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**IMCO / FAO / UNESCO / WMO / WHO / IAEA / UN
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OF MARINE POLLUTION
- GESAMP -**

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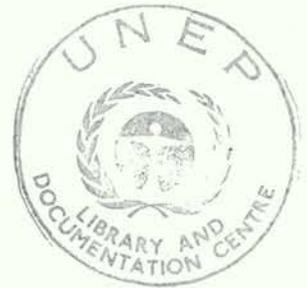
REVIEW OF HARMFUL SUBSTANCES



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IMCO/FAO/UNESCO/WMO/WHO/IAEA/UN Joint Group of Experts
on the Scientific Aspects of Marine Pollution (GESAMP)

REVIEW OF HARMFUL SUBSTANCES

UNITED NATIONS
New York, October 1976

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Explanatory note

This document is the edited and approved version, which appears in English only, of the Review of Harmful Substances which has been discussed, revised and approved by plenary sessions of the Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP). In this sense all marine pollution experts attending the first to the seventh sessions of GESAMP have participated in the preparation of the Review. However, the detailed work, most of it done between GESAMP sessions, has been the responsibility of a series of working groups under the chairmanship of Dr. H. A. Cole. Those experts who participated in the working groups are listed in annex II of the Review, together with the technical secretaries of the sponsoring GESAMP organizations who assisted them in their work.

Financial support for the latter stages of the group's work and for the publication of the Review was provided by the United Nations Environment Programme (UNEP).

Abbreviations

BP	Boiling point
FP	Flash point
LC 50	Lethal concentration, 50 per cent (concentration of solute in ppm required to produce a 50 per cent mortality of the test animals)
MP	Melting point
ppm	Parts per million
SG	Specific gravity

1. INTRODUCTION

1.1 Pursuant to United Nations General Assembly resolution 2566 (XXIV) this report presents a first Review of Harmful Substances which may have deleterious effects on man's health and his economic and cultural activities in the marine environment and coastal areas.

1.2 Having regard to the importance of the living resources of the sea as a major source of protein-rich food and the need to develop these resources further wherever practicable, the present document has been prepared primarily with these considerations in mind. Other effects of the introduction of potentially harmful substances into the marine environment will warrant more extended treatment than has been possible to give in the present review, in particular the hazards to human health to which special consideration will be given in a later revision. It should also be emphasized that the review is concerned with the oceans as a whole, implying among other things that the dynamics, time-variability and circulation of the ocean have been borne in mind in the preparation of the report.

1.3 The present Review reflects the state of knowledge available to the experts at the time of its compilation, i.e. the years 1972-1974. Scientific knowledge is continually changing and developing, and as it does so, changes will be required in this Review. For this reason, this document will be updated regularly. It is strongly recommended that the most up-to-date version of it should be used whenever possible.

1.4 A bibliography of major source materials is included as annex I. This listing is not intended to be exhaustive but to represent the important reference works used by the experts. In addition, use was made of unpublished material available to individual experts. Some of this has now been published and appropriate references are included in the bibliography.

1.5 A large number of experts in many fields participated in the preparation of the Review which has taken place over several years. A list of these experts is attached as annex II.

1.6 The Review is intended to be used by administrators and others concerned with the over-all management of waste disposal who require both general and specific information and evaluations of the hazards of various substances in the marine environment. Although the tables provide a valuable means for rapidly finding the degree of importance of various substances as pollutants, the reader is urged to refer to the text for more detailed information and specifications. Use of the tables without reference to the text could be misleading.

1.7 This Review deals expressly with substances in the marine environment. It should be noted that the World Health Organization (WHO) has much more detailed information on, and is making a continuous assessment of, the hazard to man posed by many of these substances under a variety of environmental and other exposure situations. WHO documentation should be consulted for a fuller appreciation of the hazards to man.

1.8 Similarly, more extended and detailed reviews of the hazards associated with radioactivity are available from the International Atomic Energy Agency (IAEA).

2. GENERAL NOTES ON THE REVIEW

2.1 A general problem that arises in connexion with the toxicity of certain metals is that the interaction between them is not well understood, although it has clearly been demonstrated that in the presence of one element, the anticipated toxic effect of another may not be fully observed. Cadmium and zinc, lead and calcium react in this way. The interaction of mercury and selenium is noted below.

2.2 It should be noted that bioaccumulation of heavy metals is a reversible process and that, with many organisms, the increased metal levels that occur following an acute exposure will fall once the source of pollution is removed.

2.3 It is stressed that the toxicity effects of metals can only be considered in relation to the valency state(s), solubility, stability of complexes and many other factors. This is particularly true of the short-term effects. Consideration of longer-term effects must also take into account the forms to which the metals and other materials are converted in the marine environment.

2.4 Some chemical substances may be altered by marine organisms or they may have a synergistic effect with another substance resulting in a higher level of acute toxicity than would otherwise have been expected. Little is known about the mechanism by which some of these processes take place. There is evidence that in some instances trace elements may trigger toxicity cycles in marine organisms; further investigation of ecological conditions which may lead to the production of biotoxins is highly desirable.

2.5 With regard to the sources from which pollutants originate, it is generally agreed that this is where measures of prevention or control can be most effectively applied. To facilitate further consideration of the desirability and feasibility of national control measures and international agreements, the main routes by which marine pollutants are currently known to reach the sea are indicated in table 2.

2.6 Attention is also drawn to the fact that the cargoes carried by ships include a wide variety of noxious substances, falling within the categories listed in Table 1, which may be discharged into the sea either by accident (such as in collision, stranding, fire or storm damage) or deliberately, such as in the tank cleaning and ballasting operations of a tanker or other bulk cargo vessel. A particular pollutant may therefore be subject to control under separate regulatory agencies, one associated with transport by sea (e.g. by legislation arising from the Intergovernmental Maritime Consultative Organization (IMCO) Conventions) and the other with its use or production ashore. Because of differing conditions under which the discharge is made however each regulatory agency may be obliged to apply quite separate and distinct measures of control in respect of the substance in question. In response to a specific request from IMCO, a panel of IMCO and GESAMP Experts was set up in 1972 to review the environmental hazards of

noxious substances other than oil transported by ships. The report of this panel (GESAMP IV/19/Supp.1) has now been published and has been used as a reference document for evaluating the hazards of harmful substances for the purposes of the International Convention for the Prevention of Pollution from Ships, 1973. It must be emphasized that that report relates only to the particular circumstances under which discharges occur in maritime transport and should not be used for other purposes, particularly the control of continuous discharges from direct outfalls which are generally located in inshore waters.

2.7 The Group is not aware of any situation in which the release of radio-active materials to the sea by the nuclear energy industry has produced adverse biological effects. This situation has resulted from the very firm control imposed by national Governments over this industry since its beginning. The work done on the study of the dispersion, effects and fate of radio-active materials in the marine environment has been, and continues to be, extensive. It has had the result that the status of radio-active materials as potential pollutants of the marine environment is more clearly defined than that of most other materials recognized as serious pollutants.

2.8 The routes by which marine pollutants enter the sea have been identified under the following main headings:

- (a) disposal of manufactured and industrial products or of the waste resulting from them by direct outfall or via rivers;
- (b) disposal of domestic sewage by direct outfall or via rivers;
- (c) run-off from the land of materials used in forestry, agriculture, or public health activities;
- (d) deliberate dumping of material from ships;
- (e) operational discharge of polluting materials by ships in the course of their normal tasks;
- (f) accidental release of material from ships or submarine pipelines;
- (g) exploitation of the sea-bed for petroleum or other mineral resources; and
- (h) transfer of pollutants to the ocean from the atmosphere.

These descriptions are included in table 2 and the importance of each of them as a route by which different categories of pollutants enter the sea has been shown by the use of a number of symbols. To aid in the study of Table 2 each category of pollutant is the subject of an explanatory note which gives, where appropriate, further information on main uses, principal sources and pathways to the marine environment, mode of occurrence and distribution, toxicity, breakdown products, degree of persistence and accumulation in biological materials, and known effects.

Attention is called to the fact that there is an increasing number of potentially harmful substances that may appear in effluents discharged into the

marine environment many of which have not so far been covered in the Review. These substances are present in industrial wastes frequently as a result of complex manufacturing processes.

2.9 Although to an increasing extent measures of prevention and control, both national and international, are being introduced for certain pollutants, the Group recommends that further consideration be given especially to those categories shown in table 1 as "important" or "significant" with a view to improving the effectiveness of existing legislation and, where necessary, taking further action nationally and, where appropriate, internationally (e.g. on a regional basis) to limit or control their discharge into the sea.

3. NOTES ON MAJOR CATEGORIES OF MARINE POLLUTION

3.1 Domestic sewage

When discharged untreated, domestic sewage has five major characteristics:

(a) a high bacterial content, presence of parasites and possibly virus concentrations, contaminating molluscan shellfish (necessitating purification or heat sterilization) and limiting the use of bathing areas;

(b) dissolved organic and suspended constituents which give a high biochemical oxygen demand;

(c) settling solids (organic and inorganic) depositing on the bottom - the organic component undergoes decay with consequent oxygen depletion;

(d) high nutrient concentrations (mainly phosphorus and nitrogen compounds) leading to enrichment of receiving waters and potential hypertrophication;

(e) floatables, which may be organic or inorganic materials on the surface or in suspension, constituting a serious amenity problem and interfering with primary production and affecting self-purification.

By reason of these characteristics sewage affects recreation, utilization of seafood, public health and general amenities. The production characteristics of the receiving waters may be altered and there is a possible connexion with the development of toxic blooms of algae.

One of the reasons for the need to control pollution by sewage is the maintenance of shellfish quality. The standards of treatment and/or dilution required for this purpose are somewhat higher than those presently demanded for other public health or amenity purposes. Filter-feeding molluscan shellfish concentrate bacteria and viruses along with other particulate materials and the consumption of contaminated shellfish may give rise to enteric infections. The transmission of the viral disease, infectious hepatitis, by consumption of raw shellfish contaminated by sewage is well documented. Methods of purifying shellfish from the effects of bacterial contamination are available and are extensively used in many countries but are not yet fully acceptable in all situations.

Various degrees of treatment of domestic sewage eliminate or reduce some of the foregoing polluting characteristics: primary - normally eliminates the settleable solids and floatables and proportionally reduces the microflora; secondary - clarifies the effluent from the finer colloidal suspensions, mineralizes organic substances (reducing the biochemical oxygen demand) and disinfection can provide a further removal of pathogenic forms; tertiary - removes the plant nutrients by biological or chemical action, or by a combination of the two, and reduces the suspended solids still present as well as decolorizing

the effluent. Much coastally discharged sewage receives no treatment beyond comminution or maceration; this accelerates breakdown and is an improvement from the amenity standpoint but only marginally reduces bacterial or viral contamination and nutrient content. Where practicable, separation of storm water and foul sewage systems is highly desirable, to prevent interference with treatment processes during periods of heavy rainfall.

Other household wastes which enter the municipal sewer include detergents and optical brighteners (dealt with in another section of this report), pharmaceuticals, house and garden pesticides and other chemicals, and oily and other discharges from small businesses and garages, may also be important. However, apart from the considerations mentioned above, the major problems of municipal sewage disposal arise from the inclusion of industrial wastes with materials discharged from municipal sewers. The tendency to replace sewage treatment works by long outfalls, discharging well away from the shore into deeper water, has led to the inclusion of greater quantities of industrial wastes with domestic sewage. Such wastes may contain toxic and persistent materials (e.g. metallic wastes) in concentrations which, if they were accepted by a treatment plant would reduce its efficiency. Such pipeline discharges may adversely affect marine resources, particularly shellfish and young fish on coastal nursery grounds. Pre-treatment at source of industrial wastes before discharge to sewers should become standard practice. There has been a similar tendency to replace estuarine discharges by long trunk sewers leading to marine outfalls. Careful siting of all such outfalls in relation to dilution characteristics of receiving waters, other existing or projected outfalls, and presence of exploitable marine resources is essential.

The practice of disposing of sludge from coastal sewage treatment works by dumping at sea may be harmful because such wastes may contain significant amounts of absorbed metals e.g. mercury and other metals, and also pesticide residues and other persistent chlorinated hydrocarbons. These factors and possible biological effects, e.g. interference with benthic fauna, need to be considered in deciding disposal procedures for sewage sludges and the selection of dumping zones (see GESAMP VII, annex V).

3.2 Pesticides

The term "pesticides" covers a wide range of substances of differing chemical composition and class of target organism. They are considered here under seven headings, organochlorine compounds, organophosphorus compounds, carbamate compounds, herbicides, mercurial compounds, miscellaneous metal-containing compounds and polychlorinated biphenyls. The latter are not pesticides, but have been widely used in industry and can conveniently be discussed in the same group as organochlorine pesticides.

3.2.1 Organochlorine compounds

Much information is available on this group of pesticides, some of which have been in use for more than 30 years. The most commonly used are probably DDT, BHC,

Dieldrin, Endrin, Aldrin and Endosulfan; all are used as insecticides, either for agricultural or public health pest control. Use is frequently on a fairly large scale and spraying from the air is a common means of application in some areas. Not all the material sprayed will reach the target area (less than 50 per cent in some instances) and some will inevitably be lost to the atmosphere. Of this, a proportion will reach the sea by exchange with the atmosphere, in rain or absorbed on air-borne particulate matter. Since organochlorine compounds are strongly absorbed on particulate matter and are relatively insoluble in water, it is unlikely that they will reach river systems except under flood conditions where soil particles are washed into rivers. Although comparatively non-volatile, organochlorine compounds may be lost from the soil by evaporation and particularly by codistillation with water. In addition, soil erosion by wind may carry a proportion of the applied chemical into the sea. Aerial transport accounts for at least 50 per cent of the material reaching the sea.

Mothproofing of wools and woollen garments and carpets may lead to discharge of insecticidal formulations (e.g. Dieldrin) directly to rivers and hence to the sea. Recent analyses of sewage and sewage sludges suggest that these may also be an important route of entry of pesticides to the sea.

Estimates of the proportion of the annual production of organochlorine pesticides reaching the sea have ranged as high as 90 per cent but a more accurate estimate may be 40-60 per cent.

Once in the sea, organochlorine pesticides may be concentrated either in surface slicks or by marine organisms. Some will be carried to the sea-bed on particulate material and a certain amount will remain dissolved in the sea water at a very low concentration. From analyses of marine animals, some of the organochlorine pesticides, particularly DDT, are known to be distributed on a world-wide basis. Concentrations in coastal waters can be determined, but oceanic waters contain levels below the normally accepted detectable level, i.e. 1 part in 10^{12} . Owing to the lipophilic/hydrophobic character of organochlorine pesticides, they are particularly likely to be concentrated in any oily material, e.g. fish oils. They are, therefore, found in appreciable concentrations in many marine organisms, especially those with a high lipid content and those organisms highest in the food chain. Residence time in the environment has not been accurately determined for all of them but seems to be generally of the order of years rather than months.

Although some have been used for more than 30 years, the precise mode of action of organochlorine pesticides is not fully understood. It is, however, generally accepted that they affect the transmission of impulses in the central nervous system. Recently, subtle sub-lethal side effects have been recognized, e.g. on calcium deposition in birds' eggs. Their acute toxicity to marine organisms is now fairly well documented. Crustacea are particularly sensitive; DDT concentrations as low as 0.003 ppm in water have been shown to be lethal to shrimps, but fish can tolerate concentrations up to two orders of magnitude higher - at least for a short time.

There is no evidence that the proper use of organochlorine pesticides has adversely affected human health, nor have there been any incidents where humans have been affected by eating fish contaminated with organochlorine pesticide residues. Effects on fish and shellfish populations have been demonstrated in certain estuarine environments, particularly in North America. Most of the incidents have been kills as a result of spray operations, but at least two instances have been reported where reduced breeding success of estuarine fish has been attributed to organochlorine pesticide residues arising from routine usage on the land. Predatory birds are particularly vulnerable; the reduction in numbers of brown pelicans, bald eagles and peregrine falcons in North America is attributed primarily to DDT and allied chlorinated hydrocarbons.

3.2.2 PCBs

Polychlorinated biphenyl compounds (PCBs) are sold under a variety of brand names. There is a variety of formulations depending upon the degree of chlorination of the biphenyl molecule; the greater the degree of chlorination the higher the viscosity. PCBs have had a wide range of industrial uses, particularly in the electrical industry. Because of widespread contamination of the environment, usage has now been restricted in a number of countries to applications where loss to the environment is unlikely. The routes of entry to the marine environment are still under investigation, but any industrial use inevitably involves some losses which may eventually reach the sea. Analysis of sewage sludges has revealed that most sewage contains some PCBs. The dumping of waste materials containing PCBs is probably largely on land. PCBs are highly resistant to burning and unless incineration is properly carried out (a temperature of over 800°C is required), burning of materials containing PCBs will simply release them to the atmosphere for subsequent rain-out into the sea. Disposal by dumping in the sea of wastes containing PCBs, except as trace contaminants, is forbidden under the terms of the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (London, 1972).

In occurrence and distribution, as well as persistence and accumulation, PCBs behave in much the same way as organochlorines and much that has been written above regarding these pesticides will also apply to PCBs. They have been in use for a slightly longer period and, at least in the marine environment, are just as widely spread as DDT and their persistence and concentration in marine biota is, if anything, greater rather than less than that of DDT.

The mode of action of PCBs is not well understood but may be similar to that of organochlorine insecticides. Certainly PCBs have been implicated in shell thinning of birds' eggs. The acute toxicity of PCBs is in general lower than that of organochlorine pesticides. There is some evidence, however, to suggest that they have a high chronic toxicity; it may take a matter of weeks before a short-term low-level exposure takes effect. This may be attributable to impurities in certain formulations.

In incidents of accidental ingestion or gross industrial exposure, illness and even death have been reported in humans, but there are no known ill effects

on man which can be associated with levels of PCBs in marine products. Even in estuarine environments, PCBs have not been implicated in any damage to marine life, although in some areas quite high levels have been reported in fish. The presence of high concentrations of PCBs in the livers of sea birds was suggested as a possible contributory cause in a large-scale bird kill off the United Kingdom coast in 1969, but it is now generally accepted that natural causes played the major role in causing this bird mortality.

3.2.3 Organophosphorus compounds

This group of compounds includes Malathion, Parathion, Azinphos-methyl and Chlorfenvinphos and, with the carbamate compounds, is to some extent replacing the organochlorine insecticides. In chemical terms, they are more varied than the organochlorines, although they all contain phosphorus. They are relatively soluble in water, and may be carried into rivers, and hence the sea, in substantial amounts, by run-off from land. Spray losses and evaporation of sprayed material, followed by rain-out over the sea, is a second probable route of entry to the marine environment. Industrial usage is probably small and therefore an insignificant source of pollution.

Most organophosphorus compounds are chemically less stable than the organochlorine type and they are therefore much less persistent in the environment. Most are hydrolysed on contact with water and they are much less hydrophobic than organochlorines. As a result bio-accumulation is likely to be unimportant.

Because they are less persistent and non-accumulative, not much effort has been applied to the study of the role of organophosphorus compounds in the sea. They are likely to be present in true solution and, since they are not particularly lipophilic, they are unlikely to be concentrated in surface slicks. Because they are not persistent, it seems unlikely that they will be found in ocean waters and there appear to be no reports of their occurrence in waters other than estuaries.

Organophosphorus compounds act on the nervous system by inhibition of cholinesterase activity. Their acute toxicity to marine animals is reasonably well documented and appears to differ widely according to the particular compound used, e.g. Azinphos-methyl was lethal to Crangon crangon at a concentration of 0.0003 ppm but Morphothion had no effect on the same species at 0.3 ppm. The mammalian toxicity of some organophosphorus compounds is high but residues have not so far been detected in marine organisms other than a few estuarine species and no cases of poisoning through the eating of organophosphorus pesticide-contaminated fish have been reported or indeed seem likely to occur.

3.2.4 Carbamate compounds

These compounds, which are based on carbamic acid, are of two basic types, the N-dimethylcarbamates e.g. Isolan and Dimetan, and the M-methylcarbamates, e.g., Carbaryl and Zectran. In general, they are less soluble in water than the

organophosphorus compounds but more so than the organochlorides. Some of these materials, particularly Carbaryl (Sevin), are now in fairly widespread use. They are likely to reach the sea by all the routes quoted for organophosphorus compounds. The main usage of carbamates is in agriculture but Carbaryl is to some extent replacing DDT and may be used in future malaria control operations. It also has a small-scale role in mariculture as a means of controlling crustacean pests in shellfish cultivation programmes. This provides a direct route of entry to the marine environment.

None of the carbamate compounds is particularly stable; they are attacked by acids and alkalis and it is probable that slow hydrolysis will occur once they reach the sea. They can be relatively easily metabolized and the data available for marine animals suggest that, once taken in by, for example, a bivalve, they can be completely metabolized and/or excreted within 2-3 weeks. They are therefore unlikely to pose much of a hazard as a result of persistence or accumulation. Carbamate compounds have not been detected on a wide scale in sea waters or marine animals but they are known to be readily absorbed on silt and small concentrations may be found in estuarine sediments following local use on land and in mariculture.

Carbamate compounds are cholinesterase inhibitors; a few also show activity against other enzyme systems. A few of these compounds are also used as herbicides and they might be expected to have minor effects on the phytoplankton in local areas. The toxicity of carbamate compounds to marine animals follows the same highly variable pattern, depending on compound and species, which they exhibit in the terrestrial environment. Carbaryl is moderately toxic to crustaceans but not to fish or molluscs. With the exception of Isolan, all the carbamate compounds are of low mammalian toxicity, and harm to human health, either directly or indirectly, through eating fish or shellfish, seems improbable. Isolan is of a lower mammalian toxicity than the organophosphorus compounds.

3.2.5 Herbicides

Herbicides are a mixed group of compounds, most of which have water solubilities of the order of tens of ppm or more. They include urea-based compounds such as Linuron, dipyridyl compounds such as Diquat, and acid ester hormone type compounds such as MCPA and 2,4-D. The major routes to the marine environment are probably direct water transport from the land or spray drift and subsequent rain-out over the sea. Most of these compounds are likely to be found in dissolved form but a few, e.g., Diquat, are strongly absorbed by particulate matter and will be largely associated with sediments or suspended material. Very little attention has been paid to herbicide compounds to date and the extent of their distribution in the marine environment is a matter of speculation. Most are comparatively short-lived but a few, e.g. 2,4,5-T and Picloram, have half lives up to 5 years. The genetic damage attributed to 2,4,5-T is now generally considered to be due to the presence of impurities.

Few of the herbicides are particularly toxic to fish and it seems unlikely that appreciable effects would be noticed. The main effect of herbicides in the

marine environment might be expected to be on the phytoplankton but very few data appear to be available on this subject. Tests with unialgal cultures at the United Kingdom Fisheries Laboratory, Burnham-on-Crouch with 2,4-D, Dalapon and two triazine compounds (Atrazine and Simazine) suggest that at least some herbicidal compounds tend to stimulate growth of algae rather than to kill them. Dalapon is used in *Spartina* grass control in salt marsh areas but does not seem to cause mortality of marine creatures at the levels normally used. Paraquat has a high mammalian toxicity if directly ingested and there is no known antidote, but its toxicity to marine life is low and it is strongly absorbed on particulate material.

3.2.6 Mercurial compounds

A variety of organic mercurial compounds is used in agriculture and horticulture for the control of seed-borne and fungal diseases. They have been used extensively in the past as slimicides in the paper industry. Calomel is used in some areas as a fungicide and insecticide.

Most of the mercury compounds used have a low water solubility and, in addition, are strongly absorbed on to soil particles. They are therefore only likely to find their way into the aquatic environment in times of flood. Mercury compounds are readily converted under anaerobic conditions to methyl mercury. There is some evidence to suggest that dimethyl mercury is readily volatilized and could subsequently find its way into the sea. The importance of this and other routes has still to be established and modes of entry into the marine environment are the subject of study at the present time.

Mercury occurs naturally in the marine environment as a result of the normal processes of weathering of rocks. The data available at present suggest a concentration of mercury in sea water in the range 0.03 to 0.3 ppb. Methyl mercury concentrations are probably about 1/1000 of this level. Locally higher concentrations have been recorded in coastal waters and are attributed to industrial pollution. Most mercury compounds decompose to the ionic form which is then available for methylation. Mercury as an element is a highly conservative and persistent substance in the marine environment. Although the inorganic form does not pose much of an accumulation hazard, methyl mercury is very readily taken up by marine organisms and accumulated in the food chain. Methyl mercury has a high mammalian toxicity and produces nervous disorders and death at low levels of dietary intake. One ppm of mercury is considered by many national Governments to be an unacceptably high level for food fish. However, such levels appear to have no ill effects on the fish and in certain species are even considered to be the norm by some authorities. Only in instances of extremely high mercury pollution have definite ill effects been observed in marine organisms. Normal levels of mercury in fish are probably in the range 0.01 to 0.2 ppm. Certain pelagic fish e.g. tuna and swordfish, contain somewhat higher levels but these do not seem to have changed during this century.

3.2.7 Miscellaneous metal-containing pesticides

In addition to the compounds already discussed, there are a small number of metal salts and organo-metal compounds which are used as pesticides, e.g. Bordeaux mixture (copper salt), lead arsenate and fentin acetate. These compounds have appreciable solubilities in water and are likely to be transported to the sea by land run-off and drainage. Their contribution in terms of quantity of metal ions or compounds added to the sea is negligible compared to those from other sources, e.g. lead from automobile fuels, copper from industrial wastes. It seems unlikely, therefore, that harmful effects in the marine environment would arise from their use on the land. Most of the metal-containing pesticides are toxic to fish and improper use has caused fish kills in inland waters. It is therefore, conceivable that, in the marine environment, local damage may occur, e.g. in estuaries, but the risk to humans is negligible.

3.3 Inorganic wastes

Most of the elements listed in the periodic table are present in sea water in at least one form of ion or complex and their introduction does not necessarily constitute pollution, although similar amounts discharged to fresh water areas might do so. In addition, because sea water has a high buffering capacity when compared to fresh water it is able to absorb some inorganic pollutants, e.g. acids, with relatively little change. These are two important factors which must be borne in mind when considering inorganic substances as marine pollutants.

Of the various inorganic compounds or ions which are likely to enter the marine environment a number can be selected as potential pollutants in certain circumstances - the remainder might, at the worst, be defined as contaminants.

3.3.1 Acids and alkalis

The production of many inorganic chemicals and some organic chemicals may give rise to large quantities of waste acid or alkali which may be discharged to the marine environment. Sulphuric and hydrochloric acids are most likely to be discharged, but smaller quantities of nitric acid may also be discharged. The effects of nitrate and sulphate are considered below but chloride, already present in large amounts in the sea, cannot be considered as a pollutant. The alkalis involved are lime, sodium hydroxide and, to a lesser extent, potassium hydroxide and ammonia. The ammonium cation is considered separately below but sodium and potassium fall into the same category as chloride.

Sea water has a considerable buffering capacity, i.e. it can absorb relatively large amounts of acid or alkali with comparatively small changes in pH. Discharges of unneutralized acid or alkaline effluents are frequently made into estuaries and quantities of waste acids are dumped by barge away from the shore. A second major source of acid is the burning of fossil fuels which releases quantities of sulphur dioxide and acid oxides of nitrogen into the atmosphere (50-80 million tons annually). These may subsequently be rained out over the sea, but although rainfall containing sulphur dioxide (i.e. acidic) may have affected the pH of some

Swedish lakes, a similar effect on the sea seems unlikely. Burning of chlorine-containing compounds, particularly substances such as PVC, gives rise to large quantities of HCl gas, which on dissolution, e.g. in rainwater, is a further source of acid and one which may grow in extent.

Although the effect on the pH of sea water of acids from the atmosphere cannot be detected, pH changes can be detected over relatively small areas in the proximity of discharges of acid or alkaline wastes both in estuaries and in the open sea in the wake of a discharging barge. It must therefore be concluded that discharges of acids or alkalis have only a local effect and that their distribution, although possibly world-wide, is completely accommodated by the carbon dioxide buffer system and has no effect.

The acute toxicity of both acids and alkalis to some marine animals is documented and, presumably because of the buffering capacity of the sea water, moderately high concentrations - several hundreds of ppm - have no effect. Fish and small crustacea can detect concentrations of acids and alkalis below the acutely toxic level and will avoid such concentrations. The toxic action of both acids and alkalis is probably mainly associated with the effect that they have on the oxygen-carbon dioxide transfer across the gill surface. At higher concentrations their corrosive action would undoubtedly be lethal.

3.3.2 Nutrients and ammonia

Phosphate enters the sea via rivers and directly from outfalls via sewage, where its origin is largely polyphosphate from detergent formulations. Small amounts may also be discharged by industry and some will enter as runoff from agricultural land. Sewage effluents contain nitrate and ammonia + nitrite both of which are oxidized by bacteria to nitrate. Ammonia may reach the marine environment in sewage effluents and as a result of its use in industrial processes and in agriculture. In addition large quantities of ammonium sulphate are produced as by-products in certain industrial processes. Some of this is considered waste and is discharged to the sea.

The concentration of ammonium ion in sea water is low (generally of the order of 5-50 $\mu\text{g}/\text{l}$) although locally it may be high near a discharge of nitrogen-containing waste. It is one of the intermediates in the bacterial decomposition of nitrogen-containing compounds which eventually terminates at nitrate. Ammonia is not therefore a persistent substance and large-scale distribution of high concentrations is unlikely. Nitrate and phosphate are essential nutrients in the productivity of the marine environment. Over-abundance of these ions in freshwaters can lead to hypertrophication with blooms of phytoplankton, followed by deoxygenation and anaerobic decay. Such phenomena have been recorded in the marine environment in fjord and estuarine areas (e.g. Oslo Fjord) and may become a problem in some enclosed seas. Both nitrate and phosphate are absorbed on particulate matter and the sediments provide a reservoir and means of storage of excess nutrients. Although persistent, neither nitrate nor phosphate constitute accumulation hazards within marine animals and there is no evidence to suggest that concentrations less than grossly excessive would be toxic.

3.3.3 Cyanide

Wastes containing cyanide are discharged to rivers, estuaries and on open coasts from a variety of industrial premises, e.g. metal plating plants, gas works and coke ovens, and from the scrubbing of steel works gases as well as a number of chemical processes. Direct discharges such as these account for most of the cyanide entering the marine environment, but small quantities are dumped directly into the sea, usually in deepwater. Discharge of HCN, NaCN, KCN and similar simple cyanides leads to the formation of HCN, with some subsequent dissociation to CN⁻. It is now generally accepted that HCN is much more toxic to aquatic life than CN⁻ and at pH 8 only about 7-10 per cent of the HCN is dissociated. Cyanide is biodegradable and treatment methods are available which can eliminate the need to discharge cyanides. The biodegradability of cyanide and the readiness with which it forms complexes with certain metal ions, e.g. copper and iron, means that large-scale distribution of cyanide is unlikely and that any detrimental effects would be local in nature.

3.3.4 Antimony

The over-all crustal abundance of antimony is of the order of 0.1-0.2 ppm, and except where antimony minerals are found, there is little local enrichment. Oxide minerals are known, but almost all the production is from sulfide minerals, including complex sulphides and subsequently with other metals.

World production is mainly from South Africa, China, Bolivia, Mexico, Morocco, Yugoslavia, Turkey, the United States of America and the USSR. Smaller quantities of antimony are produced from Czechoslovakia, Australia, Austria, Italy, Peru and Thailand. A considerable amount of antimony is recovered from scrap (principally lead-antimony alloy) and recycled. There has been little change in the world antimony production from 1964 to 1973 at about 65-72,000 tons per annum. The recovery of antimony from its ores is by volatilization and pyrometallurgical techniques and a number of different processes are in use.

The chief use of antimony is as an alloying element, particularly with lead, to form plates for storage batteries, as a cable covering, in type metal, fusible alloys, etc. Antimony sulphides and trioxide are used as pigments and there are smaller uses in the glass industry, in the striking surface of match boxes and in ammunition.

Smelting of antimony ores is carried out in both the countries in which the ore is produced and in industrialized countries. Antimony concentrates, crude antimony sulphides and metallic antimony are transported by sea. Loss of a shipment could give rise to a local problem.

Only small quantities of antimony are likely to be introduced to the sea by weathering (estimated at 1,300 tons annually), or by fossil fuel burning. Normal levels in sea water are reported to be of the order of 0.1-0.5 µg/l. Freshwater streams have been reported to contain about 2 µg/l.

There does not appear to be any information on the toxicity of antimony to marine animals but in freshwater acute toxicity levels of between 10 and 20 mg/l have been recorded for crustacea and fish. Normal contents of antimony in marine organisms are reported to be between 0.7-50 mg/kg for bivalve species representing a concentration factor over sea water of the order of 10^4 - 10^5 . Shrimp were reported to contain between 0.05 and 0.8 mg/kg dry weight and fish 0.019-0.13 mg/kg dry weight. In higher marine animals, e.g. seals, antimony could not be detected at 0.01 mg/kg (detection level).

Adverse effects on health have been noted in those exposed industrially and therapeutically to antimony compounds. There are certain similarities to arsenic but unlike arsenic it shows no tendency to be stored in tissues and also shows differences in toxicity. Contact with polluted sea water and consumption of seafoods from polluted areas are unlikely to constitute a hazard.

3.3.5 Arsenic

Arsenic is widely distributed in crustal rocks but at only a very small

concentration - an over-all abundance of about 2 ppm has been suggested. Rocks are known which contain much higher quantities, usually in the form of the mineral arsenopyrite (FeAsS). Strictly speaking, the word arsenic refers to the element, although in commercial practice it is often used for arsenious oxide, As_2O_3 , known also as white arsenic.

World production of arsenious oxide, from the flue dusts obtained from the roasting of arsenical ores, exceeds 30,000 tons per annum; France and Sweden being the major producers. There is important production also from Germany, Portugal, Spain, Namibia, Mexico, Brazil and Peru. Many other countries have produced small quantities. In addition considerable quantities of arsenic-containing materials are disposed of as waste products.

Arsenious oxide is used in the manufacture of insecticides, wood preservatives, anti-fouling paint, and weed killers. Smaller uses include as a constituent of some vitreous enamels, and in the metallic form as an alloying element with e.g. lead, antimony and copper.

Weathering of the earth's crust is said to introduce up to 72,000 tons per year via rivers and the burning of fossil fuels a further 700 tons, mainly from coal. This latter figure however is low in comparison with the recent estimates of atmospheric input from all sources via rain to the North Sea of 1,000 tons per year. Considerable amounts are likely to enter the sea as a direct result of metal processing operations in which arsenic is evolved as the oxide and discharged in flue gases or washings.

In the Clyde Estuary (Scotland) arsenic is reported to be present in the surface sediment at an average level of 21 mg/kg in the area where sewage sludge is deposited. The "background" level in this estuary is reported to be about 8 mg/kg. Sediments off the United States of America coast contained 3-15 mg/kg arsenic and deep sea sediments contained similar amounts. Much higher concentrations were, however, found in sediments in the vicinity of an arsenic smelter in the United States of America (290-980 mg/kg).

In sea-water arsenic occurs normally in concentrations of the order of 2 μ g/l. Fresh-water streams contain a similar amount. Two valency states are possible and both the trivalent (arsenite) and pentavalent (arsenate) have been reported. The most likely form however is arsenate since arsenite is readily oxidized.

Elemental arsenic is virtually non-toxic to marine organisms; the trivalent form is more toxic than the pentavalent form. Most of the toxicity data refer to the arsenite form and the acutely toxic level is reported to be within the range 1-10 μ g/l for a wide variety of marine organisms, and the in-tissue levels associated with death of Crangon exposed to arsenic in solution ranged from 10-100 mg/kg. The normal background levels observed in marine animals are usually lower e.g. molluscs 0.4-1.3 mg/kg, crustacea 1-10 mg/kg, fish 0.1-10 mg/kg, but much higher concentrations have been recorded in apparently healthy animals e.g. 120 mg/kg in mussels, 170 mg/kg in prawns and up to 100 mg/kg in fish (all concentrations on a wet weight basis).

Certain inorganic arsenic compounds are known to be carcinogenic and are highly toxic to man on acute or long-term administration, producing gastrointestinal, skin, liver and nerve tissue injuries, possibly by affecting enzymes containing sulfhydryl groups with which arsenic forms additive compounds. Although certain arsenic compounds readily penetrate the skin, it is most unlikely that arsenic-polluted sea-water would contain a sufficiently high concentration to cause acute or long-term injury to those exposed to it. Organic arsenic compounds are generally of much lower toxicity, probably because they are more rapidly eliminated from the body than the inorganic forms. In the forms in which arsenic is present in food it is well absorbed but is also rapidly and almost completely eliminated in urine so that accumulation in tissues is unlikely except with high intake levels. All foods contain arsenic and the richest sources of dietary arsenic appear to be seafoods, especially shellfish and crustacea; severe or prolonged pollution of the sea with arsenic must be avoided in those areas from which these species are taken, especially if seafoods form a substantial proportion of the normal diet of the population.

3.3.6 Beryllium

Beryllium is a rare and dispersed element. Although most rocks contain a few ppm, local concentrations are rare. Production is entirely from the silicate mineral beryl, which contains 7-8 per cent beryllium.

The world production is not known, as significant contributions from the United States of America and the USSR are not recorded. Remaining production is about 6,000 tons per annum, largely from Brazil, with significant amounts from Uganda, Rwandese Republic and Burundi, South Africa, Zaire and Argentina.

The production of beryllium is a difficult and hazardous process, and as a consequence is undertaken only in the more highly developed countries, where stringent precautions are in force.

Beryllium has important uses in nuclear reactors, where it is used as a moderator for neutron flux, as a copper-beryllium alloy for non-sparking safety tools and other purposes, as a casting alloy, and in the form of the oxide as a refractory material.

Only very small quantities of beryllium - 410 tons per year - enter the atmosphere annually as a result of fossil fuel burning; a further 5,600 tons has been estimated to enter the sea as a result of weathering.

The normal concentration of beryllium in sea-water is reported to be of the order of 0.0006-0.005 $\mu\text{g}/\text{l}$ and concentration factors for aquatic organisms have been reported to be of the order of 10^3 .

There appears to be no information on the toxicity of beryllium to marine organisms. In freshwater its toxicity decreases markedly with increasing hardness of the water, e.g. the LC 50 for fathead minnows increased from 0.2-30 mg/l with a corresponding increase in hardness of 12-500 mg/l (calcium

carbonate). It therefore seems likely that the toxicity to marine organisms would be less than that reported for freshwater.

Severe toxic effects have been produced in workers who have touched or inhaled beryllium and its compounds during their production and use. The particular ill-effect depends on the route, frequency and degree of exposure, as well as on the particular individual exposed. Various types of skin changes occur in beryllium disease and lung disease can be acute in onset, develop over a period of years or become chronic after an acute episode. Only a small fraction of beryllium taken by mouth is absorbed. Most of that absorbed is excreted in urine and faeces but some accumulates in body tissues, particularly in bones, and is slowly excreted over a period of years. However, tissue levels are extremely low even in those exposed to high concentrations.

Although beryllium is dangerous industrially there is no evidence that the quantities and types of beryllium compounds likely to occur in the marine environment or in seafood taken from polluted waters will be in any way hazardous to human health. However, data are limited and caution is necessary.

3.3.7 Cadmium

Cadmium occurs naturally in association with zinc (and lead) and its production is entirely from zinc concentrates (sphalerite-ZnS). Its level of abundance in crustal rocks is low (about 0.2 ppm) but it occurs widely. Independent minerals are few and rare. It occurs widely in animals and plants.

World annual production is in excess of 15,000 metric tons and increased steadily up to 1969 after which there has been a slight fall. Areas of production are similar to those of zinc. Cadmium recovery from zinc and lead concentrates takes place mainly in industrialized countries. Only very small quantities are recycled.

Cadmium is used mainly in pigments (e.g. in paints, ceramics and glass), bearing metals, in fusible and other alloys, in batteries and in nuclear reactors, and in plating for corrosion inhibition and electrical contacts.

Probably the main mode of entry to the marine environment is from effluents derived from the plating industry. Sewage contains relatively small concentrations. Sewage sludge from Swedish municipal plants is reported to contain on average 16 mg/kg dry weight of cadmium. Glasgow sewage sludge (one observation) contained 12 mg/kg and the sediment in the deposit area in the Clyde Estuary, Scotland, contained 3-7 mg/kg dry weight compared with a background value in the "uncontaminated" area of 0.4 mg/kg. United Kingdom values of the cadmium content of sewage sludge range between 2.3 and 60 mg/kg dry weight.

There is a very small contribution from the burning of fossil fuels; discharge to the atmosphere from this source has been estimated at two tons per annum world wide. However, measurements of concentrations in rainfall over the

North Sea indicate an input via aerial deposition of 230 tons per annum. There are no global estimates for the amount of cadmium reaching the sea through river discharges. The cadmium input to the North Sea by the Rhine has, however, been estimated to be 50-100 tons per annum.

Cadmium is transported by ships as a component of zinc and lead ores and metals. There is some movement by sea of refined cadmium metal and as pigment (largely CdO). Spillage will result in slow leaching but no serious hazard to marine life.

Toxicity of cadmium to marine animals varies with compounds, species and stage of development. Values are reported to be within the range 0.1-100 µg/l. Marine larvae and algae seem to be particularly susceptible. Accumulation appears to be via the food rather than by direct uptake from the water. Whole body burdens associated with death range from 2 mg/kg for shrimps to 40-100 mg/kg for oysters. "Normal" contents of cadmium in animals from areas not specially exposed to industrial effluents are for fish <0.2-10 mg/kg, and for crustacean muscle tissue <1.0-20 mg/kg. Molluscan shellfish may contain somewhat higher concentrations e.g. 20 mg/kg in scallops from the English Channel. Very much higher values have been found in shellfish from the Bristol Channel (United Kingdom), an area directly exposed to contamination from a nearby smelter.

The average cadmium content of open ocean sea-water has been estimated at 0.02 µg/l; British coastal waters yielded values between <0.01 and 0.62 µg/l. "Contaminated" waters have yielded values up to 10 µg/l.

Sediments from coastal areas not exposed to industrial effluents contain 0.47-1.9 mg/kg, deep sea clays yielded, however, only 0.4 mg/kg. Sediment from the Bristol Channel, exposed to industrial pollution, ranged 1.6-4.7 mg/kg dry weight. Organic matter from bottom sediments collected from a contaminated area off Finland is reported to have yielded up to 130 mg/kg dry weight of cadmium.

Cadmium vapour and cadmium salts can induce acute toxic injury to the lungs, gastro-intestinal tract and kidneys but such injury is unlikely to occur on contact with polluted sea water or consumption of seafoods. Cadmium is virtually absent from the body at birth. Although only 5-10 per cent of ingested cadmium is absorbed it is only very slowly excreted, the biological half-life being between 16-33 years, and it gradually accumulates with age, mainly in the kidneys and the liver. Kidney damage is likely to occur in man when the concentration in the cortex of that organ reaches a level of about 200 mg/kg net weight. In Japan, long-term ingestion of high levels of cadmium in food and water, resulting from industrial pollution in localized areas, has been implicated as a contributory cause of an illness syndrome comprising kidney damage with bone disease. Although shellfish have been shown to accumulate cadmium, there is at present no indication that consumption of their flesh leads to human disease except in areas of high industrial pollution. However, because the human body is virtually unable to eliminate absorbed cadmium, every effort should continue to be made to reduce to a minimum contamination of the marine environment with this metal.

3.3.8 Chromium

Crustal rocks vary greatly in chromium content, from less than 1 ppm in some granites to almost 1 per cent in some basic rocks. Some minerals have "chrome-bearing" forms which may contain much more. The principal ore of chromium is chromite FeCr_2O_4 , which is the only ore from which chromium is produced on any scale.

The world's production of chrome ore is principally from the Philippines, Turkey, South Africa, Rhodesia and the USSR. There are many other smaller producers. World production of chromite has risen steadily in recent years and is now 7.5 million tons per annum (1973).

Chromium is used as an alloying element in the production of stainless steels, armour plate and certain cutting steels. In the form of chromite it is used in the manufacture of chrome refractories, and in the chemical industry it is used to produce chromates and bichromates. These have a wide variety of uses including tanning, dyeing, chromium plating and production of chrome pigments.

Shipment is largely as the mineral concentrate; loss would not give rise to any hazard to marine life.

Input to the atmosphere of chromium from the world-wide combustion of coal and oil has been estimated at 1,500 metric tons per annum, a part of which may subsequently be deposited in the sea. This would appear to be a relatively small proportion of total atmospheric input when compared to preliminary estimates of the atmospheric input to the North Sea - 2,000 tons per year. The global contribution to the ocean by river discharges has been estimated at 236,000 tons per annum. The superficial sediments at the mouths of the estuaries of the Rhine and Ems have been reported to contain respectively 160 and 180 mg/kg of chromium.

The "normal" concentration of chromium in open sea water is stated to be 0.3 $\mu\text{g}/\text{l}$; coastal waters may yield about twice this figure. Near-shore sediments in areas not exposed to industrial effluents are reported to contain approximately 10-100 mg/kg. "Normal" sewage sludges from Swedish plants gave an average content of 50-200 mg/kg of chromium, whereas plants contaminated with industrial effluents yielded 1 mg/kg dry weight of chromium in the sludge. Sewage sludge from plants in the United Kingdom contain from 7-2,400 mg/kg dry weight. In the New York Bight the mean content of samples from sediments well away from the dumping zone was <10 mg/kg, whereas near the centre of the sewage sludge dumping area the mean value was 105 mg/kg. A single sample of Glasgow (Scotland) sewage sludge contained 660 mg/kg. Sediments from the deposit area in the Clyde ranged in chromium content from 48-308 mg/kg, while the Clyde "background" range is reported to be 38-106 mg/kg. There appear to be no recent estimates for deep sea deposits.

Chromium contents in marine organisms are usually below the limit of detection, but values of 0.5 mg/kg wet weight have been obtained from fish taken from English coastal waters. Rather lower figures have been obtained by French workers. However, the soft parts of invertebrates from the Clyde Estuary

sludge dumping area ranged in chromium content from 13-42 mg/kg dry weight; the highest value was given by the whelk (Buccinum undatum).

In the marine system the hexavalent form of chromium is usually considered to be the most toxic and has been suggested as the cause of ulceration in fishes. Threshold concentrations vary between 1 ppm for Nereis sp. to 40-60 mg/l for Carcinus and 33 mg/l for Crangon. Oyster larvae are killed by concentrations of 5-10 mg/l and 1 mg/l chromium reduced the rate of photosynthesis in Macrocystis by 20-30 per cent after seven to nine days' exposure. The concentration factors reported for marine organisms are quite large, e.g. 10,400 for soft-shelled clams and 60,000 for Crassostrea.

High concentrations of chromium salts are irritant to the gastrointestinal tract, skin, eyes, mucous membranes and lungs and prolonged skin contact can cause dermatitis. Human exposure in chromate-producing industries is associated with an increased incidence of lung cancer.

However, these ill-effects occur only on prolonged contact with concentrations as high as those found in the industrial environment and concentrations to be found in even heavily polluted water are unlikely to be hazardous.

Chromium is present in human tissues and takes part in some metabolic reactions. It does not accumulate to a significant extent in the body. Chromium compounds are poorly absorbed from the gastrointestinal tract and amounts which are known to occur in fish would be harmless to man.

3.3.9 Cobalt

Cobalt is a dispersed element, most rocks containing from less than 1 to about 10 ppm. Local enrichment is rare, and deposits are not sufficiently concentrated to be worked for cobalt alone. The production of cobalt concentrates is associated with the winning of other metals, especially copper, nickel and gold. The principal minerals of cobalt are sulfides and arsenides and often include other metals.

World production is almost entirely from sulfide ores and principally from Canada, Zaire, Zambia, the United States of America and Finland. Smelting of ores takes place in the country where they are produced. Total world production is now of the order of 25,000 tons, having risen steadily in recent years.

Cobalt is used principally in high temperature alloys, high-speed steels, non-magnetic and other alloys. Other uses include in the ceramic industry as pigments, enamels and glazes, and in glass making, where it is used not only to produce blue and blue-tinted glass but also in small quantities to neutralize yellow tints from iron or selenium.

Shipment is principally as cobalt metal and cobalt alloys. Loss would not give rise to any hazard to the marine environment.

The "normal" cobalt content of open ocean sea water is stated to be very low - 0.03 µg/l. It is a constituent of nuclear fall-out and it has been estimated that cobalt-60 entering the sea in this way from the atmosphere, in the North Pacific, remains for about five years in the surface waters. The burning of coal and oil is said to contribute globally 700 metric tons of cobalt per annum to the atmosphere, some of which will later reach the sea. The contribution via river discharges of naturally occurring cobalt results from the weathering of rocks and is estimated to be 15,200 tons annually. The contribution from sewage may be judged from the estimate of 8-20 mg/kg dry weight as the cobalt content of "normal" sludge from Swedish municipal plants, while "contaminated" sludge from similar plants receiving industrial effluents is given as 50 mg/kg dry weight. In sewage sludge from Glasgow (Scotland) 7.5 mg/kg dry weight was found in one sample.

In near-shore sediments from areas not exposed to industrial pollution the cobalt content ranges from 7.7-8.6 mg/kg dry weight, but an average figure for near-shore sediment is said to be 13 mg/kg. In the Solway Firth, United Kingdom, which is relatively free from industrial effluents, the cobalt content of silts and clays gave a mean value of 16 mg/kg dry weight. Muds at the mouths of the Rhine and Ems contained respectively 43 and 40 mg/kg dry weight. Near the centre of the sewage sludge dumping area in the Clyde Estuary, Scotland, values ranged between 30 and 40 mg/kg dry weight, with a mean value of 34 mg/kg. Similar values are found rather widely in this estuary. In surf clams (*Spisula solidissima*) from off Delaware Bay, United States of America, the cobalt content was found to be less than 0.10 mg/kg drained weight of meat - the limit of measurement of the method. Nevertheless, cobalt is an essential element for many biota and is normally concentrated in marine organisms by factors of 10^2 - 10^4 ; the higher values have been recorded in experiments with crustacea; in fish and seaweeds the values are usually below 100.

There is very little information on the toxicity of cobalt to marine life. In freshwater acute toxicity varies considerably with species and values of 16-5000 mg/l have been reported. For marine life the only value available suggested that 200 mg/l cobalt chloride was not toxic to fish (mummichogs).

Acute exposure to high concentrations of cobalt salts can cause gastrointestinal irritation, facial flushing, pancreatic damage and a lowering of blood pressure. Long-term administration of relatively large amounts causes nerve damage, alteration of thyroid and bone marrow activity, and heart disease which may prove fatal.

Cobalt is, however, an essential element for man: it is also a component of vitamin B₁₂. It seems unlikely that polluted water or contaminated fish could increase the amount ingested to a level which might be hazardous to health.

3.3.10 Copper

Although not abundant, copper is widely distributed in crustal rocks with an over-all abundance of about 45 ppm. It occurs mainly as sulfides of which the most common is chalcopyrite (CuFeS_2). Most copper deposits show an oxidized zone with carbonate minerals such as malachite and azurite. Oxide and native copper are also known.

Production exceeds 7.5 million tons per annum, largely from sulphide ores. Major producing countries include Australia, Canada, Chile, Japan, Peru, Philippines, Poland, South Africa, the USSR, the United States of America, Zaire and Zambia. There are many other smaller producers. Copper is extensively recycled in industrial countries.

Major uses are for electric wiring, switches, plumbing, plating, roofing and building construction, alloys (e.g. brass and bronze), domestic utensils, agricultural chemicals, wood preservatives, protective coatings, pigments, china and glass and wallpaper manufacture.

Copper reaches the marine environment from copper mines and a large number of industrial processes, e.g. artificial fibre production, agricultural chemicals, wood preservatives, wallpaper manufacture, etc. Contribution to the atmosphere from the burning of coal and oil is estimated to be 2,000 tons per annum. Natural weathering of rocks has been estimated to contribute in river discharges about 325,000 tons per annum. Old mine workings and mine dumps continue to release copper for an indefinite period; in some areas it is now worth while to recover the metal from such leachings.

World-wide carriage in ships is mainly as copper metal; smaller amounts are carried as concentrates (about 500,000 tons in 1970). Formulated products are transported as packaged goods. Spillage of metal or concentrates would result in slow release to the sea and no hazard to marine life. Spillage of packages of copper salts would create local problems.

Copper is present in all sewage being derived from food, copper plumbing and due to mixing with industrial wastes. Sewage sludge from Swedish municipal plants is reported to contain 0.5-1.5 g/kg dry weight. Glasgow sewage sludge contains 320 mg/kg and other values from the United Kingdom range between 100 and 1000 mg/kg dry weight.

In the New York Bight sludge dumping area, copper content of sediments ranged from 80-240 mg/kg dry weight in contrast to a nearby "uncontaminated" area which yielded 3 mg/kg dry weight. An area near the centre of the sludge dumping ground in the Clyde Estuary, Scotland, gave values between 40 and 210 mg/kg dry weight.

In near-shore areas, far removed from industrial plants, the superficial sediments gave values ranging from 2-26 mg/kg dry weight. Deep sea clays, on the other hand, gave average values of 250 mg/kg dry weight. Muds at the mouths of the Rhine and Ems are reported to contain 470 and 150 mg/kg dry weight

respectively. The calculated input from the Rhine to the North Sea is between 1,000 and 1,500 tons per annum. Deposition from the atmosphere with rain has been estimated to introduce about 13,000 tons of copper each year to the North Sea.

An average value for the copper content of open sea water is 2 $\mu\text{g}/\text{l}$. Coastal waters around the United Kingdom gave values ranging from 0.05-1.7 $\mu\text{g}/\text{l}$. Copper is removed from sea water by adsorption on organic matter and by deposition with clay minerals and manganese nodules (which may contain up to 2.2 per cent Cu.)

Acute toxicity to marine animals is usually reported to be of the order of a few ppm for adults of numerous species. Larvae are consistently more sensitive (0.01 ppm for sea urchin larvae) and similar levels have been shown to affect photosynthesis and growth in algae. In many molluscs and polychaetes there appears to be no regulation and concentration factors of 100-1000s are common. For example in Ostrea high levels are accumulated (100 mg/kg in the so-called "green oysters") but the copper is present as inert granules in the leucocytes. In Nereis accumulation occurs and death can result at body burdens of 200 mg/kg. However, there is evidence of genetic (?) selection for copper resistance. Fish and crustacea appear to be able to regulate their body burdens, though in Crangon, for example, detoxification is by formation of granules.

"Normal" levels of copper in fish appear to be of the order of 20 mg/kg dry weight; shellfish yield higher values e.g. mussels about 75 mg/kg, edible crabs 360 in the muscle to 1000 mg/kg dry weight in the "brown meat" (gonad and hepatopancreas).

Large doses of copper salts produce injury to the gastrointestinal tract and liver and this may cause death. Exposure to such large doses by contact with sea water or seafood is not possible. Copper is an essential element for man. Food and water provide man with a daily intake of about 4 mg copper. Normally any excess of copper ingested is rapidly excreted so that the element does not accumulate in tissues and chronic toxic injury is unlikely to occur following contact with polluted water or ingestion of seafood from any area polluted with copper.

3.3.11 Lead

The natural abundance of lead in the crustal rocks of the earth is about 15 ppm. It is ubiquitous in soils, plants and animals. Lead as an exploitable mineral occurs widely as the sulfide galena (PbS) which is the main source of production of the metal; sulfate and carbonate ores are also found but are of very minor importance. Smelting is carried out both in the mining areas and in the receiving countries. Large quantities of lead are recycled in all industrial countries, especially from batteries, cables, piping and sheeting.

World primary production is about 3.5 million metric tons; production appears to have tended to stabilize during recent years following a steady rise during the 1950s and 1960s. The principle world sources are Australia, Canada,

Mexico, the United States of America, Bulgaria and Yugoslavia, mostly from relatively small mines. Lead ore production on a lesser scale occurs, however, in many countries.

The main uses of lead are in storage batteries, anti-knock petrol additives (e.g. tetraethyl and tetramethyl lead), radiation shielding, in tank construction and lining in the chemical industry, in ammunition, fusible alloys, pigments, sheet and pipe, cable coverings, type metal, vibration damping in heavy construction, decorative pottery, glass and foil.

Lead reaching the atmosphere from the burning of coal and oil has been estimated at 3,600 metric tons per annum. World-wide introduction of lead to the sea by river discharge as a result of weathering of rocks has been estimated as being between 110,000 and 180,000 metric tons. Over 10 per cent of the present annual primary production of lead is used in leaded motor fuels where it functions as an "anti-knock" agent. However, its use for this purpose can be expected to decline, both in terms of the concentration and the total amount as control measures take effect. Much of the lead is released to the atmosphere in exhaust fumes and part of this subsequently finds its way into the sea. Using lead in this way was estimated in 1972 to introduce 2×10^5 metric tons of lead into the marine environment annually. For the North Sea the atmospheric input, estimated at 15,000 tons per year, comprises a significant proportion of the total input of lead. The 1966 level of lead in a Greenland glacier has been shown to be 500 times the level of 800 BC. Atmospheric input is considered to be the cause of the elevated lead concentrations noted in coastal waters adjacent to industrial and heavily populated coasts. Locally, however, smelting activities may have much greater effect. Lead is present in enhanced concentrations in river discharges from mineralized areas and mining activities, including long disused workings; these may contribute substantial quantities to the marine environment. Lead also occurs in the effluents of many chemical factories.

Lead is present in sewage: the mean content of sewage sludge in Sweden is stated to be 324 mg/kg dry weight; in areas receiving wastes from particular industries the lead content may, however, reach 1 g/kg dry weight. The lead content of sewage sludges from the United Kingdom ranged from 5-750 mg/kg. Much of the lead reaching the sea will be in particulate form.

Carriage of lead by ships is on a world-wide scale; it is shipped mainly as metallic lead and lead sulphide concentrates. The loss of a cargo of either (there have been some recent wrecks of ore-carriers) would result in slow leaching into the sea water without creating a serious hazard to marine resources.

Acute toxicity levels (LC 50 values up to 96 h) to marine animals have been reported to be between 1 and 10 $\mu\text{g}/\text{l}$. Lead nitrate at a concentration of 0.15 $\mu\text{g}/\text{l}$ reduced growth of a marine ciliate protozoan by 8.5 per cent in laboratory experiments. Toxicity was increased when lead was associated with zinc or mercury. Lead accumulates in animal tissues and is only very slowly excreted. Concentration factors in fish are of the order of 10^3 and in invertebrates of the order of 10^4 . In crustacea lead tends to be stored in the exoskeleton and the digestive organs. Lead is an enzyme inhibitor and impairs cell metabolism.

In marine animals it is probable that, at least in acute exposures, it acts by damaging gill surfaces and hence inhibits oxygen-carbon dioxide transfer. The mode of entry, however, is primarily with food rather than from sea water. Larvae of marine animals are generally more susceptible than adults e.g. embryos of the American oyster (Crassostrea virginica) gave an LC 50 in the range 2.20-3.60 (mean 2.45) $\mu\text{g}/\text{l}$ for lead nitrate.

Lead is persistent in the marine environment and marine sediments are probably the main storage point. Normal open sea water concentration is 0.02 $\mu\text{g}/\text{l}$ but in near-shore areas concentrations in surface waters can be between 10 and 100 times those in the open ocean. Surveys of the North Sea about 10 years apart (1961 and 1970) showed no significant change in the lead content of surface waters. Near-shore marine sediments, not affected by local sources of lead contamination, contain 1-20 ppm of lead. Sediments in the Severn Estuary (United Kingdom) ranged from 130-200 ppm; there are smelters nearby and old mining areas in the drainage basin. Deep sea clays, however, are reported as containing 80 ppm of lead.

The acute toxicity of inorganic lead is relatively low in man but when exposure continuously exceeds the rate at which it can be excreted from the body it accumulates in the tissues and finally provokes the illness known as chronic plumbism. In those countries where adequate surveys have been made the intake of lead in food and water (the main sources of lead) is lower than that likely to constitute a health hazard. However, lead accumulates in shellfish, particularly bivalve molluscs, and high concentrations of lead in their flesh seem to be associated with elevated levels of the element in near-shore sediments. No instances of human poisoning from eating such shellfish have been recorded but the rapid increase in the level of lead in the surface layer of the sea in this century must be viewed with some concern where shellfish form a substantial proportion of the human diet.

3.3.12 Manganese

Manganese is usually classed as a "minor" rather than a "trace" element in crustal rocks, ranging from 0.05-0.2 per cent. Local concentrations occur in some sedimentary rocks and also in the form of accretions known as "manganese nodules" on the deep sea floor. These nodules may contain also appreciable quantities of some non-ferrous metals especially copper, cobalt and nickel.

The principal ores of manganese are oxide minerals, particularly pyrolusite MnO_2 . Silicates and carbonates are known, but these are not important sources of manganese.

There is widespread production, transport and usage of manganese ores; the largest production being from the USSR, India, Brazil, South Africa, Morocco, Zaire, the United States of America, Japan, Mexico, Australia, China and Gabon. Total production has risen from 4 million tons in 1953 to about 8 million tons contained metal in 1973.

Manganese is used extensively as an alloying element for steel and in other aspects of steel production. Large quantities of manganese dioxide are used in the production of dry batteries and smaller quantities in glass manufacture, in glazes for pottery and making coloured bricks. Manganese salts have many uses in the chemical industry as mordants, dyes, oxidants, pigments, catalysts and intermediates.

Manganese is carried by sea largely as manganese dioxide in bulk ore carriers. Small quantities are shipped as ferro-manganese. Spillage of either of these would not result in a hazard to marine life.

Manganese occurs at the level of $200 \mu\text{g}/\text{m}^3$ in United States urban air and the air/ocean ratio is 700:1. This, it is estimated, may result in an increase of 15 per cent in the manganese content of the upper 200 m of the ocean.

The burning of coal and oil is estimated to contribute to the atmosphere only 7,000 metric tons of manganese annually, part of which will later reach the sea. The total annual input of manganese to the North Sea from the atmosphere has been preliminarily estimated to be 6,000 tons per year.

River discharges have been estimated to contribute globally both in solution and in particulate matter in total 2.2 million metric tons of manganese per annum, much of which is ultimately deposited as manganese dioxide or in manganese nodules on the ocean floor, carrying with it substantial quantities of a number of other metals.

The manganese content of "normal" open ocean sea water is stated to be $0.3 \mu\text{g}/\text{l}$, but values up to $1.9 \mu\text{g}/\text{l}$ have been quoted. Streams are reported to yield on average $7 \mu\text{g}/\text{l}$. Filtered Atlantic water collected west of the British Isles gave values ranging between 0.03 and $0.09 \mu\text{g}/\text{l}$. North Sea values ranged from 0.24 - $0.54 \mu\text{g}/\text{l}$; the English Channel was similar. Substantially higher values (range 0.22 - $14.6 \mu\text{g}/\text{l}$ in filtered sea water) were obtained from the eastern Irish Sea, which receives drainage from large industrial areas and rivers rich in minerals. In the Irish Sea significantly greater amounts of manganese were found in shore-line water than off-shore. Values obtained in 1970 from British coastal waters were not significantly different from those obtained 10 years earlier. In all areas approximately 75 per cent of the total manganese was in suspended particulate matter.

Muds from the Solway Firth (United Kingdom) are reported to contain on average $360 \text{ mg}/\text{kg}$ of manganese, with a range of 180 - $720 \text{ mg}/\text{kg}$. Sandy silt from Saanich Inlet, British Columbia, also yielded $360 \text{ mg}/\text{kg}$. On the other hand the Clyde Estuary, in the area where sewage is deposited, gave figures ranging from 500 - $1000 \text{ mg}/\text{kg}$ with a mean of $911 \text{ mg}/\text{kg}$. A single analysis of the sewage sludge itself gave $762 \text{ mg}/\text{kg}$ of manganese. "Normal" sludge from Swedish plants gave 200 - $500 \text{ mg}/\text{kg}$ dry weight. Even higher values have been reported from the muds at the mouths of the Rhine and Ems, viz. 2600 and $3300 \text{ mg}/\text{kg}$ respectively.

Generally it appears that cations are more toxic than anions, e.g. MnO_4^- - but Mn^{2+} , the most likely form to occur in sea water, is more toxic than Mn^{3+} . There

is little information on the toxicity of manganese to marine organisms; acute toxicity to fish is reported to range from 1-1000 $\mu\text{g}/\text{l}$. Oyster larvae are reported to be killed by 14-19 $\mu\text{g}/\text{l}$ and algae are claimed to be damaged by concentrations as low as 5 $\mu\text{g}/\text{l}$. Certain species appear to have a striking ability to accumulate manganese e.g. scallops (concentration factor 50,000) but in fish 100-fold appears usual and a value at which the fish can regulate further uptake. Concentration factors for manganese in algae have been reported as Fucus sp. 2.3×10^4 (18 observations) and Porphyra umbilicalis 7.0×10^3 (20 observations).

Actual concentrations of manganese ranged from 64-99 mg/kg dry weight for Fucus sp.; 29 mg/kg (two areas) for Porphyra; and 31-42 mg/kg for Patella (soft parts). Values obtained for surf clams, Spisula solidissima, from off Delaware Bay ranged from 0.68-2.79 mg/kg drained weight of shellfish in May/June 1967. Average values for the Northern Quahaug (Mercenaria mercenaria) are reported as 3-7 mg/kg.

In the industrial environment, inhalation of manganese and its compounds over a prolonged period has led to damage of the nervous system, liver and lungs. Manganese is poorly absorbed through the skin and from the gut where ill-effects are seen only at concentrations high enough to cause severe irritation. Manganese is an essential element for man. Tissue levels are probably regulated by alterations in the excretion rate. Manganese is present in many foods, occurring at low concentrations in seafoods. Human contact with manganese-polluted water and consumption of manganese contaminated seafoods do not at the present time present a health hazard.

3.3.13 Mercury

The abundance of mercury in crustal rocks is low, a figure of 0.06 ppm has been quoted. It does, however, tend to be more abundant in the rocks from certain areas, where it may appear as the sulfide mineral, cinnabar (HgS). The total world production has been fairly stable in recent years at about 9,000 tons per annum. The chief producers are Italy, Mexico, Spain and the USSR, with some production from China, Turkey, the United States of America and Yugoslavia. In general, local smelting is utilized.

The most important single usage of mercury is still in the chlor-alkali industry. Recently introduced methods of treatment of the effluent have greatly reduced the discharge of mercury from these plants. It has, however, a wide variety of other uses, e.g. agricultural chemicals, pharmaceuticals, electrical switches and instrumentation, mercury vapour lamps, extraction of gold and silver, in high quality anti-fouling paints, in dentistry and in the dyeing industry.

Mercury is also used as a catalyst in the production, inter alia, of acetaldehyde and vinyl chloride and it was this latter use at Minamata in Japan which led to the deaths of more than 40 people, and lasting injuries

to a greater number. Because of its relatively high vapour pressure (10 mg/m^3), losses to the environment occur during smelting operations and whenever metallic mercury is used.

In addition to these sources of mercury, which between them probably account for 4-5,000 tons added to the sea each year, some will reach the atmosphere from the burning of coal and oil, part of which will be rained out over the sea. The global atmospheric input has been estimated at 3,200 tons per annum. Input to the ocean by river discharges derived from the weathering of rocks has been estimated to be about 3,500 tons.

Mercury is transported by sea, primarily as the metal in flasks or as formulated packaged products. The role of leaching of the metal into the sea is uncertain, since it has been reported that metallic mercury can accumulate in hollows in the sea bed and may become covered by sediment. Under these conditions some conversion to alkyl mercury may still occur.

Mercury is present in most sewage, being derived from numerous sources, including food, dental fillings and minor industrial uses. The mean content of "normal" sewage sludge from Swedish plants is stated to be 4-8 mg/kg. Figures for United Kingdom sewage sludges range from 2.6-50 mg/kg with an average of about 9 mg/kg. The input from sewage to the North Sea has been calculated to be about 22 tons per annum. There is evidence that mercury released to the marine environment is rapidly absorbed on sedimentary material and this is reflected in the high concentrations noted in muds off major estuaries, e.g. the Rhine. The input to the North Sea from the Rhine has been estimated to be 100 tons of mercury per annum. The superficial sediments at the mouths of the Rhine and Ems were found to contain 18 and 3 mg/kg of mercury respectively.

The normal content of mercury in open ocean sea water lies within the range 0.01-0.1 $\mu\text{g/l}$. Equatorial waters are reported to yield figures one or two orders of magnitude lower than the average for temperate waters and it has been suggested that this results from uptake by plankton.

Regardless of its state on entry into the marine environment, mercury compounds are liable to be converted into methyl mercury under anaerobic conditions. Acute toxicity of ionic mercury varies both with the species and with its stage of development from 0.005-10 mg/l. Organic mercury compounds are much more toxic than ionic mercury, e.g. 18 per cent of *Plumaria* juveniles were killed by 0.044 mg/l methyl mercury (of mercurous chloride 3.12 ppm). Similarly propyl mercuric chloride was more toxic than ethyl mercuric chloride which was more toxic than methyl mercuric chloride. The figures for acute toxicity are time-dependent - apparently with a very low threshold. The corollary to this is a slow elimination or detoxification mechanism. This is seen from the half-life of alkyl mercury which is much longer than that of inorganic mercury. Half-lives for *Tapes*, *Mytilus*, *Carcinus* and fish have respectively been reported as 480, 1,000, 400 and 250-1,000 days. Concentration factors for alkyl mercury are also higher, for example *Venus* rapidly accumulated 30-40 mg/kg from 0.3 mg/kg mercuric chloride but 70 mg/kg from methyl mercury.

The significance of residue levels is uncertain. It is thought that the action of mercury is selective, binding at -SH groups of proteins etc., especially at lipid-rich sites, e.g. nervous tissue. However, the site of accumulation is dependent on the form of mercury. Levels of 200 mg/kg (total body burden) caused behavioural disorders in seals; 15 mg/kg mercury caused death in fish; 30-100 mg/kg death in shrimps. Behavioural abnormalities were apparent at concentrations only slightly less than this. It has been suggested, at least for seals and possibly for other marine animals, that the toxic action of mercury can be blocked by parallel accumulation of selenium almost up to the lethal concentration.

The human toxicities of elemental mercury and of inorganic and organic mercury compounds are different. Poisoning by elemental mercury has been found to occur only following inhalation of the vapour or prolonged contact with finely divided metal; the nervous system is chiefly affected. Inorganic mercury is concentrated in the kidney and large doses damage that organ. However, inorganic mercury is excreted from the body at a moderately high rate (a half-life of about three months) and chronic poisoning by concentrations which would occur in sea water or seafood is unlikely. The toxicity of alkyl mercury compounds is higher than that of the aryl and alkoxy compounds. Acute poisoning by organomercury compounds has occurred only on industrial exposure and following the consumption of organomercury-treated seed intended only for agricultural purposes. Long-term exposure of man to organomercury compounds damages the central nervous system; in localized areas this has occurred following the ingestion over a long period of seafoods containing high concentrations of methyl mercury compounds originating from industrial pollution. The accumulation of organomercury compounds in marine species used as human food has led to a need for some countries to introduce a ban on fishing and on the sale of contaminated fish in some areas where industrial pollution has been high. Since inorganic mercury compounds are in part transformed into organomercury compounds in the sea, contamination of the sea by all forms of mercury should be reduced to the minimum.

3.3.14 Nickel

Crustal rocks vary greatly in nickel content, from a few ppm to about 0.5 per cent in some basic rocks. There is enrichment of certain secondary rocks in nickel (some bauxites and laterites for example) with pockets that may be exploitable at times of nickel shortage. Although nickel is more abundant than copper, lead or zinc, there are fewer deposits. These are mainly sulfide ore bodies - some of which contain no more than 1 per cent nickel, with other non-ferrous metals such as cobalt and copper. The silicate mineral garnierite is also an important source of nickel.

The greater part of the world production is from sulfide ores in Canada. Other major producers include the USSR, New Caledonia, Cuba and the United States of America; Australia is expected to become a major producer. There is smaller production from Finland, Indonesia, Poland, South Africa, Rhodesia and only very small quantities of nickel from other countries. World production amounted

to 0.67 million tons in 1973. There is appreciable recovery and recycling of nickel metal.

The principal use of nickel is as an alloying element, both in steels, especially stainless steel, and in high temperature alloys. Smaller quantities of nickel metal are used in the electronic and electrical industry and nickel salts are used in electroplating, vitreous enamelling and as a catalyst in hydrogenation processes.

Nickel ores are smelted largely in the countries in which they are produced, and the nickel shipped as metallic nickel and nickel alloys. There is also some shipment of nickel ore for smelting in industrialized countries. Loss of a shipment is unlikely to cause a hazard to marine life.

The annual rate of introduction of nickel to the sea via rivers resulting from the natural weathering of rocks has been estimated at 170,000 tons. World-wide burning of coal and oil is estimated to discharge to the atmosphere only 3,700 metric tons per annum of nickel, some of which will later reach the sea. However, for the North Sea, the annual contribution from the atmosphere from all sources has been estimated by direct-measurement at 5,000 metric tons per annum.

The "normal" content of nickel in open ocean sea water is stated to be 2 $\mu\text{g}/\text{l}$. Waters of the United States eastern coast are said to show a five to tenfold increase in nickel content. Atlantic waters west of the United Kingdom, after filtration to remove suspended material, yielded values ranging from 0.29-0.66 $\mu\text{g}/\text{l}$. North Sea values were slightly lower. Filtered shore-line samples from the North Sea yielded 0.1-6.0 $\mu\text{g}/\text{l}$. Concentrations in the English Channel and the western Irish Sea were very similar but in the eastern Irish Sea, in an area receiving substantial industrial drainage and river discharges from mineralized areas, the level was approximately twice as high. Shore-line sea water, from the same area, gave figures up to 9.8 $\mu\text{g}/\text{l}$ of nickel. The suspended material from these shore-line areas in the Irish Sea yielded about 50 times the nickel found in the sea water.

An average value for the nickel content of near-shore sediments is stated to be 55 mg/kg, but analyses from some areas unaffected by industrial development gave values from <2-6 mg/kg in superficial sediments. Deep sea clays, on the other hand, contained 225 mg/kg and nickel is present in significant quantities in the manganese nodules found abundantly on the sea floor in certain areas.

Sewage contains substantial quantities of nickel, even when uncontaminated by industrial effluents, e.g. the "normal" sludge from 100 Swedish municipal plants is stated to contain 25-100 mg/kg dry weight; "contaminated" sludge from Swedish plants contained 500 mg/kg dry weight of nickel. A single analysis of sewage sludge from Glasgow (Scotland) gave 82 mg/kg dry weight, while the superficial deposits near the centre of the sludge dumping area averaged 50 mg/kg dry weight with a range of 24-70 mg/kg. In the New York Bight the "natural" values in the sediment are very low (3-8 mg/kg dry weight), but near the centre of the dumping area average 24 mg/kg dry weight.

Nickel is concentrated from sea water by many marine organisms, e.g. oysters and clams, by a factor of about 4000, cockles by even more.

Concentration factors for nickel in dry material of brown seaweeds (Fucus sp., mainly F. vesiculosus), an edible seaweed (Porphyra umbilicalis) and limpets (Patella vulgata) from around Britain are stated to be 2.8, 1.1 and 3.6×10^3 respectively. The soft parts of a range of crustacean and molluscan species from the Clyde Estuary sludge deposit area ranged in nickel content from 8.5-9.2 mg/kg dry weight, with the highest values from shrimps and the lowest from whelks (Buccinum undatum).

In freshwater acutely toxic levels to fish have been reported between 0.5 and 10 mg/l but toxicity in sea water seems to be lower e.g. 48 h LC 50 to Crangon crangon 125 mg/l, Ostrea edulis 100-150 mg/l; Pandalus montagui were however quite susceptible (14 ppm) and Crassostrea larvae were killed by 1.2 ppm.

Large doses of nickel salts taken by mouth cause acute gastrointestinal irritation, but poisoning in man, even by the large amounts at one time used therapeutically, is almost unknown. Nickel is poorly absorbed and any that enters the tissues is rapidly eliminated in urine and faeces and there is no evidence of accumulation in the body.

Severe dermatitis occurs in industrial workers and others in frequent contact with the metal, and it is possible that nickel (in some form) is carcinogenic to those working in nickel refineries, however, there is no evidence that ordinary exposure to the low concentrations of nickel which occur in the marine environment constitutes a health hazard. And at the present time, with the present levels of nickel in the marine environment, the consumption of seafood is unlikely to be harmful. A hazard could arise if increasing amounts are to be discharged into the sea.

3.3.15 Phosphorus (elemental)

Phosphorus is normally found in the sea in the form of phosphate, either particulate organic or inorganic. If discharged in elemental form, however, it remains largely in that state and is potentially highly toxic. There have been some instances of elemental phosphorus being discharged to the marine environment from factories producing phosphorus from phosphate ores and from ships carrying phosphorus both in bulk and in drums. Much of the phosphorus becomes locked in the sediments where it remains virtually unchanged for a considerable period; the fraction remaining in the water is slowly oxidized to phosphate. One large-scale incidence of toxicity arose on the coast of Newfoundland from a factory discharge. Large numbers of herring, cod and other species were killed; in some species extensive haemolysis and reduction of haematocrits was observed.

3.3.16 Selenium

Selenium is largely associated with sulfur minerals in the crustal rocks and has an abundance of about 0.09 ppm. A few selenides are known, but these are of rare occurrence. The bulk of world production is from anode slimes that result from the electrolytic refining of copper, plus a smaller contribution by extraction from flue dusts of certain pyrometallurgical processes, including the burning of pyrites.

The world production of selenium reached 1,200 tons in 1970, largely from the United States of America, Canada, Japan, Sweden and Mexico, with smaller amounts from Belgium, Finland, Yugoslavia and Peru. There is also a small amount of selenium recovered and recycled.

The principal uses of selenium include glass manufacture, rectifiers and photoelectric cells. Smaller quantities are used in the production of rubber and plastics, as a catalyst, in dyeing and in pharmaceuticals.

The burning of coal and oil has been estimated to contribute 450 tons of selenium per annum to the atmosphere globally; some of this will later reach the ocean. Weathering processes are reported to introduce about 7,200 tons per annum of selenium to the world oceans.

Selenium is stated to be present in open sea water at a concentration of about 0.5 µg/l. Streams are said to yield on average 0.2 µg/l.

Information on the effects on marine life of concentrations of selenium in sea water greater than normal does not appear to be available. However, selenium is present in easily detectable concentrations in a number of marine animals, for example, crustacea about 0.6 mg/kg dry weight, flounder 0.3 mg/kg, oysters 0.6 mg/kg and scallops 0.5-1.4 mg/kg dry weight. In various fish from Japan, selenium levels were reported to be 0.17-0.77 mg/kg dry weight, while from Canada levels in marine fish were between 0.8 and 1.9 mg/kg dry weight. Fish appear to be able to regulate their selenium content and the biological half-life is reported to be of the order of 10-30 days.

Selenium has been found to be especially high (approximately 100 mg/kg dry weight) in Antarctic seal and penguin livers. Levels in common or harbour seals, (Phoca vitulina), from the Netherlands varied from 0.3-14 mg/kg in fresh brain tissue and from 5-370 mg/kg in the fresh liver of the same species. The highest values were found in the older animals. In the grey seal, (Halichoerus grypus), from the Netherlands the fresh brain contained 0.26 mg/kg (one example) and the liver 1.6-182 mg/kg. Most of the harbour and grey seals were dead or dying and contained large amounts of mercury.

Hood seals (Cystophora cristata) from the Arctic gave much lower values of selenium, 0.6-12 mg/kg, in a mixture of adults and juveniles (seven examples). Four observations from harp seals (Pagophilus groenlandicus), taken north-east of Jan Mayen, gave very low values 0.4-2.3 mg/kg, from fresh tissue.

There is a remarkable correlation between the levels of mercury and selenium in seals; in the liver this indicates a molar ratio of 1:1. A similar correlation has been found in dolphins and porpoises. It is known that selenium compounds may protect man from the toxic action of mercury; it seems that they may exert a similar effect in marine animals.

Acute and long-term exposure of workers to selenium fumes has caused a variety of ill-effects and animals receiving high dietary concentrations of selenium compounds have developed impaired vision, liver injury, anaemia and paralysis leading to death. Selenium and its compounds are not readily absorbed through the skin and concentrations high enough to cause skin injury could not occur in the open sea. While selenium, because of its insolubility, is itself relatively harmless when taken by mouth, soluble selenium compounds are highly toxic and when taken over prolonged periods have been implicated in causing cancer in animals.

However, selenium is an essential element for several animal species and possibly also for man. The human dietary selenium intake varies considerably in different areas, mainly due to differences in the selenium content of grain foods, but there are no convincing reports that even high selenium diets have caused ill-health in man. It is unlikely that consumption of seafood would increase dietary selenium to a sufficient extent or for a sufficiently prolonged period to produce adverse effects on health. Nevertheless, concern could arise where the discharge of selenium compounds occurs.

3.3.17 Silver

Silver is a rare element, with a crustal abundance given as 0.08 ppm. The important ores of silver, themselves rare in occurrence, are all sulphides, often complex sulphides with other metals. The production of metal is divided equally between recovery from lead-zinc sulfide ores and ores of copper, nickel, gold and tin. There is also some production from ores worked exclusively for silver.

Primary production, amounting to 9,600 tons in 1973, is largely in those countries where the ores are mined. The major producing countries are Australia, Canada, Mexico, Peru, the United States of America and the USSR, with smaller but important production from Bolivia, Chile, France, Germany, Honduras, Japan, South Africa, Sweden, Yugoslavia and even smaller quantities from a number of other countries. Silver is extensively recycled from photographic residues and to a lesser extent from obsolete coinage metal.

There is still some use of silver as a coinage metal. Large quantities are stored as a monetary reserve and as tableware. Small amounts are used in brazing alloys and in the electrical and electronic industries and as plating metal, but the chief uses of silver are in photography, in silverware, for electroplating and in jewellery.

The burning of fossil fuel has been estimated on a global basis to add to the atmosphere 70 tons of silver per annum, some of which will later reach the sea. The contribution from streams through the weathering of rocks has been estimated on a world-wide basis to be 11,000 tons per annum.

Silver levels in the sea appear to range from 0.01-0.3 µg/l. Stream water is said to contain 0.03 µg/l. Filtered shore-line sea water from two localities in the Irish Sea gave values between 0.02 and 0.24 and 0.03 and 0.16 µg/l respectively. The silver in the particulate fraction in these two sets of samples was 47 and 69 per cent of the total. There is evidence that approximately half of the silver reaching the ocean from radio-active fall-out may be retained in the upper ocean over a period of one decade.

The silver content of surface sediments from coastal areas far removed from industrial development seems to range from 0.5-3.0 mg/kg, and deep sea clays have been found to contain even less (0.11 mg/kg). In the Solway Firth (United Kingdom) all values were <0.2 mg/kg dry weight.

Brown seaweeds (Fucus sp.) from the coastal waters around the United Kingdom gave values ranging between 0.20 and 0.35 mg/kg, the highest values coming from the North Sea. The edible seaweed Porphyra umbilicalis ranged (mean values) from 0.09-0.13 mg/kg in the Irish Sea, while the soft parts of limpets (Patella sp.) from the same area yielded mean values of 1.3-2.1 mg/kg. Concentration factors were 5.0×10^3 for Fucus, 1.9×10^3 for Porphyra and 3.1×10^4 for Patella. Silver content of Fucus seaweeds was very similar in 1961 and 1970 when all British coastal areas were compared. Concentration factors in the livers of fish are stated to be 5×10^5 . Bivalve molluscs can accumulate silver to a notable extent and levels of 20 ppm in Crassostrea, 17 ppm in Mya and 8 ppm in Ostrea are reported to be "normal". The highest concentrations are reported to be found in the heart and kidney.

The toxicity of silver to freshwater species appears to be extremely high and threshold levels as low as 0.005 ppm have been reported for fish. In the marine environment toxicity appears to be of the same order, with the 48 h LC 50 value for Crassostrea larvae being reported as 0.0058 mg/l.

Although some ill-effects, including accumulation in tissues, have been noted following therapeutic use of silver salts or on prolonged industrial exposure, no hazard to health can be expected from contact with polluted sea water or from eating contaminated seafood.

3.3.18 Sulphur (as sulphite)

Sulphite may enter the marine environment in wastes from certain industrial processes e.g. the pulp industry and rayon manufacture. Sulphur dioxide produced from the burning of fossil fuels will also enter the sea as sulphite from the atmosphere. The sulphite ion is not stable in sea water; under normal aerobic conditions it will be oxidized to sulphate. Under anaerobic conditions sulphite and sulphate may be reduced by bacteria to sulphide which is toxic and obnoxious on amenity grounds. Sulphite is also toxic to marine life and, although not stable in

the marine environment, is known to have caused damage to marine life near effluent discharges. Sulphate is not toxic to marine life and is present naturally in sea water in relatively high concentration (2.76 g/l); it cannot therefore be considered to be a pollutant.

3.3.19 Titanium dioxide wastes

The industrial production of titanium dioxide from titanium ores can give rise to large volumes of a waste which is characterized by its high proportion of acid and ferrous sulphate. This particular waste is considered worthy of special attention since in many instances the waste is discharged, completely untreated, into the sea either from a pipeline or from barges.

The ferrous ion is very rapidly oxidized to ferric ion which precipitates in colloidal form as the hydrated hydroxide over a considerable area in the locality of the discharge or dumping. Although the effect of the acid is lost relatively rapidly, ferric hydroxide is persistent and remains in or on the sea bottom for considerable periods. No ill-effects on human health or living resources, except in the immediate vicinity of the discharge, have been reported, but amenities might be affected in coastal areas owing to deposition of ferric hydroxide in the intertidal region. The nature of this waste is likely to change in the future as new methods replace the old sulphuric acid process; these use a different one and the sulphuric acid in the waste is to some extent replaced by hydrochloric acid.

3.3.20 Vanadium

Vanadium is widely distributed in small amounts in both igneous and sedimentary rocks, with an over-all abundance of about 200 ppm. Basic rocks tend to contain more vanadium than others, but there is a wide variation within each group of rocks. It occurs naturally as a base element in plants and animals.

World production increased substantially up to 1969 but has now stabilized at about 12,000 tons per annum.

The principal sources of vanadium minerals are in the United States of America and South Africa, mostly in the form of small, local concentrations of fairly rare minerals, especially vanadinites. There is also production in South Africa and Finland from particular iron ore deposits in which vanadium exists as a minor constituent. There has also been some production from deposits of the sulfide mineral patronite in South America, from vanadiferous phosphate ores, from certain iron ore slags and from the ash obtained by burning certain oils originating from South America that are particularly rich in vanadium.

There are a number of small uses, as a catalyst, in alloys e.g. ferrovanadium, in pigment production and photography, etc.

River discharges have been calculated to introduce 312,000 tons of vanadium each year to the oceans of the world. Fossil fuel burning is estimated to contribute 12,000 tons to the atmosphere, a part of which may subsequently reach the sea with rain. Only small quantities will reach the sea in industrial effluents.

The toxicity of vanadium compounds in freshwater is low and decreases with increasing hardening of water. There seem to be no data for marine animals but toxicity is probably even lower than in freshwater animals.

Vanadium is concentrated by certain classes of marine animals, especially ascidians and echinoderms, in which it is present in the blood as haemovanadine. Concentration factors can be very high up to 10^5 or even slightly more. Certain echinoderms may contain up to 57 mg/kg dry weight (internal tissues) while certain ascidians (whole body) may contain 620 mg/kg dry weight. It will be recalled that some ascidians are eaten, e.g. in the Mediterranean and in Japan. Other invertebrates are reputed to contain 5-40 mg/kg, while fish range from 1.6-1.8 mg/kg dry weight.

Open ocean concentration of vanadium is stated to be 1 $\mu\text{g}/\text{l}$ while coastal waters may contain 3-4 $\mu\text{g}/\text{l}$.

Vanadium compounds are of moderately high acute toxicity and have been said to cause a wide range of effects when administered to mammals. However, no ill-effects to man are likely to occur from contact with sea water even if it is contaminated with vanadium compounds since the normal diet provides man with about 2 mg of vanadium each day, an intake which greatly exceeds any exposure from consuming present day seafoods.

3.3.21 Zinc

Zinc occurs naturally as the sulphide mineral sphalerite (ZnS) which has a wide variety of common names, and in lesser quantities as carbonate, smithsonite (calamine) and silicate minerals. It occurs very widely in small quantities as a component of rocks and soils; average terrestrial abundance is of the order of 40 ppm. Zinc compounds are ubiquitous in animals and plants.

Zinc production is largely from the sulphide mineral and world production is rather more than 5 million tons per annum; it has almost doubled since 1953 but now appears to be stabilizing. Chief producers are Australia, Canada, Germany, Italy, Japan, Mexico, Poland, the United States of America and Zaire, with smaller production from many other countries.

Deposits of zinc sulfide are frequently associated with lead sulfide and all zinc sulfide ores contain a small proportion of cadmium. The main uses of zinc are for galvanizing or otherwise coating iron and steel sheets and wire which have a very wide application e.g. in roofing, agriculture, etc. Zinc is also used in artificial fibre manufacture, in battery cases, alloy manufacture (e.g. brass and in diecast alloys), paint manufacture, in plating as an alternative to cadmium, electrical fuses and anodes, and cable wrappings.

Large amounts of zinc are discharged to rivers in chemical wastes e.g. from some artificial fibre manufacturing processes. Sewage contains large quantities of zinc mainly derived from food (zinc is poorly absorbed by the gut) and galvanized domestic utensils and water cisterns. Swedish sewage sludge analyses give an average content of zinc of 2500 mg/kg dry weight (range 1-10 g/kg). Similar figures have been obtained from United Kingdom analyses e.g. the Greater London Council sewage averages 3500 mg/kg of zinc. Other sources of zinc in the sea are mining wastes and the dissolution of sacrificial anodes fitted to ships' hulls for protection against electrolytic corrosion.

Zinc in river discharges derived from the dissolution and weathering of rocks has been estimated at 720,000 tons per annum on a global basis. Burning of fossil fuels is estimated to contribute 7,000 metric tons per annum of zinc to the atmosphere part of which will ultimately reach the sea.

There is world-wide transport by ships of zinc ingots and sulfide concentrates (in 1970 in excess of 400,000 tons). Spillage of a cargo would result in slow leaching of salts but negligible hazard to marine life. The acute toxicity of zinc compounds to marine animals is generally reported as being within the range 1-10 mg/l, but concentrations as low as 0.006 mg/l may induce abnormalities in sea urchin larvae under laboratory conditions. Acute exposure leads to gill damage in fish, but uptake by marine organisms is primarily via food rather than directly from sea water. Zinc sulphate at a concentration of 0.125 mg/l is reported to reduce growth of a marine ciliate protozoan by 8.3 per cent; toxicity was increased when the zinc was associated with lead or mercury.

Larvae of marine animals are generally more susceptible than adults e.g. the LC 50 (96 h) value for European flat oyster (Ostrea edulis) larvae is reported to be 0.1 mg/l while that for adults of the same species is 100 mg/l, growth of the larvae was impaired at 0.05 mg/l. Larvae of the American oyster (Crassostrea virginica) gave an LC 50 of 0.31 mg/l of zinc chloride (range 0.22-0.37 mg/l). Fifty per cent of the larvae of several marine invertebrates were killed in two hours by 5.30 mg/l of zinc as citrate. Concentration factors for zinc in marine animals range from 2,000-100,000 depending upon the species; the lowest values are derived from fish and the highest from oysters.

The normal concentration of zinc in open sea water is reported to be 3 µg/l. Coastal waters give values ranging from 2.50 µg/l. Marine sediments in areas removed from industrial contamination may contain from 4-39 mg/kg, but concentrations in deep sea clays were found to be 165 mg/kg. A sandy silt from Saanich Inlet, British Columbia, yielded 89 mg/kg of zinc. In contrast values from sediments taken from the Bristol Channel, United Kingdom, an area containing an active smelter and old mine workings, ranged between 400 and 600 mg/kg. In the New York Bight sediment values from the area uncontaminated from dumping ranged between 16-20 mg/kg whereas near the centre of the sewage dumping area the mean value was 254 mg/kg. The amount of sewage dumped in the area exceeded 10,000 tons per day in 1964-1965. In the Clyde Estuary (Scotland) sediments from the sewage dumping area contained 136-826 mg/kg.

Zinc is an essential element for man and is a constituent of several cellular enzymes. It occurs ubiquitously in food which normally provides man with an intake of 10-15 mg zinc per day. Gastrointestinal upsets can be caused when high concentrations of soluble zinc salts are taken by mouth but the concentrations necessary to produce this effect are much higher than could occur in even highly polluted water. Constant exposure to low concentrations of zinc salts does not cause its accumulation in human tissues or produce chronic toxic effects.

3.4 Radio-active materials

The group considered that they were more concerned with the problems arising from exposure to radiation, and not with other problems associated with specific radionuclides such as bioaccumulation or acute toxicity. Radio-active substances are naturally present in the marine environment, in solution, in crustal rocks and in sediments. There are two main sources of artificial radio-activity in the marine environment, fall-out from nuclear weapon testing and wastes from nuclear power production, including fuel processing.

Uncontrolled inputs of artificial radio-activity to the marine environment still occur as a result of nuclear weapon testing. At the reduced level of testing in recent years this input approximates the rate of loss of this category of material due to radio-active decay. Under these conditions the global ocean inventory of weapon test origin will remain roughly the same with an average annual input some 10 times greater than the present input from nuclear power operations. Moreover, the introduction of waste radio-active materials from this latter source

is subject to strict control, usually under special legislation, designed to reduce hazards to public health or harm to marine resources to negligible proportions.

Whilst greater in over-all magnitude, weapon test fall-out may be regarded as a diffuse input and the consequential concentrations in any sector of the marine environment, except possibly in the vicinity of maritime test areas, will be low. There may be some bias with respect to latitude or, in the case of fresh fall-out, between hemispheres, according to the location, scale and frequency of testing. In contrast, inputs from waste management activities in association with nuclear power production will tend to be discrete point inputs leading to higher but localized contamination.

It follows that in terms of the governing criteria for human radiation exposure, waste management policies will have major significance for the radiation exposure of individual members of the public. Weapon testing, in spite of its lower concentration, will on the other hand, by virtue of its wide distribution, continue to contribute the major share to population radiation dose commitment from the marine environment. Provided there are no serious changes in the scale of weapon testing or the philosophy and practice of radiation protection, both categories of exposure will be of minor significance.

Continued development of nuclear power may gradually change the balance of this picture, with the exploitation of nuclear energy for peaceful purposes contributing an increasingly large share of the radiation exposure. Several hundred nuclear power plants are expected to be in operation within the next 20 years. Strict maintenance of high levels of control and surveillance should, however, serve to ensure that the situation is contained well within acceptable bounds under routine conditions. However, because of the high level of radio-activity of some wastes and the long half-lives of some of the substances, there are materials that must be prevented from escaping into the marine environment for centuries.

High level radio-active waste must, of course, remain under stringent surveillance in high integrity storage or be introduced to the environment in such a way, as for example burial in remote geological strata, as to ensure that there is no possibility of radiation exposure of man or other elements of the biosphere.

There remains the consideration of nuclear accidents, and whilst the probability of occurrence of accidents of significant magnitude are acceptably low at individual nuclear sites, the over-all probability of an accident will increase as the total number of sites increases. Accidental release of radio-active materials may be caused by human error, equipment failure, earthquake, sabotage or war. The first three factors can be and are catered for in the design, construction and operation of nuclear installations to an extent that accidents of such origin are reduced to a very low frequency. The prevention of accidents due to war and sabotage presents different problems not specifically catered for in design and construction but amenable to treatment to some extent in operation and control. Accidents whose origin, probability of occurrence and magnitude warrant contingency planning are not likely to be on such a scale as to present problems which are other than national in character. It is inconceivable that the frequency of occurrence of such accidents which would be acceptable to national regulatory

authorities could pose a serious problem to the marine environment. As with routine disposals, the present stringent standards of construction, operation and control should ensure sensible management of these problems.

There are three different types of radio-active substances, namely those that give rise to α (alpha), β (beta) or γ (gamma) emissions (or mixtures of these). Each of these activities has a characteristic energy. Different isotopes have different half-lives and pathways in the marine environment and these, together with the different types of emissions lead to different degrees of hazard. For more complete and detailed information see, e.g. IAEA Information Circular 205/Add.1, 10 January 1975 (Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter).

3.5 Oil and oil dispersants

Prior to about 1950, petroleum was refined in the country of origin, and the world traffic was largely in refined products. The newer refineries have been built in the developed countries, giving rise to the growth of a new trade in the carriage of crude oil by sea from the oil producing areas to the user countries. The massive and continual rise in oil consumption has resulted in the construction of larger and larger vessels for this trade. At the present time the largest ships carry 0.5 million tons of oil.

Annual world production has risen from 1,260 million tons in 1962 to 2,600 million tons in 1972; this is expected to rise to 3,500 million tons by 1980.

This rise in oil consumption has led to a world-wide search for newer sources of supply, and an increasing proportion of the world's needs is now and will continue to be met from off-shore oil fields. These will increasingly be sited on the deeper parts of the continental shelf, as the technology of deep-sea drilling develops.

These changes in the world's trade in petroleum and petroleum products since about 1950 have led to a massive increase of oil pollution of the marine environment, especially of beaches, largely from shipping. There has been considerable national and international activity to limit, and where possible to prevent, this pollution by oil. An international conference convened in 1954 by the United Kingdom concluded the International Convention for the Prevention of Pollution of the Sea by Oil, 1954, which was subsequently deposited with IMCO. Amendments to this convention, designed to further limit the quantities of oil discharged at sea, were adopted in 1962 and 1969, although the latter have yet to be brought into force internationally. Further limitations on the operation of tankers and other vessels were developed by an international conference convened by IMCO in 1973. This resulted in the International Convention for the Prevention of Pollution from Ships, 1973, which was designed to achieve "the complete elimination of intentional pollution by oil and noxious substances other than oil and the minimization of accidental spills".

Oils and oil products can enter the marine environment from submarine seeps, from shipping operations and marine accidents, both on the high seas and in port (up to 1 million tons per annum) and by discharge to rivers, sewers, and so finally to the sea. Aerial transport of oil derived from internal combustion engines may transfer substantial quantities to the sea.

In general, oil is lighter than water and tends to spread fairly rapidly, forming a thin layer which moves over the surface under the influence of winds and tides. Though found widely over the oceans it is most frequent around the main routes by which oil is carried from producing areas to the refineries and along trade routes and near the population centres they connect.

In temperate and tropical zones oils are biodegraded and also polymerized; under the action of light and oxygen density increases and the particles may become dense enough to sink to the sea floor. In very cold waters such as the Arctic the rate of biodegradation appears to be very slow. A fresh crude oil can lose up to 30 per cent by evaporation in 30 hours. A much smaller amount can dissolve in the water. These effects tend to increase the density to the sinking point.

Oils with high wax content or which are very viscous do not degrade so rapidly and are frequently found on beaches as lumps or smears of so-called "tar". "Tar balls" are ubiquitous in many ocean areas, particularly on major tanker routes and may be derived from tanker washings.

When highly dispersed, oil may be moderately toxic to marine life but under normal field conditions toxicity is low. The species most at risk are those living in the littoral zone where oil may be deposited on a falling tide. In such circumstances, shellfish have become tainted and edible seaweeds both reduced in growth and made unsaleable. Observations in temperate zones have shown that a single heavy contamination of the flora and fauna of the intertidal zone has a negligible effect though repeated applications (every tide) of a much smaller amount - a hardly visible film - eventually leads to a reduction in the number of species and in some cases, absence of life. In tropical areas marine life may be more sensitive to damage by oil.

In inland estuarine waters or enclosed bays or similar situations, the effect of the more toxic aromatic fractions, together with the reduction in dissolved oxygen resulting from biodegradation, may produce more marked mortality in many species.

It is believed that traces of hydrocarbons may affect fish behaviour such as the return of salmon to the "home" river. Some oils contain carcinogens and their reported occurrence in organisms in the food chain as the result of oil pollution could, if proven, lead to some risk to man as the ultimate consumer.

Oil pollution is popularly regarded as an important contaminant of the ocean very largely because it is visible, and is a great despoiler of coastal amenities. It also kills sea birds, particularly the diving birds, which, being washed ashore in an oiled condition, arouse great concern.

Considerable attention continues to be paid to methods for the recovery of oil from the sea surface. Satisfactory methods are now available for confined waters under calm conditions but it is still difficult to apply such methods to the open sea. Sinking techniques are now regarded as less desirable because of the tendency of sunken oil to return to the surface or to move substantial distances and so affect living resources. Fishing gear dragged along the bottom may become contaminated by oily residues. However, it may be necessary to use such methods as an emergency measure in the event of a massive release of oil such as could occur following a tanker casualty.

Improvements have been made in the formulation and usage of oil dispersants. Those now available are of low toxicity to marine life and are more effective at lower concentration, enabling better use to be made of new and more efficient application equipment. The use of absorbents for removing surface oil, although well developed for inland waters, has not proved of value in open sea conditions.

For a further consideration of the effects of oil reference should be made to the Reports of the GESAMP Working Group on the Impact of Oil on the Marine Environment (GESAMP VII and VIII, GESAMP Reports and Studies Number 6).

3.6 Organic chemicals

The number of organic chemicals known to man at the present time exceeds 1 million. A wide range of these substances occur naturally in animals and plants and in natural products such as petroleum. Only a small proportion of the total is used by man in the pure state and only a comparatively few compounds are produced in large quantities. Currently 70 per cent of the world's organic chemicals are produced directly or indirectly from petroleum and it is estimated that the proportion will exceed 90 per cent by 1980.

As a starting point in the review of the potential pollution risk posed by organic chemicals, a number of substances were selected each of which are known to be carried in large quantities by ship (more than 25,000 tons per year) or which might create a hazard to marine life if released to the sea. In making this selection, use was made of the Report of an Ad Hoc Panel of IMCO and GESAMP Experts to Review the Environmental Hazards of Noxious Substances other than Oil Transported by Ships (GESAMP IV/19/Supp. 1) and a study by Norway for IMCO on the bulk carriage of chemicals by sea. The Norwegian study was prepared as a background document for the 1973 IMCO Marine Pollution Conference and summarizes the replies to a questionnaire on the quantities, type of ship, etc. involved in bulk transport of chemicals. Because replies to the questionnaire were not received from all countries, the totals given for annual carriage cannot be regarded as the complete world-wide carriage figures. They do, however, provide a satisfactory basis for an assessment of the marine pollution hazard arising from the bulk carriage of chemicals. Where the amount carried is said to be in excess of 25,000 tons per annum, the chemical was regarded as a candidate for the review and the Norwegian study data on quantities shipped are quoted.

In considering the selected organic chemicals as harmful substances, the view was taken that the major risk to the marine environment arises as a result of chronic exposure to continuous discharges from factories, etc. However, where it is known that substantial amounts (>25,000 tons per annum) are moved by sea, there is a significant risk of severe short-term pollution following spillage of ships' cargo. Comments are made on the effect such a spillage might have; these are equally applicable to accidental massive losses from a factory or storage facility. Where marine transport is known to be important for other substances listed in this review, similar notes will be added as part of the continuing process of revision and updating.

It has not been possible to cite world production figures of organic chemicals but it was noted that other groups had recognized the need to establish these wherever possible.

In compiling notes on the organic substances included in the Review, the Working Group assembled information on the following points:

- (1) Nature of the substance and principal purposes for which it is used;
- (2) Extent to which it is transported by sea;
- (3) Principal ways in which it may reach the marine environment, e.g. as waste from particular industrial processes or uses, from tank washings, by aerial transport, etc;
- (4) Effects on marine life, including bioaccumulation or tainting;
- (5) Hazard to human health by ingestion directly or via seafood, by skin or eye contact or inhalation, for example when bathing in an area affected by a substantial spillage;
- (6) Effects on amenities, e.g. by interference with leisure activities, objectionable smell or persistence;
- (7) Nature of breakdown products produced in the marine environment, their toxicity and persistence.

3.6.1 Acetone CH₃ COCH₃, dimethyl ketone, 2-propanone

Acetone is a very widely used solvent, especially in paints, varnishes and the pharmaceutical industry; it is also used as a delustrant in cellulose acetate fibre manufacture and as a general degreasing agent. The compound is manufactured on a world-wide scale, with plants in most developed countries. Because of its very wide scale usage as a solvent, substantial amounts are likely to enter the sea in effluents discharged to rivers or via pipelines. Transport by sea is largely in chemical tankers.

Acetone is readily miscible with water, highly volatile (B P 56°C) and inflammable (F P - 20°C); the vapour will ignite above water solutions of 2-3 per cent.

Its acute toxicity (LC 50) to aquatic life is in the range 100-1,000 ppm. It is readily degradable and is unlikely to be persistent in the marine environment; its degradation products are unlikely to be more toxic than the parent compound.

Exposure to concentrations of vapour well above those that are recognizable by odour may cause eye, nose and throat irritation in man; the liquid produces transient eye irritation.

Even a substantial spillage would be unlikely to create an amenity problem. Its smell is not objectionable (it is used in many paints).

3.6.2 Acrolein, $\text{CH}_2 = \text{CH} \cdot \text{CHO}$, propenal, acrylic, aldehyde, allyl, aldehyde, acraldehyde, acrylaldehyde

This substance, an unsaturated aldehyde, has a disagreeable odour, resembling burnt fat. It is a clear, colourless liquid but is more usually tinted or coloured yellow. It is used as an intermediate in the production of acrylic and other plastic materials and is manufactured on a large scale by the dehydration of glycerol and by the oxidation of propylene. It is not normally carried in bulk, but any increase in usage may require the use of demountable tanks.

Acrolein is unstable and polymerizes readily to give disacryl. It undergoes oxidation in air to form acrylic acid.

It is lighter than water (SG 0.841) but fairly soluble in it (about 22 per cent in freshwater). It is very volatile (BP 52.5°C) and has an appreciable vapour pressure at normal atmospheric temperatures. Its flash point is less than 0°C and in view of its flammability and low boiling point, a spillage could be a fire and explosion hazard.

Acute toxicity to marine life (LC 50) is less than 1 mg/l, and sublethal effects (decreased shell growth of oysters) have been recorded at less than 0.1 mg/l. It is repellent to fish.

The vapour causes strong irritation to the skin, lungs and eyes, but is readily detectable by smell at concentrations below that likely to be harmful. Acrylic acid, to which it is oxidized, has similar properties. Acrolein is unlikely to accumulate and does not have long-term toxic effects.

Spillage on or near to a beach would cause an amenity problem on account of its smell and fire hazard.

3.6.3 Acrylonitrile $\text{CH}_2 = \text{CHCN}$, propene nitrile, vinyl cyanide

This substance is mainly used in the manufacture of synthetic rubber and plastics and as a synthetic fibre for textiles (e.g. "Acrilan" and "Courtelle"); it is also employed as a grain fumigant.

Small quantities are found in wastes from manufacturing plants. Some may be lost to the air during manufacture.

It is transported in bulk by sea on a world-wide scale, mainly between developed countries. (Amount carried in 1970: 93,453 tons: maximum cargo about 800 t; 200 t per tank. Maximum release from rupture of two tanks possibly 400 tons.)

Although lighter than sea water (SG 0.80), it is soluble in water (31 g/l in fresh water) and is unlikely to remain on the surface of the sea due to its solubility and volatility (BP 77.3°C). However, hydrolysis is unlikely to be rapid at the pH of sea water. A substantial spillage, resulting for example from a collision at sea, would create a fire and explosion hazard (F P 0°C , explosive limits 3-17%).

If released to the marine environment in substantial quantities, it would constitute a significant hazard to marine life (LC 50 1-10 ppm). It is not bio-accumulated but longer term low-level effects are uncertain. Breakdown products in the sea are likely to be less toxic than acrylonitrile.

The vapour is acutely poisonous and beaches affected by a spillage would have to be cleared. It would, however, evaporate rapidly in favourable circumstances, e.g. high temperatures and breezes. The polymer is harmless but acrylonitrile is unlikely to polymerize on the beach.

3.6.4 Allyl alcohol, $\text{CH}_2=\text{CH}.\text{CH}_2\text{OH}$, 2-propen-1-ol, propenol-3, vinyl carbinol

This substance is an unsaturated alcohol, with a pungent odour. It is a colourless liquid, but frequently tinted yellow. It is used in the preparation of resins and plastic materials, and to a smaller extent in the preparation of some pharmaceuticals. It is manufactured from glycerol by dehydration and subsequent reduction and from allyl chloride by hydrolysis. It is carried largely in drums.

It is miscible with water in all proportions. It is not very volatile (BP 97°C), nor does it have an appreciable vapour pressure at normal atmospheric temperatures. It is inflammable, flash point 32.5°C .

Its acute toxicity to marine life is in the range 1-10 mg/l. Development of eggs of bivalves was adversely affected at concentrations of about 1 mg/l.

Liquid and gaseous allyl alcohol are irritant to the skin, mucous membranes, lungs and eyes. It is readily absorbed from the gastrointestinal tract and through the skin, causing severe liver damage at comparatively low dosage levels. However,

low concentrations are easily discernible by taste and smell and concentrations likely to be injurious in a short period of time will be painful to the eyes and nose.

Spillage on or near a beach would cause a short-term amenity problem on account of its smell and fire hazard.

3.6.5 Allyl chloride $\text{CH}_2=\text{CH}.\text{CH}_2\text{Cl}$, 3-chloropropene, chloropropylene

This substance is a clear colourless liquid with an irritating smell. It is used as a chemical intermediate and in paints, varnishes and adhesives. It is made by high temperature chlorination of propylene. It is normally carried in drums and demountable tanks, but not so far as a bulk liquid.

It is lighter than water (SG 0.938). It is only slightly soluble in water, with which it reacts slowly to form allyl alcohol. It is very volatile (BP 44.6°C), and is a fire hazard.

For acute toxicity to marine life and hazard to human life see allyl alcohol.

Spillage on a beach would create a short-term amenity problem on account of the smell and fire hazard.

3.6.6 Benzene C_6H_6 , benzol

Benzene has many industrial uses: for example, in solvents; as a starting material for the manufacture of "hard" detergents and of cumene used in the production of resins; as a lubrication oil additive and in the making of nylon; as a chemical intermediate in the production of acetone and phenol.

Benzene is carried in bulk by sea on a world-wide basis (amount carried in 1970: 279,852 tons).

Its solubility in sea water (2000 ppm) is somewhat above that of toluene; its flashpoint is very low (-17°C) and it is also an explosive hazard (explosive limits 1-8 per cent). If spilt, it floats on the sea (SG 0.88) and evaporates readily (BP 80°C).

Benzene has an acute toxicity to marine life (LC 50) in the range 10-100 ppm but it is not bioaccumulated. Breakdown products are less toxic than the benzene which is a human hazard because it damages liver and bone marrow. It is metabolized and excreted by human beings. Frequent exposure may lead to leukaemia; high concentrations of vapour have a narcotic effect.

It has a strong but not highly objectionable smell. A nearby spillage might cause a fire or explosive hazard on a beach, but this would be a short-lived situation.

3.6.7 Carbon disulphide CS_2 , carbon bisulphide

This substance is mainly used for the production of rayon and cellulose films and in the manufacture of carbon tetrachloride and xanthates which are employed as flotation agents. It is also widely used in small quantities as a solvent for a number of elements. Small quantities only are shipped in bulk (amount carried in 1970: 595 tons); extreme care is required when it is moved in drums.

It is heavier than sea water (SG 1.26), very volatile (BP $46^{\circ}C$) and highly inflammable (F P $-30^{\circ}C$). It presents an acute fire and explosive hazard and may ignite spontaneously at $100^{\circ}C$, e.g. by contact with hot steam pipes. It is very slightly soluble in sea water (about 0.3 per cent).

Carbon disulphide has an acute toxicity (LC 50) to marine life of less than 1 ppm and it is bio-accumulated. It decomposes in the sea by oxidation.

The liquid is an irritant to the skin and eyes and is absorbed through the skin. The vapour is absorbed rapidly on inhalation; its ingestion then causes vomiting, liver and kidney damage and respiration failure. It can also cause permanent damage to the nervous system. The presence of the liquid or vapour on beaches would present a major health hazard.

3.6.8 Carbon tetrachloride CCl_4 , tetrachloromethane, perchloromethane

It is used in the manufacture of aerosol propellants and refrigerants, and as a solvent, degreasing agent and agricultural fumigant. It is also used in the chlorination of paraffin wax to produce "cerochlors", plasticisers for paints, etc. Usage is world-wide, principally among industrialized countries.

Carbon tetrachloride is not a problem in effluents, the main losses being to the air by evaporation (BP $77^{\circ}C$) where it may be broken down by ultraviolet light.

Carbon tetrachloride is carried in bulk tankers (amount carried in 1970: 114,203 tons; maximum load about 1,000 tons; usually in small chemical tankers).

Solubility in fresh water is 750 ppm and probably less in sea water. It is heavier than sea water (SG 1.59) and is not inflammable. Acute toxicity to marine life (LC 50) is in the range of 10-100 ppm, with rapid uptake and loss from the tissues. The observed concentration in Irish Sea coastal water was 1×10^{-10} or 10^{-11} ; concentration in fish was higher in the same area. Some difficulties however, were experienced in identifying peaks in the records. Muds may take up carbon tetrachloride to the extent of x2 in the immediate vicinity of effluent discharge. The breakdown products of carbon tetrachloride in the sea are not fully known.

The liquid can be absorbed through the skin and the vapour, which is heavier than air, may be inhaled. Exposure to either liquid or vapour may cause severe liver damage.

The smell is distinctive but not highly objectionable. Following a major spillage, carbon tetrachloride might be driven up on to the beach over a period.

3.6.9 Chlorobenzene C_6H_5Cl , monochlorobenzene, benzene chloride, phenyl chloride

This liquid is used as an intermediate in the production of phenol from benzene, as a starting material in dyestuffs manufacture, and in the production of fine chemicals. It is also employed as a solvent and as a heat transfer medium. It reaches the environment largely by evaporation but may be present at the level of a few ppm in some liquid industrial effluents. It is transported by road and rail and in ships, but not in bulk.

Chlorobenzene is moderately volatile (BP $132^{\circ}C$), heavier than water (SG 1.11), inflammable (F P $28^{\circ}C$), and explosive (explosive limits 1.8-9.6 per cent).

Its acute toxicity to marine life is rather high (96 hour LC 50 about 2.5 ppm) and it can accumulate rapidly in fish, largely in the liver. Chlorobenzene is broken down by microorganisms to hydrochloric acid and phenol, which eventually breaks down to carbon dioxide and water. In the atmosphere it is broken down by ultraviolet light in about two weeks. It may accumulate in sediments depending upon organic content and concentration in the overlying water.

Ingestion of the liquid and inhalation of high concentrations of the vapour can depress the nervous system and cause liver damage; the vapour is slightly irritant.

There is likely to be a health hazard only in areas close to a large spillage.

3.6.10 Chloroform $CHCl_3$, trichloromethane

Chloroform has many uses: in toothpastes and pharmaceutical products; as a flavouring in foods; as a solvent; and in making aerosol propellants and refrigerants. It presents a minor fire hazard and is, therefore, not used in major industrial processes, but it is employed in small amounts in a wide variety of ways. An important route to the marine environment may be through the atmosphere. It is mostly carried in small drums (25 litres) with ethanol as a stabilizer and there is little bulk carriage (amount carried in 1970: 3,621 tons).

Chloroform is more volatile than carbon tetrachloride (BP $61^{\circ}C$.) and more soluble in sea water (about 1.5 per cent). It is heavier than sea water (SG 1.49).

Its effects on marine life, so far as they have been assessed, are similar to those of carbon tetrachloride (96 hour LC 50 about 30 ppm). The breakdown products of chloroform in the marine environment are likely to be less toxic than the parent compound.

Ingestion of liquid and inhalation of vapour depress the nervous system and cause liver damage. The liquid is only slightly irritant to the skin but can cause severe eye injury. Health is likely to be affected only following a spillage close to a beach on to which the liquid might be brought by successive tides.

3.6.11 Cresol $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$, methylphenol, cresylic acid, tricresol

This substance is normally a mixture of 3 isomers, 1,2, 1,3 and 1,4 hydroxymethylbenzene. Cresols have a very wide usage, mainly in the manufacture of disinfectants and synthetic resins, but also in the production of tricresyl phosphate, salicylaldehyde, coumarin and herbicides. They are produced in many countries. Trade is world-wide and includes carriage in bulk (amount carried in 1970: 25,697 tons).

These substances are marginally heavier than sea water (SG 1.03 - 1.05). They are slightly volatile (BP 195 -205°C) and soluble in water (about 2 per cent). They are inflammable (F P 80-86°C) but do not present a major fire risk.

They have an acute toxicity to marine life (LC 50) in the range 1-10 ppm and are liable to taint fish and shellfish at very low concentrations with consequent interference with marketing. They are biodegradable, the breakdown products being less toxic than the parent compound.

Cresols are highly irritant and rapidly damage skin; they are hazardous to human beings on oral ingestion or following absorption through the skin. Solutions are somewhat less harmful.

A large spillage near a beach would create an amenity problem.

3.6.12 Crotonaldehyde $\text{CH}_3\text{CH} : \text{CH CHO}$, methyl acrolein, crotonic aldehyde

This is used mainly for making 2-ethyl-hexanol and acetate solvents; it is also widely used as a chemical intermediate. The main routes of loss to the sea are via industrial effluents and leakages. It is not known to be transported on a large scale.

It is lighter than sea water (SG 0.86), moderately volatile (BP 102°C), soluble in water (about 15.5 per cent) and inflammable (FP 13°C), but has a low vapour pressure; explosive and fire hazards are minor.

Acute toxicity to marine life (LC 50) is in the range 1-10 ppm, it is biodegradable but not bioaccumulated. Breakdown products are less toxic than the parent compound.

Both liquid and vapour are strongly irritant; splashes of liquid in the eye may cause blindness. Exposure to liquid, vapour (TL_v 2 ppm) and solutions is extremely hazardous and beaches affected by a spillage would have to be cleared for a period. It has a pungent smell.

3.6.13 Cumene $C_6H_5CH(CH_3)_2$, isopropylbenzene, cumol

This is an intermediate in the production of phenol and acetone. It is also used in the manufacture of plastics and as a solvent. World-wide carriage is in bulk (amount carried in 1970: 151,075 tons).

Cumene is lighter than sea water (SG 0.86) and practically insoluble. It is moderately volatile (BP $152^\circ C$) and highly inflammable (FP $45^\circ C$).

Its acute toxicity (LC 50) to marine life is in the range 10-100 ppm. If released to the sea, the bulk would be lost by evaporation; any that dissolved would be degraded.

Although very high concentrations of the vapour are narcotic, cumene is unlikely to harm human health.

A large spillage near a beach might create a short-lived amenity problem because of the fire risk.

3.6.14 O-dichlorobenzene $C_6H_4Cl_2$, 1,2-dichlorobenzene

This substance is used in the manufacture of isocyanates and dyestuffs, as a solvent and in the production of paint-strippers, as a pesticide and also as a degreasing agent for metals, wool and leather. Losses to the environment will occur via effluents from industrial use, discarding of used solvents and paint-strippers and by evaporation. It is transported by road and rail tankers and by ships but not in bulk.

It is only slightly volatile (BP $180^\circ C$), heavier than sea water (SG 1.31) and practically insoluble (about 100 ppm in sea water). It is inflammable (FP $65^\circ C$).

O-dichlorobenzene is highly toxic to fish (LC 50 about 1 ppm) and is accumulated and lost very rapidly (within one week), with high concentrations in the liver, but very much less in the flesh. It may also accumulate in sediments, depending on organic content and concentration in overlying waters. There is very little information on biodegradability or breakdown products in the sea but it can be metabolized and excreted by mammals.

Although high concentrations of both vapour and liquid can lead to depression of the nervous system and liver and kidney damage, a human health hazard is unlikely except from prolonged or frequent contact with liquid which might be washed up on beaches.

It is otherwise unlikely to create an amenity problem; the smell is penetrating, but not unpleasant.

3.6.15 P-dichlorobenzene $C_6H_4Cl_2$, 1,4-dichlorobenzene

This substance is a solid (MP 53°C). Its main uses are as a deodorant, moth repellent and soil fumigant, and in the manufacture of dyestuffs and fine chemicals. Losses to the environment will occur mainly by evaporation (it is widely used as a deodorant). It is transported largely in drums.

It is heavier than sea water (SG 1.46); slightly volatile (BP 174°C) and practically insoluble (about 75 ppm). It is inflammable (FP 65°C).

P-dichlorobenzene has an acute toxicity to fish (LC 50) of about 1.5 ppm; there is no information regarding its bioaccumulation but it is probably similar to O-dichlorobenzene. Biodegradability and breakdown products have not been investigated.

The risks of injury to human health are extremely low although any drums cast up on the shore would represent a hazard since ingestion may lead to liver damage.

It is otherwise unlikely to create an amenity problem.

3.6.16 Epichlorohydrin $CH_2-O-CH-CH_2Cl$, γ -chloropropylene oxide

The biggest single use of this chemical is in the production of epoxy and phenoxy resins; smaller quantities are used as a solvent for cellulose esters, in the manufacture of glycerol and in curing propylene-based paints.

Trade is mainly between the developed countries (amount carried in 1970: 2,445 tons). The maximum ship consignment is likely to be around 500 tons, with a maximum tank size (normally stainless steel) of 200 tons. The bulk of the material transported is carried in drums.

Epichlorohydrin is heavier than water (SG 1.18), moderately volatile (BP 118°C) and inflammable (FP 34°C); it is slightly soluble in water (about 1 per cent) and if released in small quantities in factory effluents will probably be completely dissolved. Accidental spillages of larger amounts will sink.

Although its acute toxicity (LC 50) to marine life is in the range 1-10 ppm, it is unlikely to be accumulated by marine animals and is probably readily broken down by bacteria and other aquatic life. The final breakdown products and intermediates are likely to be of lower toxicity than the parent compound.

Repeated contact with the liquid may cause allergic sensitization in man.

Because of its volatility and strongly irritant vapour, a large spillage would cause a short-term but substantial amenity problem.

3.6.17 Ethyl alcohol C_2H_5OH , ethanol, alcohol

Ethyl alcohol is produced in many countries. Its main uses are in production of acetaldehyde as a solvent and in production of alcoholic drinks. It has many minor uses and is consequently present in small quantities in many industrial effluents. Trade is world-wide; sea transport is in bulk (amount carried in 1970: 59,477 tons) and in demountable tanks.

Ethyl alcohol is lighter than (SG 0.80) but completely miscible with sea water. It is volatile (BP $78^{\circ}C$) and inflammable (FP $9-11^{\circ}C$).

Its acute toxicity to marine life (LC 50) is in the range 10-100 ppm. It is not accumulated and is rapidly biodegraded to substances which are harmless. A major spillage might result in a deoxygenation problem in confined waters.

No human health hazard or amenity problem is likely to arise from the release of ethyl alcohol to the marine environment.

3.6.18 Ethylbenzene $C_6H_5C_2H_5$, phenylethane

This substance is used in the production of styrene monomer and as a solvent. Its main route to the sea will be in wastes from manufacturing plants and possibly by transport through the atmosphere. It is transported in bulk chemical tankers (amount carried in 1970: 125,726 tons), mainly in the North Atlantic.

It is lighter than sea water (SG 0.87), practically insoluble, moderately volatile (BP $136^{\circ}C$) and highly inflammable (FP $20^{\circ}C$).

Its acute toxicity to marine life (LC 50) is in the range 10-100 ppm; it is not likely to be bioaccumulated and the breakdown products are expected to be less toxic than the parent compound.

The liquid and high concentration of vapour are somewhat irritant to skin and eyes and prolonged exposure will depress nervous activity. Human health is unlikely to be harmed except on prolonged exposure to liquid.

Apart from deposition of liquid on beaches resulting from a substantial nearby spillage, there would be no amenity problem.

3.6.19 Ethylene dibromide $\text{CH}_2\text{Br CH}_2\text{Br}$, EDB, 1,2-dibromoethane, glycol dibromide

This substance is a heavy colourless liquid with a sweet odour, but may be tinted or coloured yellow. It is used as a grain fumigant, a solvent, an anti-knock reagent (especially in aviation fuels) where it acts as a lead scavenger, and as a chemical intermediate. It is made by direct bromination of ethylene. It is carried largely in drums; bulk transport is not known.

It is much heavier than water (SG 2.17) and slightly soluble in it (about 0.4 per cent). It has an appreciable vapour pressure at normal atmospheric temperatures, but is not particularly volatile (BP 132°C). It does not constitute a fire hazard; it was formerly used as a fire extinguisher, but this use had discontinued as it emits toxic fumes when heated to decomposition.

The acute toxicity to marine life is in the range 10-100 mg/l. There may be short-term bioaccumulation, and the material is known to be both carcinogenic and mutagenic.

High concentrations of ethylene dibromide vapour are irritant; prolonged contact with the liquid causes skin injury. It is readily absorbed by the lungs, skin and from the gastrointestinal tract. Solutions resulting from spillage at sea are unlikely to be hazardous to human health.

The only amenity problem is that which could arise from high concentrations of the vapour.

3.6.20 Ethylene dichloride $\text{CH}_2\text{Cl.CH}_2\text{Cl}$, 1,2 dichloroethane

This substance is a solvent for gums, fats and waxes. It is used in the manufacture of paints, varnishes and other surface coatings and in the production of artificial fibres and plastics, e.g. acetyl cellulose, vinyl chloride and PVC. It is also used in the production of automobile anti-knock compounds. The principal source of contamination of the marine environment is from wastes arising from industrial processes; tanker washings are relatively unimportant. World-wide tanker trade is in bulk (amount carried in 1970: 241,356 tons).

It is heavier than sea water (SG 1.26), slightly soluble (about 1 per cent), and volatile (BP 85°C); spillage could create a fire risk (FP 15°C).

Acute toxicity to marine life (LC 50) lies above 100 ppm, with short-term accumulation only. This substance cannot be detected in the marine environment by present analytical methods. Breakdown products in the marine environment are likely to be less toxic than ethylene dichloride.

The vapour irritates the eyes, nose and throat and exposure to either liquid or vapour causes nervous system depression and liver and kidney damage. There is likely to be a health hazard only in areas close to a large spillage.

If spillage occurs close to a beach there would be a minor amenity problem, since ethylene dichloride, though heavier than water, might be brought ashore by successive tides.

3.6.21 Ethylene glycol $\text{CH}_2\text{OH}\cdot\text{CH}_2\text{OH}$, 1,2 ethanediol

This compound is the simplest of the glycols. Its major uses are as a coolant and an anti-freeze and de-icing compound, but recently large amounts of ethylene glycol of high purity have been used in the manufacture of Terylene. Smaller quantities are widely used, e.g. in cosmetics, printing inks, brake fluids and laminate plastics.

Because of its low volatility (B P 197°C), the major route to the sea is likely to be via effluent discharges from factories or in town sewers (from car radiators) or by direct spillage and chemical tanker washings.

World trade is extensive, especially of the high purity fibre-grade compounds; large amounts are carried in ordinary chemical tankers (amount carried in 1970: 169,167 tons) with a maximum tank size of 500 tons.

Ethylene glycol is heavier than water (S G 1.12) but is very soluble in water and has a low volatility. It is, however, readily degradable and has an acute toxicity to aquatic life (LC 50) above 1,000 ppm. The final products of biodegradation and any intermediates will be of low toxicity to marine life.

The liquid is not harmful to human skin but 60 ml is reported to be a fatal dose when taken by mouth. Harmful concentrations of vapour are unlikely to occur at sea.

Except where large amounts are spilt in enclosed bays or estuaries when deoxygenation may occur, the material does not seem likely to cause any problem in the marine environment.

3.6.22 Methyl alcohol CH_3OH , methanol, carbinol, wood alcohol

This substance is used as an industrial solvent, as raw material for formaldehyde and methyl ester production and as an anti-freeze in automobiles. It is employed as a denaturant for ethyl alcohol. It is produced in many countries; world-wide carriage is in bulk chemical tankers (amount carried in 1970: 617,601 tons).

Methyl alcohol is lighter than sea water (S G 0.79), volatile (B P 65°C), completely miscible with water, highly inflammable (F P 12°C) and explosive (explosive limits 6-37%).

It has an acute toxicity to marine life (LC 50) above 1,000 ppm. It is not bioaccumulated and the breakdown products in the sea will be harmless. A substantial spillage in confined waters might produce deoxygenation.

Although ingestion of liquid and inhalation of high concentrations of vapour depress the nervous system and cause respiratory failure and blindness (which may be permanent), methyl alcohol is unlikely to present a health hazard under conditions which may be encountered following spillage at sea.

There is no amenity problem.

3.6.23 Methylene chloride CH_2Cl_2 , methylene dichloride, dichloromethane

This is a solvent used in the spinning of acetate yarn and as a paint stripper, both industrially and domestically. It is usually recovered from cellulose acetate yarn processing and main losses will be by evaporation. It is transported on a world-wide scale (amount carried in 1970: 30,329 tons).

It is heavier than water (S G 1.33) but is soluble in water (about 2 per cent) and very volatile (BP 40°C). It is inflammable.

It is not bioaccumulated and acute toxicity to marine life (LC 50) is more than 100 ppm. There is no information on biodegradability, but photo-chemical breakdown in ultra-violet light is rapid. It cannot be found in the marine environment by present methods of analysis. The breakdown products are likely to be less toxic than methylene chloride.

This substance depresses the nervous system and the vapour has been used as an anaesthetic. Because of its high volatility, spillage in the sea is unlikely to present a health hazard.

3.6.24 Naphthenic acid

This is a mixture of carboxylic acids, mainly with cyclic structures, obtained from crude petroleum by alkali extraction. They are used in the production of metal naphthenates which are subsequently used as rot preventatives in wood, cellulose products and natural fibre ropes, and as paint driers. The commercial grade is normally dark in colour with a strong unpleasant smell. This substance is mostly moved in drums, but occasionally in bulk tankers (amount carried in 1970: 1,963 tons).

It is lighter than sea water and practically insoluble; it is not volatile.

Acute toxicity to marine life (LC 50) is in the range 1-10 ppm; it may possibly result in tainting of fish and shellfish. It is likely to be biodegraded, the breakdown products possibly having a similar toxicity.

Naphthenic acid is unlikely to be harmful to man but, because of its strong persistent smell, a substantial spillage could create an amenity problem.

3.6.25 Phenol C_6H_5OH , carbolic acid

This is a single substance with no isomers. Its former main source, coal tar distillation, has now been largely superseded by synthesis from benzene. It is generally used as a chemical intermediate, for example in production of resins, including bakelite-type and epoxy resins, and also in the production of pharmaceuticals, disinfectants, herbicides (2, 4-D type) and lube additives. It has many industrial uses and is contained also in a number of household products. It may, therefore, be present in many industrial and domestic wastes. It is detectable at very low levels. Phenol is carried in road and rail tankers and in ships (amount carried in 1970: 28,970 tons); it may be molten or as a 60 per cent solution in water or as a solid.

It can be very objectionable as a contaminant of potential water supplies, e.g. from desalination and can be tasted at concentrations as low as 20 ppb after chlorination. Disposal of wastes containing phenol is usually carefully controlled in developed countries.

Heavier than sea water (SG: 1.07) but miscible and very soluble, phenol is a significant hazard to marine life, (LC 50: 10-100 ppm). Tainting of fish and shellfish may occur at very low concentrations and can produce severe difficulties in marketing. Although chemically stable, phenol is biodegradable but the speed of this process in the sea is not known. It will react with proteins but action on marine life has not been closely studied. Breakdown products are likely to be less toxic than phenol.

High concentrations are caustic and hazardous to human beings on oral ingestion or on contact with the skin through which it can be absorbed. Dilution markedly reduces the hazard.

A large spillage near a beach would create a significant but short-lived amenity problem.

3.6.26 Phthalate esters

These are esters of o-phthalic acid (1,2 - $C_6H_4(COOH)_2$) and alcohols ranging from C_1 to C_{13} with various isomers. They are used mainly as plasticizers in the production of PVC, polyvinyl acetate, cellulose nitrate and a few other plastics where flexibility is required. They are also used as solvents, insect repellants, alcohol denaturants and in cosmetics. The main routes of loss to the sea will be effluents from manufacturing plants and from plastic production. They are present in domestic sewage. They are transported in road tankers and containers and in bulk shipments (approx. 126,000 tons), the latter mainly as di-octyl phthalate.

Some phthalates will float on the sea but others will sink slowly. They are not volatile (BP above $283^{\circ}C$), practically insoluble in water and virtually non-inflammable.

Although widely found, the toxicity to marine life of phthalates is in general very low but will vary with the alcohol used. One of the most widely used - di-octyl phthalate - has a very low acute toxicity but work on di-butyl phthalate shows a 96 hour LC 50 in the range 1-10 ppm. Di-octyl and di-butyl phthalates are accumulated by some invertebrates and fish from water by factors of 1,400 to 3,600 times. There are indications that natural synthesis can occur in biological material. Hydrolysis and metabolism of the alcohol part of the molecule are likely to occur but the fate of the phthalic acid in the sea is not known. The rate of breakdown will vary between esters.

Human health is unlikely to be harmed by direct contact with the esters, and there is no evidence that fish contaminated with small quantities are a danger to human health.

An amenity problem might arise from a substantial spillage in close proximity to a beach because of their physical nature and persistence.

3.6.27 Styrene monomer $C_6H_5CH:CH_2$ - vinyl benzene, phenylethylene

This compound is used in the production of polystyrene and other plastics, artificial rubbers and resins. The monomer is unstable and is normally shipped with small quantities of paratertiary butyl catechol added as a stabilizer (20 ppm). It is shipped in bulk on a world-wide scale (amount carried in 1970 - 476,206 tons), maximum single shipment being 1,000 tons. Small quantities of the monomer may enter the sea in effluents or in chemical tanker washings but the most commonly encountered form is the expanded polymer which is widely used in thermal insulation and as a packaging material.

The monomer is a colourless inflammable liquid (F P 32°C) which is lighter than water (S G 0.91) and practically insoluble. It would float on sea water and, because the stabilizer is readily soluble in water, the monomer would probably polymerize to a solid unless dispersed by wave action. It is moderately volatile (B P 145°C).

Styrene monomer has an acute toxicity to marine life (LC 50) in the range 10-100 ppm. The polymerized material is not toxic to man and is only very slowly degraded. Degradation products of the polymer and the monomer in the marine environment are not fully known, but are unlikely to be more toxic than the parent compound. The familiar expanded polystyrene beads are produced by heating small beads of polystyrene containing occluded pentene. These beads are almost neutrally buoyant in sea water and have been found in several areas of the world, e.g. the United States and the United Kingdom. They have been found in the gut of fish where they may cause blockages and have been reported to absorb compounds such as PCBs.

3.6.28 Tetramethyl lead and tetraethyl lead $Pb(CH_3)_4$ and $Pb(C_2H_5)_4$, lead tetramethyl and lead tetraethyl (TML and TEL)

These two substances are colourless, mobile, oily liquids with slight but not unpleasant odours. They are made from a sodium-lead alloy by reaction with methyl and ethyl chlorides. In recent years other processes have been developed. By far the greatest quantities of these substances are used as anti-knock additives to fuel. Other minor uses are in the manufacture of organomercury fungicides and other pesticidal products. They are carried exclusively in special returnable tanks and drum-sized containers.

They are heavy liquids (SG 1.99 and 1.66 respectively) and are not appreciably volatile (BP $110^\circ C$ and about $220^\circ C$ with decomposition). Tetraethyl lead is a moderate fire hazard, tetramethyl lead more so.

Acute toxicity to marine life is of the order of 1 ppm (tetraethyl lead); no figures are available for toxicity of tetramethyl lead, but this is probably of the same order. There is likely to be short-term bioaccumulation, although this is as yet not well understood.

These substances cause injury to the brain, liver and kidneys when absorbed through the skin, gastrointestinal tract and lungs following contact with liquid or vapour. As they are practically insoluble in water (20-30 mg/litre), injury through contact with polluted sea water appears unlikely.

Amenity problems are unlikely to arise except when the special containers are damaged. In view of the high density of these substances, full drums are unlikely to be washed up on beaches. However, there have been a number of incidents where empty or partly empty drums have been lost on return voyages and were subsequently stranded on beaches. Use or reuse of these drums for other purposes would be highly hazardous to human health.

3.6.29 Toluene $C_6H_5CH_3$, methyl benzene, phenylmethane, toluol

This substance is widely used in industry, especially as a solvent and chemical intermediate, and is also used in the manufacture of explosives (e.g. TNT). It is carried in bulk by sea on a world-wide scale (amount carried in 1970: 366,441 tons). The main means of entry to the marine environment will be from industrial wastes.

It is more volatile than xylene, highly inflammable (F P $4^\circ C$), and has a similar explosive risk (explosive limits 1-7 per cent). It is lighter than sea water and only slightly soluble, though more so than xylene.

The biological properties of toluene are not well known, its acute toxicity to marine life (LC 50) being in the range 10-100 ppm. It is slightly more hazardous to human beings than xylene but does not have the toxic properties of benzene. It is not a skin irritant.

Amenity risks from a spillage would be similar to those of xylene.

3.6.30 Toluene diisocyanate $\text{CH}_3\text{C}_6\text{H}_3(\text{NCO})_2$, tolylene diisocyanate

The normal commercial product is a mixture of the 2,4 and 2,6 isomers. It is used mainly in the production of polyurethane foams which are employed in upholstery and in refrigeration as thermal insulators. It is also used as a cross-linking agent for nylon 6. Trade is world-wide and the normal means of transport is in drums; in future some may be transported in bulk.

It has a sharp pungent odour, is slightly volatile (BP 251°C) and is heavier than water (SG 1.22) with which it reacts to evolve CO_2 and form phenyl ureas which are solids. It may be a solid or liquid (MP about 20°C).

The pure substance would be toxic to marine life (LC 50 in the range 1-10 ppm), but if released to the marine environment would react with sea water producing substances which are not harmful.

The liquid and vapour are markedly irritant and highly toxic to man: the vapour is harmful at a very low concentration (TLV 0.02 ppm). Because it is widely regarded as a particularly hazardous substance to man, great care is necessary in handling. Losses in manufacture or use are likely to be very small.

Losses of drum-sized quantities could, however, cause serious amenity problems at least for a short time.

3.6.31 Trichlorobenzenes $\text{C}_6\text{H}_3\text{Cl}_3$

There are three isomers, 1.2.3, 1.2.4 and 1.3.5 trichlorobenzene: the 1.2.3 and 1.3.5 isomers are solids; the 1.2.4 isomer is a liquid at ordinary temperatures (MP 17°C); and there is a commercial grade consisting of a mixture of isomers. They are formed as intermediates in dyestuffs manufacture and the liquid isomer is used as a solvent. They are transported in drums but the liquid 1.2.4 isomer is also moved in tanks. Little is known about possible losses to the environment, but these will include evaporation.

These substances are heavier than sea water (SG 1.5-1.7), practically insoluble (about 30 ppm in fresh water) and only slightly volatile (BP $208-218^\circ\text{C}$).

Trichlorobenzenes are similar to dichlorobenzenes in their toxicity to fish. The 1.2.4 isomer, the most harmful, appears to have an LC 50 of about 1 ppm. There is no information on bioaccumulation or breakdown products but the degree of bioaccumulation is likely to be at least as great as for o-dichlorobenzene. The 1.3.5 is likely to be the most stable.

A human health hazard is unlikely except by ingestion of the chemical washed up on a beach.

An amenity problem is unlikely to arise.

3.6.32 Vinyl acetate $\text{CH}_3\text{COOCH}:\text{CH}_2$

This substance is used in the manufacture of plastics, films, lacquers and paints. It is carried in bulk chemical tankers (amount carried in 1970: 85,162 tons) on a world-wide scale with added stabilizing substances, usually hydroquinone or diphenylamine.

It is moderately volatile (B P 72°C) and very inflammable (F P 1°C), and presents a serious fire risk. It will float on the sea (S G 0.93) and is moderately soluble (about 2 per cent).

Acute toxicity to marine life (LC 50) is in range 100-1,000 ppm and it is readily biodegradable.

The liquid monomer and its vapour are of low toxicity and neither the monomer nor polymer are likely to present a health hazard.

Vinyl acetate may polymerize in air and in the sea and create a nuisance on beaches if carried ashore after spillage. Such polymerized material is likely to resist breakdown but is less persistent than PVC.

3.6.33 Vinyl chloride $\text{CH}_2:\text{CH Cl}$, chlor ethylene

This is a gas (B P 13.8°C) carried as a liquid under pressure. Vinyl chloride monomer is used in making polyvinyl chloride (90 per cent of its use). It is also used in the manufacture of polyvinylidene and co-polymers for fibres and as a refrigerant. It is transported by road and ship. Escape from manufacturing plants could result in some contamination by aerial transport.

Vinyl chloride is highly volatile and inflammable (F P 78°C); it poses an explosion risk (explosive limits 4-22 per cent).

Because of its high vapour pressure and low solubility in water it would probably not remain in the sea long enough to affect marine life.

A health hazard in the marine environment is likely to occur only on exposure to concentrations of gas which might occur in the immediate proximity of a major release.

Apart from the explosion hazard it seems unlikely to create an amenity problem. However, it has recently been suggested that the monomer may be more harmful than previously thought and industrial exposure limits have been reduced.

3.6.34 Xylene $\text{C}_6\text{H}_4(\text{CH}_3)_2$, dimethylbenzene, xylol

Xylene exists as three isomers: ortho-, meta- and para-xylene. They are widely used as solvents in the manufacture of paints and other surface coatings and in the synthesis of organic chemicals. Ortho-xylene is used in the manufacture of phthalate plasticizers (phthalates are now made in most developed countries).

Paraxylene is used in making "Terylene", a synthetic fibre. Main routes to the sea by spillage, leakage from manufacturing plants and tank washings. The bulk of the xylene used in paints evaporates and there may be some transfer from the air to the sea.

Xylene is carried in bulk by sea in very large quantities on a world-wide scale (amount shipped in 1970: 603,297 tons). Bulk cargoes may be either single substances or mixtures.

It will float on water (S G 0.86), is practically insoluble, and evaporation will occur rapidly (B P 137-140°C). It is volatile and highly inflammable (FP^o29 C) and explosive (1 per cent lower explosive limit). A substantial spillage will create a fire and explosion hazard.

Xylenes are relatively stable substances whose chemical breakdown is slow, and the resulting products are less toxic. Toxicity to marine life is not well established but is not high unless emulsified into the water with other chemicals. Further investigations are needed. Xylenes are not likely to be bioaccumulated.

They are oxidized and excreted by the human body. They are mildly irritant and have a strong but only slightly objectionable smell.

Xylene would not present a serious amenity problem if spilt near a beach except for the fire risk.

3.7 Organic industrial wastes

(1) Pulp and paper mill wastes

These wastes can be harmful to receiving waters for four reasons:

- (a) toxicity
- (b) biochemical oxygen demand (BOD)
- (c) suspended solids
- (d) colour

The toxicity of pulp mill wastes is usually associated with sulphur-containing compounds, arising from the wood digestion process, and chlorinated phenolic compounds produced during bleaching of the pulp and paper.

High BOD is a characteristic of untreated sulphite pulp effluents and many fish kills have occurred because of oxygen depletion in waters receiving these high BOD wastes. Stabilization ponds with aeration and activated sludge systems are common forms of treatment.

The solid fractions of pulp and paper mill wastes may accumulate in sludge beds to produce local nuisances. These undergo decomposition and remove dissolved oxygen from water. They often form noxious gases. In addition, large areas of the bottom of receiving bodies of water may be covered with a layer of settled organic material having undesirable effects on benthic communities. By the use of improved in-plant facilities, more efficient screening and better retention in clarifiers and/or ponds, losses of solids can be reduced. The effects of pulp and paper mill wastes on the higher forms of marine flora and fauna are often sublethal rather than acute. For example, oyster quality is known to have declined in many pulp mill areas, although there is little documentation on actual mortality. The food supply of these sedentary organisms can be markedly altered owing to decline of phytoplankton caused by toxicity, turbidity and colour.

(2) Other high-BOD wastes

Certain simple organic chemicals, e.g. straight chain alcohols and wastes from food processing, breweries, distilleries, etc. exert a high biochemical oxygen demand. This characteristic is often of greater practical importance in the marine environment than their direct toxicities. Fish kills may occur in restricted bays and estuaries, especially in tropical areas, owing to decomposition, and if the wastes contain a high proportion of solids, local sludge deposits may result. When deoxygenation occurs, noxious gases are evolved and amenities are likely to be affected. Provided the wastes are adequately diluted and dispersed and local accumulations are prevented, direct acute toxicity problems can be avoided. Chronic toxicity is unlikely except in the immediate vicinity of outfalls where dispersive processes are poor.

3.8 Military wastes

The dumping of military wastes may be a significant factor in the pollution of national and international waters. These wastes may consist of organic material, biological and chemical warfare agents, heavy metals, petrochemicals, out-dated explosives, defoliating agents, pesticides, solid objects, dredging spoils and other miscellaneous inorganic materials peculiar to the military establishment. Because of the classified aspects of military operations, the exact chemical and toxicological nature of these materials is frequently unknown. Moreover, details concerning the dumping of these materials are not generally available. Nevertheless, it should be pointed out that the dumping of many of these materials may be contrary to sound conservation practice and should so far as practicable conform to the recognized conventions.

3.9 Heat

Increase in temperature arising from the discharge of power station and industrial cooling and waste waters may cause two main undesirable effects; it decreases oxygen solubility in water and increases metabolic activities of microflora and fauna generally, which in turn may result in higher BOD and local hypertrophication. When the discharge of wastes of high BOD, from domestic sources, is accompanied by thermal pollution, a local environmental degradation

may result affecting natural self-purification capacity. Fluctuating water temperatures may produce changes in biological communities. The effects of this form of pollution naturally depend on the recipient sea water temperature and that of the effluents.

In certain circumstances thermal pollution has made estuaries and enclosed reef areas unsuitable for various commercial species of fish and shellfish and, on the other hand, it may lead to the introduction and establishment of alien species some of which may be undesirable such as timber boring organisms. Special care is needed in siting power stations employing sea water for cooling in tropical areas where animals and plants may have a rather narrow range of temperature tolerance.

3.10 Detergents

Pollution qualities of detergents have been related to:

- (1) Non-biodegradability, resulting in foaming of receiving waters;
- (2) Phosphate content, leading to enrichment of receiving waters; and
- (3) To a lesser degree, direct toxicity of the ingredients.

Virtually all domestic detergents on the world markets today are biodegradable, as a result of conversion by manufacturers from the "hard" alkyl benzene sulfonate (ABS) to the "soft" lauryl alkyl sulfonate (LAS) form. The former are, however, still widely used in industry. Sodium polyphosphates remain as a major constituent (20-60 per cent) in most proprietary detergents. Because they perform vital functions related to cleaning efficiency and no generally acceptable substitute is available, manufacturers are reluctant to eliminate or even reduce the amount of phosphate in detergents. NTA (sodium salt of nitrilotriacetate) has been used as a substitute for phosphate in detergents but doubts have been expressed as to the wisdom of this; its environmental effects are not fully known. Optical brighteners added to most detergents appear to persist in the environment and their effects should be studied.

3.11 Solid objects

The dumping of containers, scrap metal and other bulky wastes liable to sink to the sea bottom and to present a serious obstacle to fishing or navigation is controlled by the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (London, 1972) and a special permit is required. In granting such special permits one of the factors to be considered is the suitability of the proposed disposal site in relation to, for example, exploitable resources and fishing areas.

The Convention also provides that the deposit of "persistent plastics and other synthetic materials, for example netting and ropes, which may float or remain

in suspension in the sea in such a manner as to interfere materially with fishing, navigation or other legitimate uses of the sea" is forbidden.

Many of the synthetic plastics are virtually indestructible. Their main effect is to interfere with navigation and fishing operations and when washed up on shores, they reduce amenities. For example, pieces of synthetic ropes and fishing nets are commonly found floating in areas of intense fishing activity, such as the North Sea, and they can immobilize vessels by getting wound round propeller shafts. Again, plastic bottles and containers thrown overboard and washed ashore are a common feature of beaches in many parts of the world. There is also increasing evidence of damage to sea birds due to their getting entangled in pieces of floating fishing net. Sunken objects may also interfere with fishing operations and some areas have been reported as being unfishable after off-shore oil drilling operations on account of the rubbish left behind. In some cases, the dumping of objects has been on such a scale as to affect the habitat of bottom-living animals. The dispersal of garbage from ships will be controlled by the provisions of the IMCO International Convention for the Prevention of Pollution from Ships, 1973. Wastes enclosed in containers may be dumped in very deep water beyond the edge of the continental shelf. Under the terms of the Convention for the Prevention of Marine Pollution by Dumping from Ships and Aircraft (Oslo, 1972), such deep water must be not less than 2,000 metres in depth and not less than 150 nautical miles from the nearest land.

3.12 Dredging spill and inert wastes

Inert wastes are introduced into the marine environment in very large quantities via rivers and pipelines, by dredging and mining operations and by dumping from barges. In shallow coastal seas dispersal away from the coast may be seriously hampered by various types of sediment traps. Frequently, solid matter discharged into the sea returns to neighbouring shores or estuarine waters, thus threatening areas where important marine, plant and animal populations are located.

Dredging and mining operations can create an excessively high sedimentation factor which can reduce the supply of light for plants, smother fish eggs, larvae, invertebrates and micro-organisms, thereby interfering with the normal bottom component of biological energy cycling. These effects may be particularly disastrous in tropical reef areas where many reef organisms such as sponges, corals and other coelenterates are especially sensitive to increased sedimentation. There is a need for accurate quantitative data regarding the effects of increased sedimentation on marine fauna and flora.

In addition to sand and silt dredged from navigable channels and harbours, and dumped at sea, there are industrial activities which result in a large volume of inert waste which may either reach the sea by pipeline as a slurry, be dumped from barges, or merely tipped on the shore. Examples are china clay, gypsum, fly-ash from power stations and colliery waste. These materials are usually inert and non-toxic but may affect marine life by settling on the sea bed, and so modifying the ecosystem, or by creating turbid conditions and reducing light

penetration. Primary production may be decreased, fish spawning grounds may be destroyed and the settlement of molluscs prevented. The bottom may be rendered unsuitable for crustacea such as lobsters, crabs and prawns, but new communities of bottom animals may be produced which may provide additional food for fish. Where dredgings include a substantial quantity of organic material, an additional BOD may be created locally and nutrients may be added. Where material is dredged from industrial harbours or estuaries it may contain significant quantities of absorbed pollutants, e.g. metals and persistent organic substances which may or may not be later released.

Table 1

DEGREE OF IMPORTANCE AS POLLUTANTS ACCORDING TO THE MAJOR
CATEGORIES OF MARINE POLLUTION RECOGNIZED BY GESAMP

Note: The ratings in this table refer to knowledge of the state of marine pollution at the present. As such they can be considered to provide guidance on future levels of pollution, provided existing controls are maintained or strengthened.

It should be noted that WHO has much more detailed information on, and is making a continuous assessment of, the hazard to man posed by many of these substances under a variety of environmental and other exposure situations. WHO documentation should be consulted for a fuller appreciation of the hazards to man.

Key to symbols: ++ important
+ significant
(+) slight
? uncertain
- negligible

Indications for control:

In relation to the prevention and control of marine pollution, the symbols in table 1 would generally imply the following:

- ++ - restrictive or preventive measures recommended
- + - restrictive or preventive measures should be considered
- ? - further investigations required pending which caution is recommended
- (+) - no special action indicated
- - no special action indicated

Category	Harm to living resources	Hazards to human health	Hindrance to maritime activities	Reduction of amenities
(1) <u>Domestic sewage</u>	++	++	(+)	++
(2) <u>Pesticides</u>				
Organochlorine compounds	++	(+)	-	-
Organophosphorus compounds	+	-	-	-
Carbamate compounds	+	(+)	-	-
Herbicides	+	(+)	-	-
Mercurial compounds	++	++	-	-
Miscellaneous metal-containing pesticides	+	+	-	-
PCBs	++	(+)	-	-
(3) <u>Inorganic wastes</u>				
Acids and alkalis	(+)	-	+	-
Nutrients and ammonia	(+)	(+)	-	(+)
Cyanide	(+)	(+)	-	-
Antimony	(+)	-	-	-
Arsenic	(+)	(+)	-	-

Table 1 (continued)

Category	Harm to living resources	Hazards to human health	Hindrance to maritime activities	Reduction of amenities
(3) <u>Inorganic wastes</u> (continued)				
Beryllium	(+)	(+)	-	-
Cadmium	+	+	-	-
Chromium	(+)	-	-	-
Cobalt	-	-	-	-
Copper	+	-	-	-
Lead	(+)	+	-	-
Manganese	(+)	-	-	-
Mercury	++	++	-	-
Nickel	-	-	-	-
Phosphorus (elemental)	++	++	-	+
Selenium	?	(+)	-	-
Silver	++	-	-	-
Sulphur (as sulphite)	(+)	-	-	(+)
Titanium dioxide wastes	(+)	-	-	(+)
Vanadium	-	-	-	-
(4) <u>Radio-active materials</u>	-	+	-	-
(5) <u>Oil</u>	+	?	+	++
(6) <u>Organic chemicals</u>				
Acetone	-	-	-	-
Acrolein	++	+	-	+
Acrylonitrile	+	+	(+)	++
Allyl alcohol	+	-	-	(+)
Allyl chloride	+	+	-	(+)
Benzene	(+)	-	(+)	-
Carbon disulphide	++	+	+	+
Carbon tetrachloride	+	+	-	+
Chlorobenzene	++	-	-	(+)
Chloroform	(+)	(+)	-	(+)
Cresol	+	-	-	+
Crotonaldehyde	+	+	(+)	+
Cumene	(+)	-	(+)	-
O-dichlorobenzene	++	-	-	(+)
P-dichlorobenzene	++	-	-	(+)
Epichlorohydrin	+	(+)	-	+
Ethyl alcohol	-	-	-	-
Ethylbenzene	(+)	-	(+)	-
Ethylene dibromide	(+)	(+)	-	(+)
Ethylene dichloride	(+)	(+)	-	(+)

Table 1 (continued)

Category	Harm to living resources	Hazards to human health	Hindrance to maritime activities	Reduction of amenities
(6) <u>Organic chemicals</u> (continued)				
Ethylene glycol	-	-	-	-
Methyl alcohol	-	-	-	-
Methylene chloride	(+)	-	-	-
Naphthenic acid	+	-	-	(+)
Phenol	+	-	-	-
Phthalate esters	?	-	-	(+)
Styrene monomer	(+)	-	-	+ a/
Tetramethyl lead	++	+	-	++
Tetraethyl lead	++	+	-	++
Toluene	(+)	-	(+)	-
Toluene diisocyanate	+	+	-	++
Trichlorobenzenes	++	-	-	(+)
Vinyl acetate	(+)	-	-	+
Vinyl chloride	-	(+)	-	(+)
Xylene	(+)	-	(+)	-
(7) <u>Organic industrial wastes</u>				
(a) Pulp and paper mill wastes	++	-	(+)	+
(b) Other high BOD wastes	+	-	-	++
(8) <u>Military wastes</u>	?	?	-	-
(9) <u>Heat</u>	+	-	-	-
(10) <u>Detergents</u>	?	-	-	-
(11) <u>Solid objects</u>	(+)	-	++	++
(12) <u>Dredging spoil and inert wastes</u>	+	-	(+)	+

a/ Relates to polymer.

Table 2

RELATIVE IMPORTANCE OF THE DIFFERENT ROUTES BY WHICH POLLUTANTS ENTER THE SEA

Note: The ratings in this table refer to knowledge of the state of marine pollution at the present. As such they can be considered to provide guidance on future levels of pollution, provided existing controls are maintained or strengthened.

Key to symbols

- 3 Important
- 2 Significant
- 1 Slight
- ? Uncertain
- 0 Negligible
- P Potentially important
- * Dependent on extent of weapons testing

Category of pollutant	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
	Manufacture and use of industrial products - disposal via direct outfalls and rivers	Domestic wastes - disposal via direct outfalls and rivers	Agriculture, forestry, public health - via run-off from land	Deliberate dumpings from ships	Operational discharge from ships in course of duties	Accidental release from ships and submarine pipelines	Exploitation of sea-bed mineral resources	Transfer from the atmosphere
(1) Domestic sewage	0	3	0	2	1	0	0	0
(2) Pesticides								
Organochlorine compounds	2	2	2	0	0	P	0	3
Organophosphorus compounds	2	1	2	0	0	P	0	3
Carbamate compounds	2	1	2	0	0	P	0	?
Herbicides	2	1	2	0	0	P	0	?
Mercurial compounds	2	0	3	0	0	P	0	?
Miscellaneous metal-containing compounds	2	1	1	0	0	P	0	?
PCBs	3	0	0	0	0	P	?	3
(3) Inorganic wastes								
Acids and alkalis	3	0	0	2	1	P	0	0
Nutrients and ammonia	2	2	3	1	0	0	0	0
Cyanide	3	0	0	1	0	0	0	0
Antimony	2	0	0	0	0	0	0	0
Arsenic	3	1	0	1	0	P	P	2
Beryllium	1	0	0	0	0	0	0	0
Cadmium	3	0	0	0	0	0	0	1
Chromium	3	0	0	1	0	0	0	0
Cobalt	2	0	0	1	0	0	0	0
Copper	3	2	1	1	0	0	0	0
Lead	2	1	0	?	0	0	0	3
Manganese	3	1	0	?	0	0	0	1
Mercury	3	2	0	0	0	P	0	3

Table 2 (continued)

Category of pollutant	(a) Manufacture and use of industrial products - direct outfalls and rivers	(b) Domestic wastes - disposal via direct outfalls and rivers	(c) Agriculture, forestry, public health - via run-off from land	(d) Deliberate dumpings from ships	(e) Operational discharge from ships in course of duties	(f) Accidental release from ships and submarine pipelines	(g) Exploitation of sea-bed mineral resources	(h) Transfer from the atmosphere
<u>(5) Inorganic wastes</u>								
<u>(continued)</u>								
Nickel	3	0	0	0	0	0	0	1
Phosphorus (elemental)	2	0	0	0	1	P	0	0
Selenium	2	0	0	0	0	0	0	1
Silver	2	0	0	0	0	0	0	0
Sulphur (as sulphite)	2	0	0	0	0	0	0	2
Titanium dioxide wastes	3	0	0	3	0	0	0	0
Vanadium	2	0	0	0	0	0	0	1
<u>(4) Radio-active materials</u>								
	3	0	0	1	0	P	0	P*
<u>(5) Oil</u>								
	3	1	0	1	3	2	1	?
<u>(6) Organic chemicals</u>								
Acetone	3	0	0	1	0	0	0	0
Acrolein	1	0	0	0	0	0	0	0
Acrylonitrile	3	0	0	P	P	P	0	?
Allyl alcohol	1	0	0	0	0	0	0	0
Allyl chloride	1	0	0	0	0	0	0	0
Benzene	3	0	0	0	P	P	0	?
Carbon disulphide	3	0	0	0	0	0	0	0
Carbon tetrachloride	3	0	0	0	P	P	0	?
Chlorobenzene	3	0	0	0	0	P	0	?
Chloroform	3	0	0	0	0	0	0	?
Cresol	3	2	2	1	1	P	0	0
Crotonaldehyde	3	0	0	0	0	P	0	0
Cumene	3	0	0	0	1	P	0	?
O-dichlorobenzene	3	0	0	0	0	P	0	?
P-dichlorobenzene	3	2	0	0	0	P	0	?
Epichlorohydrin	3	0	0	0	0	P	0	0
Ethyl alcohol	3	0	0	0	0	0	0	0
Ethylbenzene	3	0	0	0	0	P	0	?
Ethylene dibromide	3	0	1	0	0	0	0	1
Ethylene dichloride	2	1	0	1	2	P	0	?
Ethylene glycol	2	2	0	0	1	0	0	0
Methyl alcohol	3	0	0	1	0	0	0	0
Methylene chloride	3	0	0	1	0	0	0	?
Naphthenic acid	3	0	0	0	0	0	0	0

Table 2 (continued)

Category of pollutant	(a) Manufacture and use of industrial products - disposal via direct outfalls and rivers	(b) Domestic wastes - disposal via direct outfalls and rivers	(c) Agriculture, forestry, public health - via run-off from land	(d) Deliberate dumpings from ships	(e) Operational discharge from ships in course of duties	(f) Accidental release from ships and submarine pipelines	(g) Exploitation of sea-bed mineral resources	(h) Transfer from the atmosphere
(6) Organic chemicals (continued)								
Phenol	3	1	1	1	1	P	0	0
Phthalate esters	3	2	0	0	1	P	0	?
Styrene monomer	3	0	0	0	1	P	0	0
Tetramethyl lead	2	0	0	0	0	P	0	?
Tetraethyl lead	2	0	0	0	0	P	0	?
Toluene	3	0	0	P	P	P	0	?
Toluene diisocyanate	3	0	0	0	0	P	0	0
Trichlorobenzene	3	0	0	0	0	P	0	?
Vinyl acetate	3	0	0	0	0	0	0	0
Vinyl chloride	3	0	0	0	0	0	0	?
Xylene	3	0	0	P	P	P	0	?
(7) Organic industrial wastes								
(a) Pulp and paper mill wastes								
	3	0	0	0	0	0	0	0
(b) Other high BOD wastes								
	3	2	2	0	P	P	0	0
(8) Military wastes								
	?	0	0	?	?	?	0	0
(9) Heat								
	3	0	0	0	0	0	0	0
(10) Detergents								
	2	3	1	0	1	0	1	0
(11) Solid objects								
	2	1	0	3	3	1	1	0
(12) Dredging spoil and inert wastes								
	2	0	1	3	0	0	3	0

Annex I

BIBLIOGRAPHY: MAJOR SOURCE MATERIALS

The assessments and notes on particular substances appearing in the Review were based upon the examination and discussion of a large number of original papers describing studies of individual substances, or groups of substances, and available in the national agencies and departments. In addition, much use was made of published and unpublished data available to individual experts. Some, but not all, of this unpublished information has since appeared in national reports and scientific journals.

The selected references listed below have been grouped according to whether they (a) provide information over a wide range of substances or situations or (b) concentrate on particular substances or aspects of marine pollution. It must be emphasized that they represent only a small fraction of the information considered in compiling the Review.

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Annex II

PARTICIPATING EXPERTS AND TECHNICAL SECRETARIES

Dr. D. J. Baumgartner	United States
Prof. J. Brisou	France
Dr. H. A. Cole	United Kingdom
Dr. B. I. Dybern	Sweden
Prof. M. A. Fontaine	France
Dr. B. W. Halstead	United States
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Dr. G. J. Van Esch	Netherlands
Dr. M. Waldichuk	Canada
Dr. G. F. Weichart	Federal Republic of Germany
Dr. L. W. Weinberger	United States
Mr. J. Wardley Smith	United Kingdom

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Dr. L. Andren	FAO
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Mr. S. L. D. Young	IMCO

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