strain. The unit strain is proportional to the unit stress until a certain stress is exceeded. The point where this proportionality no longer holds true is termed the proportional limit. It is designated as σy, the yield stress. It is the upper limit of chronic toxicity. Loads above this point approach the acute toxicity. The symbol, σu, represents the TLm value. σw is the allowable concentration which produces no adverse effects. It is obtained by applying a safety factor to the chronic concentration, σy. The following relationship exists:

$$\frac{\sigma y}{\sigma w} = \text{overall safety factor}$$

The linear-elastic relationship occurs as long as the stress is below the proportional limit; no permanent damage is done when the load is removed. The organism will recover with no lingering effects. Wilson (1965) has shown this to be true with brook trout. The trout concentrated methoxychlor in their tissues after seven days of exposure. However, after being transferred to non-contaminated water, 41.3% of the toxicant was lost from their body tissues. The removal of the toxicant enabled the affected organism to revert back to normal. Nonlinear elastic relationships are similar to linear, except that unit stress is not proportional to unit strain. There is also no permanent residual effect after the toxicant is removed completely.

Viscoelastic behavior resembles linear elasticity except that the strain continues to increase while the load remains constant. And, there is a residual effect after the load is removed. Exposure to a constant concentration increases the severity of the effects. This type of behavior is more time-dependent than anything else. Bioaccumulation is typical of this. An organism will continue to accumulate a toxicant in its tissues as long as the compound is present in the water. After extended periods of exposure the accumulated levels may reach dangerous levels. And, if the organism is transferred to a clean environment the toxicant remains in its tissues and is not flushed out for some period of time. The toxicant may disappear eventually but that would be a result of its biological half-life.

Anelastic deformation is time-dependent, but completely recoverable. Strain at any time is proportional to change in stress, and the effects at any given instant depends on all prior stress changes.

Plastic strain is not proportional to stress and a permanent effect remains after removal of the toxicant. Plastic strain depends primarily upon the stress and for the most part independent of prior stress changes. A permanent effect like damage to body organs or biochemical processes may result from exposure. Removal of the toxicant does not insure complete reversibility of the damage already inflicted.

In the medical world pharmacologists refer to a margin of safety for a drug. This is the dosage range between the dose producing a lethal effect and the dose producing a desired effect (Loomis, 1974). Another term for margin of safety is therapeutic index. The therapeutic index is obtained experimentally. Two dose-response curves are constructed using a toxicant and a target organism. One curve represents the therapeutic effect, the second curve represents the lethal effect. This is shown in Figure 6.2. Line A is the therapeutic response, line B is the lethal response. The ED_{50} and LD_{50} doses can be determined from the graph. The therapeutic index is expressed as the following ratio:

$$\text{therapeutic index} = \frac{LD_{50}}{ED_{50}}$$

Other authors have proposed that the following ratio be used:

$$\text{therapeutic index} = \frac{LD_{1}}{ED_{99}}$$

This is a more critical evaluation of the compounds safety. If these two values are used the margin of safety is reduced. Therefore, more care or discretion is applied when dealing with that compound.

In applying this same principle to the marine environment and to a factor of safety, the ED_{50} should represent a "no effect" level. This is essentially the σw concentration shown in Figure 6.1 (pg. 80). The safe level should be below the chronic level when possible. An obstacle that would arise would be an argument over the definition of a chronic effect. It might be difficult to measure or assess effects that are subchronic. Some chronic effects will be more detrimental than others and this will have to be examined carefully. Epifanio (1971) presented chronic effects on two species of crab larvae. Exposure to 1 ppb dieldrin lengthened and prevented the crab larvae's development. However, exposure to 0.05 ppb produced no noticeable effect. This is a factor of 20 between chronic and subchronic effects.

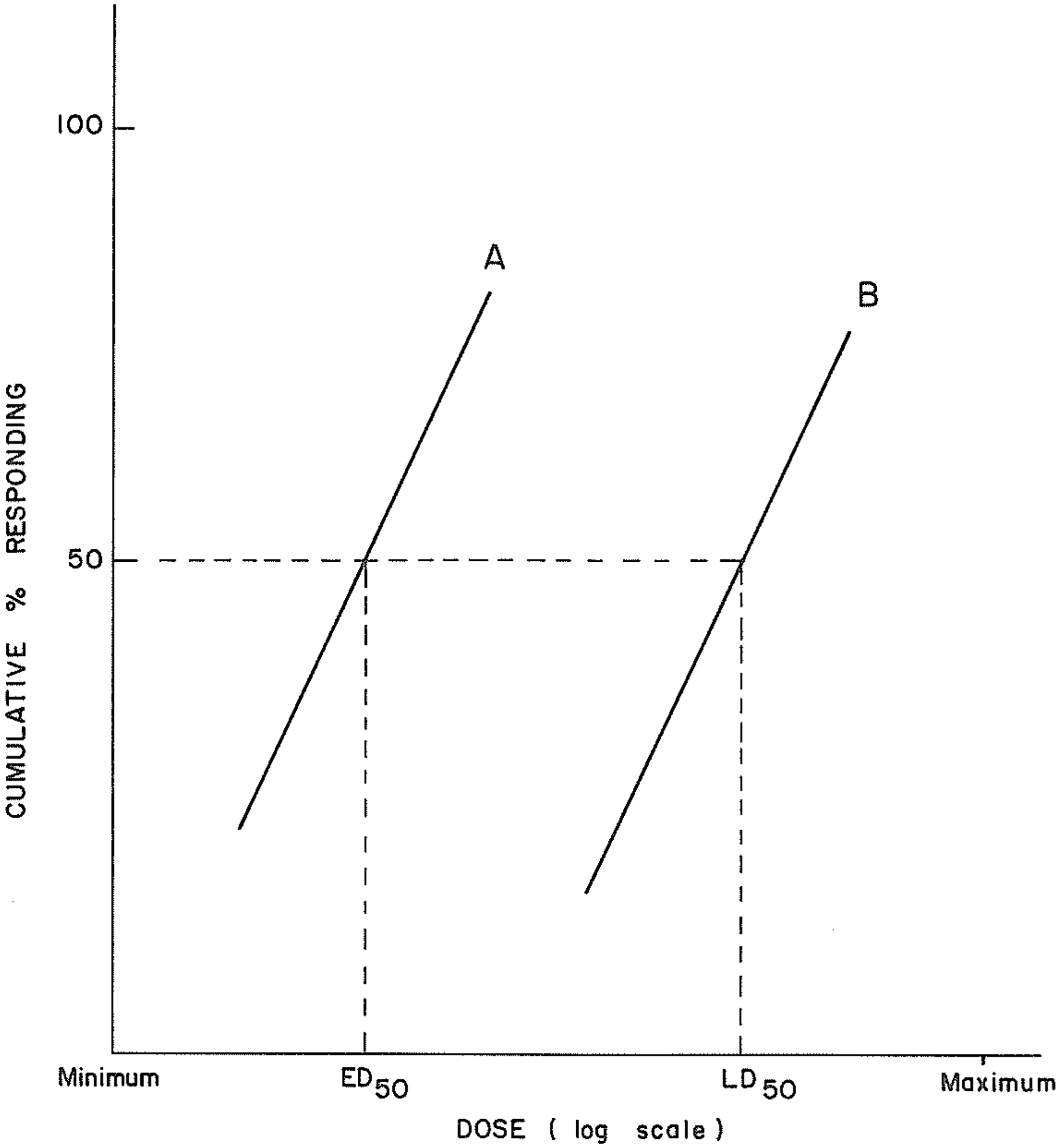

FIGURE 6.2. DOSE-RESPONSE RELATIONSHIP FOR A DRUG ADMINISTERED TO A TEST ORGANISM.

If the acute/chronic ratio were known in this case, one would only have to add the factor of 20 to it to obtain a factor of safety.

With some wastes there is a clear-cut distinction between harmful effects and subchronic effects. However, there do exist some categories of wastes where this distinction is not readily recognizable. Domestic sewage sludge and certain pharmaceutical wastes may indeed have a positive effect on marine organisms. The nutrients or stimulants present in these types of waste may actually encourage growth, provided the concentrations or dosage is not too great. Strictly controlled and monitored discharges of this nature could benefit selected areas in the ocean.

Conclusions

It is obvious that the application of a uniform safety factor will not always satisfactorily reduce the risk to the marine environment. For example the safety factor required for one class of compounds may not be applicable for another class. Certainly the safety factor necessary for domestic wastes is not as great as the one required for pesticides. There is a need to examine and define accurately the various categories of classes of waste compounds. Some categories are rather obvious; pesticides, industrial waste by-products, pharmaceutical wastes, domestic wastes, and dredge materials. These categories can also be divided into subclasses differentiating the basic constituents on the basis of chemical structure. Pesticides could be further divided into chlorinated hydrocarbons, organophosphates, carbamates, etc.

Before safety factors can be formulated for these categories much more research is needed concerning chronic or long-term effects. The research of the literature undertaken by this author has shown there to be a limited amount of data on chronic effects of industrial waste compounds. A majority of the studies involve pesticides. There definitely exists a need for more research on other classes of chemicals to bring into perspective the steps required to formulate a safety factor. With increased awareness and knowledge of the variables and relationships presented in this report, at least a start in the right direction is possible. This should encourage more research and understanding in the risk involved with ocean dumping.

The most appropriate organisms should be used for the actual testing. Thorough baseline studies of disposal sites are necessary to assess which organisms will be most affected by waste disposal, and which of these are most sensitive or vital to the marine ecosystem. Preferably the most appropriate organism should be tested when it is in its most critical growth stage.

With the development of more efficient waste disposal alternatives, ocean disposal of industrial wastes is being reduced and may even cease in the future. However, with the increasing demand for natural gas and oil, the feasibility of some alternatives is becoming economically unsound. Thus, there is a demand to return to ocean dumping. This demand may be strengthened by future high waste treatment requirements which generate greater masses of residues. Until the long-term effects of ocean disposal can be completely assessed no absolute decision concerning ocean disposal should be formulated. Thus, the quest for knowledge relating to ocean dumping should continue.

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