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PRELIMINARY INFORMATION ON SUBSTANCES LISTED, OR LIKELY TO BE LISTED, IN THE ANNEXES OF THE DRAFT PROTOCOL FOR THE PROTECTION OF THE MEDITERRANEAN SEA AGAINST POLLUTION FROM LAND-BASED SOURCES

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INTRODUCTORY NOTE

1. This document has been prepared at the request of the Second Intergovernmental Consultation concerning a Draft Protocol of the Mediterranean Sea against Pollution from Land-Based Sources, Venice, 17-21 October 1977 (see UNEP/IG.11/BD 32).

2. Its aim is to give some information (such as quantities produced, users, inputs into the Mediterranean, toxicity to man and marine organisms, etc.) on substances listed, or likely to appear, in annexes I and II of the draft protocol.

3. Because of the very short time available for the preparation of this document it was not possible to collect all available data covering the wide range of pollutants listed in annexes I and II. Therefore the present data should be taken as preliminary only and as indicating no more than approximate estimates or orders of magnitude. Data on acute and chronic toxicity, persistence, bioaccumulation and carcinogenesis, are not yet known for a number of listed pollutants. For teratogenic and mutagenic properties no information is yet available. Existing data for marine organisms are particularly scarce.

I - GENERAL NOTES

A. Organohalogen compounds

4. Substances containing C-X links, where X is an atom of halogen (F, Cl, Br. I). This definition covers several thousands of organic compounds. Some of them are not simple derivatives of hydrocarbons, but they may also contain in their structure other functional groups such as, for example, phenols, alcohols, acids, esters etc. Taking account of amounts produced, the most important are organochlorine products, followed by organofluorides and organobromides. Organoiodines are very rare.

i) Organochlorides: the following are the most important:

5.
- Aliphatic compounds with short chains (1 to 3 carbon atoms): solvents, fabrication of polymers
- Pesticides: DDT and its metabolites, cyclodiens,, (aldrin, dieldrin, endrin, endosulphan, mirex, heptachlor, heptachloroepoxide, chlordane, cyclohexane, benzenehexachloride, metoxychlore, toxaphene, pentachlorphenol, 2, 4 - D; 2, 4, 5 - T
- Polychlorbiphenyls (PCB) and polychloroterphenyls (PCT)
- EDC tar
- Hexachlorobutadiene

- Orto and para dichlorobenzene
- Chlorinated paraffins
- Chlorinated naphthalenes
- Products resulting from water treatment

6. Pesticides and PCBs usually present a high toxicity level for marine life, especially for crustacea whose metabolism is close to that of insects. Their persistence is generally high, as are their accumulation and food chain concentration properties. They are not very soluble in water, but soluble in fats. Because of this, tensio-active products (detergents) can increase their deleterious effects on marine life of organochloride compounds.

7. In the sea, they concentrate in sediments, superficial layers of water, and living organisms.

8. It seems necessary to prepare, for each individual compound, a descriptive schedule, as marked differences can exist between similar products as regards their chemical and biological properties. The substances investigated were mainly chosen on the basis of their economic importance. Data used in the tables and schedules are indicative and need more detailed investigations.

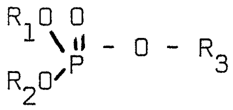
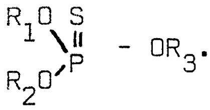
ii) Organofluorides:

9. - Chlorofluorocarbons: used in sprays and thermic fluids. These products are volatile and should not influence marine pollution.

iii) Organobromides:

10. - Polybromodiphenyls (flame retarders for plastic materials)

B. Organophosphorous compounds

11. The compounds included in the heading are organophosphoric esters, by the links  $(R_1O)(R_2O)P(=O)-O-R_3$ or  $(R_1O)(R_2O)P(=S)-OR_3$. Hundreds of these compounds are produced in industry, pesticides being the most important from the economic and environmental point of view. Industrial use plays a secondary role in marine pollution.

12. Nowadays organophosphoric pesticides, together with carbamates, replace the organochlor pesticides, the use of the latter being no longer authorized in several countries. Malathion, parathions, dimethoate, azinphosmethyl and chlorfenvinphos are the most used.

13. Almost all the organophosphoric pesticides are highly toxic to aquatic invertebrates and generally less toxic to fish. The molecules have a weak chemical stability; their compounds are hydrolysed in water in which they are fairly soluble. Their persistence in the environment does not exceed two months, except in the case of ethion and dimethoate when it can be longer.

14. No instance of bioaccumulation in marine organisms has been reported. Their toxicity to man is high, but sea-food does not contain any residues of these substances, with the exception of the very small amounts found in rare species fished in estuaries. Information on many of these compounds is incomplete.

15. Organophosphoric pesticides are also toxic to marine organisms and much more toxic to mammals than organochlor pesticides. They are not very persistent, however, and the organophosphorous compounds seldom reach crustaceans, fish and man, at the end of the food chain.

C. Persistent mineral oils and persistent hydrocarbons derived from petroleum, in particular used lubricating oils

16. Petroleum and its by-products comprise hundreds and thousands of compounds. Estimates of the input of oils into the Mediterranean vary, but they all indicate the fact that a non-negligible part comes from land-based sources: as far as the input of oils into the Mediterranean is concerned few data are, at present, available. However, the annual pollution load in the coastal zone of the Mediterranean from industrial discharges of mineral oils has been estimated at 120 x 10^3 t/y (see UNEP/IG.11/INF.5, table 7).

17. To give precise figures on toxicity, persistence and bioaccumulation of crude oils and their by-products is very difficult; they are in fact complex mixtures of different substances. It is, however, possible to consider that these products are generally of very low to low toxicity, that they have low bioaccumulation properties, and that their persistence in the marine environment varies from days to months.

18. However, some oil compounds or certain of their by-products should be considered as important marine pollutants, in particular, the following :

(i) cyclic compounds with carcinogenic properties. Such compounds are usually found in very low concentrations in crude oils and refined products, but they may be present at higher concentrations in certain industrial wastes.

(ii) waste oils including both lubricating oils for combustion engines and certain industrial oils. These products in fact are specially treated and are mixed with additives to increase their length of life. They are generally toxic, as a result of the additives or of the metal traces they contain.

D. Persistent synthetic solids

19. Persistent materials which may float, sink or remain in suspension and which may interfere with any legitimate use of the sea include mainly household refuse or certain industrial wastes containing a high amount of plastics or other solid non-biodegradable materials.

20. The disposal on land of such residues in the immediate vicinity of the sea-shore or coastal rivers, may lead, in certain cases, to their discharge into the sea.

21. Although such substances are inert, and a priori neither bioaccumulable nor toxic, their persistence in the sea can give rise to many problems. Their transportation, on long distances, by sea currents can be detrimental to extensive coastal zones by reducing touristic amenities (for example beaches strewn with detritus brought in by the sea) and endangering navigation and fisheries (obstruction of cooling-water pipes on ships, clogging of propellers, tearing of fishing nets, etc.).

E. Radioactive wastes

22. The projected growth of nuclear installations (power plants, reprocessing plants, fuel fabrication plants) will inevitably lead to routine discharge of liquid and gaseous wastes which, even after treatment, will contain low level radioactivity. Medium and high activity liquid wastes arising from fuel reprocessing are concentrated and isolated very effectively in long-term storage or they are converted to a solid state and stored in deep depositories.

23. The principal radioactive materials formed in nuclear installations are fission and activation products. Radioactive liquid wastes from nuclear fuel reprocessing plants contain, in addition, some transuranium radionuclides. Plutonium isotopes Pu^{239}, Pu^{240} and Pu^{241} present a special case because of their long half-life and alpha-emitting radiation.

24. There are three major categories of liquid wastes from reprocessing plants :

(i) low level wastes, such as wastes from fuel storage tanks, condensates from evaporators and many industrial effluents; these wastes are not discharged to the environment unless they have been treated to bring them down to lower activity level;

(ii) medium activity wastes, such as those arising from chemical decanning operations, and some plant effluents;

(iii) high activity wastes, containing the bulk (usually more than 99.9%) of the fission products.

F. Biocides and their derivatives

25. Besides carbamates and substituted ureas, the biocides not included in annex I do not constitute large chemical groups. They are numerous, but information on their utilization is scanty.

26. There are two kinds of carbamates currently used: N-dimethylcarbamates (isolan and dimetilan) and N-methylcarbamates (carbaryl and zectran). Carbaryl seems to be the product most in use.

27. Carbamates have little chemical stability and are easily hydrolysed in sea-water. They can be metabolized by marine organisms and eliminated quite quickly. Therefore the risks of bioaccumulation and of persistence are very limited. Toxicity can vary according to the chemical nature of the compounds or to the different marine species; for example, carbaryl is moderately toxic to crustaceans but not toxic to fishes and molluscs. Some are a little phytotoxic and can thus affect phytoplankton.

28. With the exception of isolan, which is less toxic than organophosphoric compounds, all the carbamates are slightly toxic to mammals. The risks from eating sea-food that might be contaminated are therefore small.

29. Other compounds worthy of attention are the triazines, disquat and paraquat.

G. Organosilicon compounds

30. These compounds have one or more Si - C links.

31. As far as pollution of the sea is concerned, the most important are polymers, above all those called polydimethylsiloxanes (PDMS) distinguished by the formula $-\underline{/}\,\mathrm{Si}\,(\mathrm{CH}_3)_2\text{-O-}\underline{/}$. These compounds, called "silicons", can be fluids, elastomers or resins. They are mainly used as medicines (antiaerophagia), in mammary aesthetic surgery and surgical prosthesis.

32. The raw materials used for the preparation of PDMS are compounds with a low molecular weight which are quickly hydrolysed into silica and volatile hydrocarbons; they are therefore not harmful to the marine environment.

33. The polydimethylsiloxanes have a strong chemical stability and are not biodegradable; consequently they are very persistent in sea-water, but they are not known to have any toxic effect at concentrations they may reach in the marine environment.

H. Detergents

34. Detergents are a common component of sewage and some industrial effluents all derived for the most part from household cleaning agents. Characteristics of detergents include (a) partial biodegradability, (b) phosphate content, leading to enrichment of nutrients in receiving waters, and (c) to a small degree, direct toxicity of the ingredients.

35. Before 1965 only "hard", non-biodegradable, detergents were produced. They were characterized as alkylbenzene sulphonates (ABS). For the past decade the more biodegradable "soft" linear alkylate sulphonates (LAS) have been produced by the detergent industries. Nowadays, LAS is the primary toxic active compound, two to four times more toxic than ABS.

36. Sodium phosphates are still a constituent in most detergents to increase their effectiveness. Because of certain negative effects of sodium phosphates, sodium salt of nitrilotriacetate (NTA) has been used as a substitute for phosphate in detergents. However, doubts have been expressed about this substitution because NTA has negative environmental effects. Also, bleachers, which are usually added to most detergents, are persistent in the aquatic environment. Their effects on marine life is also little known.

37. Toxic effects of LAS have been investigated for several fishes and acute toxic effects in the range 0.2 to 10 mg/l have been found. Data for aquatic organisms are rather scarce.

I. Pathogenic organisms

38. Pathogenic organisms present in sewage are an indication of the nature and degree of human infection in a community. Other possible contributors of pathogens to waste waters are domestic animals, farm and slaughterhouse waters, and rodents inhabiting the sewers. Principal organisms of significance to health, and the infections they cause, are as follows :

(i) Bacteria: Vibrio cholerae (cholera); salmonella sp (typhoid and paratyphoid fevers, food poisoning, gastro-enteritis); shigella (bacillary dysentery); clostridium (food poisoning, gas gangrene); staphylococcus aureus (pyogenic skin and wound infections, food poisoning); mycobacterium tuberculosis (tuberculosis), leptospira (leptospirosis, jaundice).

(ii) Viruses: poliovirus (poliomyelitis), infectious hepatitis virus (hepatitis, jaundice); adenoviruses (conjunctivitis, pharyngitis); coxsackle viruses A and B, ECHO-viruses, reoviruses (enteritis, fever, rashes, attack on central nervous system);

(iii) Protozoa: entamoeba histolytica (amoebic dysentery).

(iv) Metazoa: nematode ova (roundworm and threadworm infestations) cestode ova (tapeworm infestations).

39. At present there is no conclusive evidence of a cause and effect relationship between bathing in sewage-polluted water and the onset of serious disease, although contact with polluted water does tend to be associated with increased incidence of rhino-pharyngeal, skin, conjunctival and ear infections. In the sea, pathogens undergo dilution, sedimentation,

and differential mortality according to such factors as sunlight, temperature and salinity.

40. The greater risk of infection results from the ingestion of contaminated fish and shellfish which have been insufficiently cooked or heat-treated to kill potential pathogens. Diseases known to have been transmitted by shellfish are typhoid and paratyphoid fevers, infectious hepatitis, and gastro-enteritis of non-specific origin. Filter-feeders retain bacteria, and probably viruses, very efficiently, and can concentrate them many times more than the level in sea-water.

41. Ninety per cent of the sewage from Mediterranean coastal municipalities enters the sea untreated or inadequately treated. Viral hepatitis, dysentery, typhoid and poliomyelitis are endemic in the region, and periodic outbreaks of cholera occur. The yearly influx of tourists, which increases the population density of some areas ten times during summer months, and results in the mixing of populations with varied immunological histories, greatly complicates the epidemiological picture in the Mediterranean.

J. Thermal pollution

42. Thermal power stations are converting only approximately one third of the thermal energy produced into electricity. The rest of the heat may be described as "low quality heat" and is discharged into the environment (atmosphere, sea-water, rivers, lakes), in most cases in the form of large quantities of warm water.

43. The local increase in temperature of the marine environment arising from the discharges of thermal power stations and also of industrial cooling waters may cause three main undesirable effects: (a) it decreases oxygen solubility in water, (b) it increases the metabolic activities of microorganisms and (c) it changes toxic properties of possible pollutants. These, in turn, may result in higher BOD and may yield local hypertrophication. Usually these warm water discharges are not continuous and resulting fluctuating water temperatures may produce changes in biological communities. Final environmental effects of thermal pollution depend on the temperature of the recipient sea-water and that of effluents.

K. Substances which have an adverse effect on oxygen balance in the sea

44. A reduction in dissolved oxygen concentrations may reduce the rate of oxygen uptake by aquatic plants and animals. Therefore any change in the dissolved oxygen concentration in estuaries and coastal waters presents risk to aquatic life and may change the species composition and abundance of the aquatic organisms. As indicated by laboratory experiments, a reduction in dissolved oxygen concentration is also reflected in growth rate, swimming speed and hatching weight; it shows fractional or percentage reductions that approximately correlate with the logarithm of the deviation

of the dissolved oxygen concentration from the concentration in equilibrium with the atmosphere, at constant dissolved oxygen concentration.

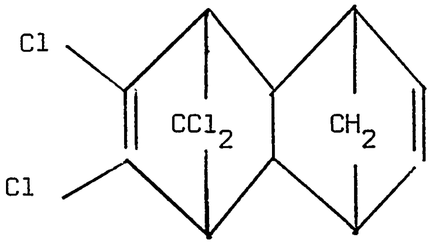
45. Typical representative substances which may affect the oxygen balance in the marine environment are pulp and paper mill wastes. Their toxicity is usually associated with sulphur-containing compounds arising from the wood digestion process, and chlorinated phenolic compounds produced during bleaching of the pulp and paper. High biochemical oxygen demand (BOD) is always present in untreated sulphite pulp effluents. High mortality of fish occurred because of oxygen depletion in waters receiving these high BOD wastes. The solid fractions of pulp and paper mill wastes could be accumulated on the bottom and during their decomposition they remove dissolved oxygen from water often forming noxious gases. The known effects of pulp and paper mill wastes on marine organisms are often sublethal rather than acute. It is known that the quality of oysters declined in such an area, although there is practically no evidence of actual mortality.

46. A number of industries release wastes of similar properties. Wastes from food-processing industries, distilleries, breweries, the pharmaceutical industry etc. could cause effects similar to those described for pulp and paper mill wastes. For substances which have an adverse effect on the oxygen balance in the sea this characteristic is usually of greater practical importance in the marine environment than their direct toxicities.

SUBSTANCE

Aldrin

Most usual form of the substance in sea-water



A) Quantities produced per year in the world

(1971) USA Estimate: 4,500,000 tons

B) Main uses of the product

- Non-phytotoxic insecticide used against soil insects
- Prohibited in agriculture in many countries

C) Main producing countries

Netherlands, USA

D) Main pathways and estimate of inputs to the sea (on a world scale)

Input from rivers after washing of soil

E) Main pathways and estimate of inputs into the Mediterranean sea

F) Concentrations found in the sea

	General bibliography	Mediterranean data
ter		(1968): 5,30 ppb

Sediments	Mediterranean continental shelf of Languedoc 2 positive samplings out of 80: 50 and 150 ug/kg
Organisms	

G) Concentrations found in effluents

- in municipal effluents

- in industrial effluents

H) Physiochemical reactions likely to occur in the sea

- Production of photoaldrin (10 times more toxic than aldrin)
- Rapid transformation of aldrin into very persistent dieldrin

Aldrin is not persistent because of its chemical reactions, but the products of its degradation are dangerous

I) Persistence and biochemical transformation in the sea

J) Effects on marine life

- Acute toxicity

LD_{50}:	invertebrates:	1 - 32 ppb
	fish:	3 - 100 ppb

- Concentration factor

very high: it can reach 140,000

- Bioaccumulation

  - Biomagnification through the food chain
  - Very slow elimination in clean water

- Organoleptic properties

K) Effects on man

Aldrin changes into dieldrin in the marine environment. Therefore this product can be ingested by man together with sea-food. These compounds do not exhibit a very high toxicity to mammals, but dieldrin is carcinogenic to mouse (not to rat). WHO/FAO established the P.D.D. (permissible daily dose) for man as 0.5 ug/kg body weight for aldrin and 0.1 ug/kg for dieldrin

L) Sea-water quality objectives currently studied in some countries

0.01 ug/l

SUBSTANCE

Mercury and its compounds

Most usual form of the substance in sea-water

Inorganic salts

A) Quantities produced per year in the world

9,000 tons

B) Main uses of the product: very diverse

- Chlorine production by electrolysis of alkaline chlorides by circulating cathode of mercury
- Electric equipment: switches, lamps, fluorescent tubes, batteries and accumulators
- Measuring apparatus: thermometers, manometers
- Mercurial fungicides: treatment of seeds, pulp and paper industry
- Colouring matter
- Pharmaceutical products
- Dentistry
- Fine chemicals
- Anti-fouling paints
- Catalysts

C) Main producing countries

Italy, Spain, Yugoslavia, Turkey, USA, Mexico, USSR, China

In general, metallurgical plants are situated where extraction takes place

D) Main pathways and estimate of inputs to the sea (on a world scale)

- Natural source from deposits at the bottom of the sea releasing mercury
- Combustion of fossil fuel (coal, petroleum) causes significant releases
- Its input through rivers (municipal discharges, discharges in sludge from treatment installations, industrial discharges) amount to 3, 500 t/y
- The input through the air is estimated at 3, 200 t/y

E) Main pathways and estimate of inputs into the Mediterranean Sea

Estimated input of 130 t/y into the Mediterranean Sea from land-based sources

F) Concentrations found in the sea

	General bibliography	Mediterranean data
Water	Normal 0.01-0.1 ug/l (open sea) (Mediterranean excluded) polluted water up to 4 ug/l	0.04-3.6 ug/l (industrial areas) generally 0.2 ug/l The seas around areas with strong tectonic or volcanic activity, usually have a high concentration of mercury

Sediments

Non-polluted areas: 60-150 ug/l

Polluted areas: more than 1 mg/l

Bay of Minamata: 7-8.50 mg/l

Organisms

molluscs:	0.02-0.2 mg/kg
crustaceans:	0.01-0.7 mg/kg
shell-fish:	0.02-2.5 mg/kg
fish (except tuna):	0.01-1.5 mg/kg
tuna:	0.2 mg/kg

tuna : 0.01 - 4.1 mg/kg

G) Concentrations found in effluents: sludges (from treatment plants)

4.8 mg/kg (Sweden)

2.50 mg/kg; average 9 mg/kg (United Kingdom)

- in municipal effluents

- in industrial effluents

H) Physiochemical reactions likely to occur in the sea

- All the organic compounds of mercury can be transformed into inorganic salts of mercury by biological, chemical and photochemical means

- Most mercury compounds settle in sediments, after adsorption on to solid particles. The release of these compounds is theoretically possible, but, because of complex laws, it is difficult to state precisely what really happens

I) Persistence and biochemical transformation in the sea

Transformation of inorganic mercury into organic mercury by micro-organisms in anaerobiotic conditions. This transformation might occur in living organisms and it is very important because the organic mercury compounds are much more dangerous to man. For this reason, any discharge of mercury, even in mineral form has to be avoided

J) Effects on marine life

- Acute toxicity
  - Inorganic compounds: it varies greatly according to species or the stage of development: LD_{50}: 0.001-10 mg/l
  - Organic compounds: much more toxic. LD_{50} can be as low as 0.04 ug/l for some larvae

- Concentration factor

It could be very high; in methylmercury salts it can reach 82,000; in organic mercury salts up to 15,000; in methoxiethylmercury salts up to 2,000

- Bio-accumulation

Very high in marine organisms, specially in those higher in the food chain. Bio-elimination in clean water is very slow and it takes 400- 1,000 days

- Organoleptic properties

K) Effects on man

Mercury, metal or mineral, is relatively less toxic and most can be excreted. On the other hand, the organic compounds accumulated in marine organisms consumed by man, can provoke lethal chronic intoxications (cf. Minamata). WHO/FAO indicate 0.3 mg as the P.D.D. for mercury of which not more than 0.2 mg in the form of methylmercury

L) Sea-water quality objectives currently studied in some countries

USA (1972) 0.05 ug/l

SUBSTANCE

Cadmium and its compounds

Most usual form of the substance in sea-water

inorganic salts

A) Quantities produced per year in the world

15,000 t/y

B) Main uses of the product

Surface treatment (cadmium-coating)
Colouring matter (paints, ceramics, glass, plastics)
Metallurgy (alloys)
Fuse plugs, batteries
Nuclear reactors
Stabilizers for plastic products

C) Main producing countries

USA, Belgium, Federal Republic of Germany

D) Main pathways and estimate of inputs to the sea (on a world scale)

- contamination of rivers by the effluents of industries for the production of cadmium (and zinc)
- contamination of rivers by wastes of surface treatment industries
- slight contamination through the air because of carbon and fuel combustion

E) Main pathways and estimate of inputs into the Mediterranean Sea

F) Concentrations found in the sea

	General bibliography	Mediterranean data
Water	0.01 ug/l (open water) 0.6 ug/l (coast) up to 10 ug/l in very polluted areas	0.4 ug/l - 5 ug/l

Sediments

0.5 - 2 mg/kg (not polluted)
1.6 - 4.7 mg/kg (polluted)

Organisms

Mytilus: 400 - 500 ug/kg commonly
fish: 0.2 - 10 mg/kg in areas with no industrial wastes
crustaceans: 1-20 mg/kg in areas with no industrial wastes
molluscs: 20 mg/kg

G) Concentrations found in effluents

Sludge: 10 - 16 mg/kg (dry weight)

- in municipal effluents

- in industrial effluents

H) Physiochemical reactions likely to occur in the sea

- No transformation into organic cadmium
- In presence of contamination, soluble compounds (chlorides and sulphates) can precipitate into insoluble compounds (carbonate, oxide and sulphite)

I) Persistence and biochemical transformation in the sea

J) Effects on marine life

- Acute toxicity

  LD_{50}: 0.1 - 100 ug/l

  Larvae and algae are very sensitive

- Concentration factor

high:	
zooplankton:	6×10^3
molluscs:	10^4
crustaceans:	10^3
fish:	$10 - 10^3$

- Bioaccumulation

Cadmium is very accumulable, but it does not seem to produce concentrations in the food chain. The concentration level in fish is usually lower than that in organisms in the first steps of the food chain. The level in predator fish is no higher than in other fish

- Organoleptic properties

K) Effects on man

Elimination is very slow in man (half-life: 16-33 years). Although only 5-10% of cadmium coming from food is absorbed, the body burden constantly increases during life; cadmium concentrates mainly in the liver and kidneys. It does not seem that eating contaminated sea-food or shell-fish could lead to serious poisoning except in very polluted areas ("Itaî-Itaî" illness in Japan). Nevertheless, since man is not able to eliminate this toxic product, it is necessary to fight against any possible input of this metal into the sea

L) Sea-water quality objectives currently studied in some countries

SUBSTANCE

Tetramethyl lead and tetraethyl lead

Most usual form of the substance in sea-water

$Pb(CH_3)_4$ and $Pb(C_2H_5)_4$

A) Quantities produced per year in the world

data available for 1975:

total production	301,000 tons
USA	175,000 tons
UK	58,000 tons
France	14,000 tons
Italy	10,000 tons

B) Main uses of the product

- as anti-knock additives to fuel
- in the manufacture of organomercury fungicides
- in the manufacture of other pesticidal products

C) Main producing countries

USA , UK, France, Italy, F.R. Germany, Japan

D) Main pathways and estimate of inputs to the sea (on a world scale)

E) Main pathways and estimate of inputs into the Mediterranean Sea

F) Concentrations found in the sea

	General bibliography	Mediterranean data
Water		

Sediments

Organisms

G) Concentrations found in effluents

- in municipal effluents

- in industrial effluents

H) Physiochemical reactions likely to occur in the sea

Decomposition

I) Persistence and biochemical transformation in the sea

Decomposition takes place and equilibrium between several chemical lead species is set up.
No data on biochemical transformation of tetramethyl lead or tetraethyl lead in the marine environment

J) Effects on marine life

Not well known

- Acute toxicity

LD_{50} to marine life is of the orderof 1 mg/l for tetraethyl lead, while no data are available for toxicity of tetramethyl lead

- Concentration factor

- Bioaccumulation

There is likely to be rapid bioaccumulation, although this is as yet not well understood

- Organoleptic properties

Slight but not unpleasant odours

K) Effects on man

These substances cause injury to the brain, liver and kidneys when absorbed through the skin, gastro-intestinal tract and lungs following contact with the liquid or vapour form. Harm through contact with polluted sea-water appears unlikely, because concentration in the sea is usually very low.

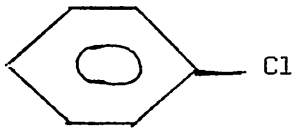
L) Sea-water quality objectives currently studied in some countries

None

SUBSTANCE

Monochlorobenzene

Most usual form of the substance in sea water C_6H_5Cl



A) Quantities produced per year in the world

Total world production (1972): approx	300,000 tons
USA production (1972): approx	800,000 tons

B) Main uses of the product

- as a medium in the production of phenol
- as a raw material in dyestuffs manufacture
- in the production of fine chemicals
- as a solvent
- as a heat transfer medium

C) Main producing countries

USA, France, USSR

D) Main pathways and estimate of inputs to the sea (on a world scale)

(Local pollutant)

E) Main pathways and estimate of inputs into the Mediterranean sea

releases by producers or industrial firms using it, during transport by ships, rail or lorries

F) Concentrations found in the sea

No published data

General bibliography	Mediterranean data

water

Sediments

Organisms

G) Concentrations found in effluents

- in municipal effluents

- in industrial effluents

H) Physiochemical reactions likely to occur in the sea

accumulates in sediments depending upon its organic content and concentration in the overlying water

I) Persistence and biochemical transformation in the sea

Biodegradable by microorganisms into hydrochloric acid and phenol which is also biodegradable

J) Effects on marine life

accumulates rapidly in marine organisms, especially in fish; critical organ: liver

- Acute toxicity

acute toxicity to marine life is rather high. LC_{50} approx. 2.5 mg/l

- Concentration factor

very high; much more experimental data needed

- Bioaccumulation

Known to be high in marine organisms, especially in fish

- Organoleptic properties

characteristic smell

K) Effects on man

Ingestion of the liquid and inhalation of large quantities of the vapour can depress the nervous system and cause liver damage; the vapour is slightly irritant

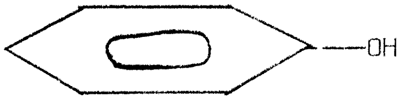
L) Sea-water quality objectives currently studied in some countries

SUBSTANCE

Phenol

Most usual form of the substance in sea water

C_6H_5OH



A) Quantities produced per year in the world

World production 1972: approx	1.500.000 tons
USA production 1972: approx	800.000 tons

B) Main uses of the product

- as a chemical intermediate in the production of plastics and resins
- in the pharmaceutical industry
- as disinfectants
- in the manufacture of some herbicides
- in the manufacture of lube additives
- in a number of household products

C) Main producing countries

UK, USA, Italy, Federal Republic of Germany

D) Main pathways and estimate of inputs to the sea (on a world scale)

- Releases from industries that are using or producing it
- Domestic wastes

Approximately 12.000 tons of phenols and cresols reach the Mediterranean sea from land-based sources. The highest concentration is in estuaries receiving industrial wastes

E) Main pathways and estimate of inputs into the Mediterranean sea

Industrial and urban areas; could be concentrated by certain marine organisms, especially in the estuarine environment

Estimated input of 12×10^3 t/y into the Mediterranean Sea from land-based sources

F) Concentrations found in the sea

Not very many data available; data for coastal water near industrial and urban areas indicate conc. up to 10 ug/l of sea-water

	General bibliography	Mediterranean data
Water		

Sediments

Organisms

G) Concentrations found in effluents

- in municipal effluents

less than 1 mg/l

- in industrial effluents

often more than 1 mg/l

H) Physiochemical reactions likely to occur in the sea

- sorption on suspended matter, detritus and sediments

I) Persistence and biochemical transformation in the sea

Biodegradable but the speed of this process in the sea is not known

J) Effects on marine life

Reacts with proteins but action on marine life has not been closely studied; data available for *Crassostrea virginica* (American oyster), *Mercenaria mercenaria* and some others

- Acute toxicity

on marine organisms: LD_{50}: 10-100 mg/l

- Concentration factor

- Bioaccumulation

Known to be accumulated by many organisms (especially fish and shellfish)

- Organoleptic properties

Tainting of fish and shell fish occurs even at very low concentrations of phenol

K) Effects on man

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

L) Sea-water quality objectives currently studied in some countries

U.S. Water Quality Criteria recommended that public water supply sources contain no more than 1 ug/l phenolic compounds

Table A. Principal organohalogen compounds

(1)

Substance	Use.Origin as marine pollutants	Total input into the oceans on a world scale	Persistence	Toxicity	Bioaccumulation Concentration factor	Remarks
1	2	3	4	5	6	7
Organohalogen compound		quantities involved				
DDT and metabolites (DDE and DDD)	use prohibited in agriculture in Western Europe; elsewhere: eradication of malaria, yellow fever and sleeping sickness	world production: 1971: 180,000 tons; 1976: 60,000 tons (25% of DDT production would reach the sea)	high persistency in soil from (4 to 30 years); the same in marine organisms which metabolize DDT into DDE and DDD	acute toxicity: LC50 from 0.01 ug/l (crustaceans) to 2 ug/l (fishes)	concentration factor. 10^6; bioaccumulation because of solubility in fats	only slightly toxic to man LD50 at 500 mg/kg; slight DDT and DDE burden in general population.
Aldrin	insecticide not toxic to plants used against soil insects; not authorized in agriculture in several countries	1971 production: USA estimate 4,500,000 tons	can change into photo-aldrin (10 times more toxic) and into dieldrin (very persistent: 10 years in the soil)	acute toxicity: LC50 invertebrates (48-96 h) at 32 ug/l, LC50 fishes (48-96 h) from 3 to 100 ug/l	concentration factor 40,000 for fishes; bio-accumulation in food chains	toxicity to man: permissible daily dose: (PDD) 0.1 ug/kg **body weight**
Dieldrin	contact insecticide; prohibited in agriculture in most of the industrialized countries; not phytotoxic	production 1971: (estimation USA) less than 450,000 tons; 1977 production (USA) interrupted	persistent (10 years in soil)	acute toxicity: LC50 invertebrates (48 - 96 h): 0.5 at 400 ug/l; fishes (96 h): from 0.9 to 35 ug/l	concentration factor 50,000, of particular importance for fish; bioaccumulation in the food chain	toxicity to man: LD50 (ingestion) 60 mg/kg; permissible daily dose (PLD) 0.1 ug/kg
Endrin	insecticide used on crops; prohibited in agriculture in several countries	production 1971: (USA estimate) less than 450,000 tons; at present, production interrupted in USA	persistent (soil: 14 years) no degradation in fresh water after 8 weeks	acute toxicity: LC50 (48 - 96 h) invertebrates from 0.25 to 45 ug/l LC50 (48 - 96 h) fishes from 0.05 to 3 ug/l	concentration factor can reach 70,000	toxicity to man, PDD: 2 ug/kg
Endosulphan	insecticide	1971 production: (USA estimate) 900,000 tons	not very persistent: less than 10 days in soil; less than 4 weeks in frsh water	acute toxicity: LC50 (48 - 96 h) invertebrates from 0.2 to 10 ug/l, LC50 (48 - 96 h) fishes from 0.1 to 100 ug/l	not very bioaccumulable	toxicity to man: PDD: 7.5 ug/kg
Chlordane	contact and ingestion insecticide, prohibited in agriculture in several countries	1971 production: (USA estimate) 10,000,000 tons: big reduction after 1971	persistent: 14 years in soil; degradation of 15% after 8 weeks in fresh water	acute toxicity: LC50 (96 h) fishes from 10 to 190 ug/l, LC50 (18 h for 7 days) for several planktonic species and **invertebrates: from 0.1 to 500 ug/l**		toxicity for man: PDD: 1 ug/kg

Table A. (cont'd)

1	2	3	4	5	6	7
Heptachlore and Heptachlorpoxyde	insecticide prohibited in agriculture in several countries	(1971) USA estimate: 2.7 million tons (has now fallen off a great deal)	soil: 14 years; water: no degradation after 8 weeks	very toxic: LC50 (2 or 4 days) invertebrates: from 1 to 80 ug/1: fish: from 0.8 to 400 ug/1	concentration factor in 5 days: 2,600; biomagnification; slow elimination in clear water	toxicity to man: permissible daily dose (PDD): 0.05 mg/kg
Mirex	insecticide prohibited in agriculture in several countries; flame retarder	(1971) USA estimate: < 450,000 tons	more than 2 years in living organisms	slightly toxic: LC50 (3 days) up to 40 ug/1 for invertebrates; sublethal effects up to 0.01 ug/1	concentration factors can reach 7,300; elimination very slow in Europe	
Polychlorobiphenyls (PCB)	in the past they were varied: nowadays, in several countries they are authorized only in closed systems: dielectrics, hydraulic fluids and heat bearers	1975 world estimate: from 60 to 70,000 tons	the most chlorinated ones: several decades; the least chlorinated ones: 1 month	LC50 (4 days) invertebrates: up to 3 ug/1; fishes: up to 280 ug/1; other effects: up to 0.1 ug/1	concentration factor can reach 240,000; biomagnification; accumulation and metabolization are more important for the least chlorinated	
Polychloroterphenyls (PCT)	in the past, similar to those of PCB: nowadays, cire perdue castings and "hot-melt" glues	1974 estimate for France: 500 tons (consumption 200 tons)	very similar probably to that of PCB		bioaccumulable	
O-dichlorobenzene	scouring solution, manufacturing medium, solvent	1972 Western Europe: 30,000 tons		LC50 (4 days) fish: 1 mg/1	bioaccumulable rapid elimination	
P-dichlorobenzene	moth-killer, manufacturing medium, deodorant	1972 Western Europe: 30,000 tons		LC50 (2 days) fishes: up to 880 ug/1	concentration factor can reach 230	
Hexachlorobutadiene	synthesis medium, possibly pesticide, hydraulic fluid, solvents, production impurity	imports to USA (1974): 100 - 250 tons (no production)	fairly persistent in the hydrosphere	LC50 (4 days) invertebrates: up to 870 ug/1 ; fishes: up to 60 ug/1	concentration factor can reach 2,000	

Table A. (cont'd)

1	2	3	4	5	6	7
Toxaphen (Polycamphene, camphechlor)	insecticide		soil: 14 years; water: 6 years; half-life: 6 months	acute toxicity: invertebrates LC50 (2-4 days): from 3 to 26 ug/l; fishes LC50 (2-4 days) from 0.5 to 50 ug/l	very bioaccumulable; concentration factor can reach 18,000; bioaccumulation in the food chain	
Hexachlorocycloxanes (HCH) (3 isomers: α, β and γ. γ- HCH (lindane) will be treated separately)	the isomers α and β are obtained. during the manufacture of lindane (1 ton of lindane requires from 4 to 6 tons of β-HCH)	ECE estimate in 1974: 16,300 tons	soil: 14 years; water: more than 4 years; β-isomer is the most stable	acute toxicity: crustaceans LC50 (2 days) from 1 to 33 ug/l molluscs: CL50 (2 days), more than 10,000 ug/l; fishes LC50 (2 days) from 50 to 20,000 ug/l	accumulation not very high in animals; concentration factor of 1,000 for α - isomer; the elimination of β-isomer is slower	toxicity to man: α - isomer has little acute or chronic toxicity β- isomer has less acute but more chronic toxicity than lindane
Lindane (γHCH)	protection of stored food stuffs against insects	USA 1971 estimate: 45,000 tons; France 1972: 2,200 tons	soil: 10 years; rapid degradation in an alkaline medium in the more complex chlorinated products	acute toxicity: LC50 (4 days), crustaceans from 5 to 10 ug/l; molluscs: more than 10,000 ug/l; fishes: from 9 to 500 ug/l	almost non-accumulable	high acute toxicity (LD50: 300 mg/k but low chronic toxicity: permissible daily dose: 0.01 mg/kg
Hexachlorobenzine HCB	pesticide, fungicide, protection of seeds			weak acute toxicity: average chronic and subacute toxicity		toxicity to man: it causes porphyria
Methoxychlore	insecticide, the use of which might increase		not very persistent in water (8 days)	very toxic LD50 (2-4 days) invertebrates: from 0.8 to 12 ug/l; fishes: from 3 to 150 ug/l	moderate bioaccumulation in fishes; no retention in fats: elimination therefore rapid	toxicity to man: permissible daily dose: 0.1 mg/kg
Pentachlorophenol (PCP) and Pentachlorophenates	wood preservation, slimicides in wood and paper industries		water: 2 months; soil: 6 months; half-life: 40 days	acute toxicity: LC50 (4 days) from 60 to 300 ug/l; sub-lethal toxicity: up to 1 ug/l		

Table A. (cont'd)

1	2	3	4	5	6	7
EDC tar (s)	wastes from the production of very important substances: vinyl, chloride, perchloroethylene; no specific use, mixture of hundreds of chemical products	1975 estimate: 400,000 tons	water: for the four main products, half-life = from 4 to 8 days	LC50 variable from 1 to 50 mg/1 (more toxic than the products taken separately)	concentration factor can reach 2,900 tons very rapid elimination	possibility of using controlled incineration avoid effects on the environment; vinyl chloride and perchloroethylene, both volatile, seem not to be present the sea
Tetrachloroparadibenzodioxine	production impurity of 2, 4, 5-T; no specific use	nowadays very small amounts present because of the production conditions chosen	soil: less than 6 years; water: probably as for soil; rapid degradation in light, when in organic solvents	fishes: LC50 from 0.1 to 10 ug/1	bioaccumulable concentration factor could reach 63,000	extremely toxic to some mammals theratogenic
2, 4-D	herbicide		soil: up to 4 weeks; water: more than 6 months	LC50 (2 days): invertebrates: up to 800 ug/1	not bioaccumulable	toxicity to man: permissible daily dose: (PDD) 0.3 mg/kg
2, 4, 5-T	herbicide		soil: up to 9 months	LC50: invertebrates: 1 ug/1; fishes: up to 320 ug/1	almost non-accumulable: concentration factor can reach 220; it does not reach the food chain	in several countries, 2, 4, 5-T is not allowe to contain more than 0.1 mg/kg of tetrachlor dioxine

Table B. Organo-phosphorous compounds

Substance	Use	Total input into the oceans on a world scale	Persistence	Toxicity	Bioaccumulation	Remarks
1	2	3	4	5	6	7
Malathion	insecticide	(1972) USA estimate: 14,000 tons	soil: 1 week; fresh water: up to 4 weeks; sea-water: up to 3 weeks	LC50 (2 or 4 days): invertebrates: up to 1 ug/l; fish: up to 20 ug/l	no bioaccumulation	
Parathion or parathion-ethyl	insecticide	(1973) USA estimate: 63,000 tons	soil: up to 6 months; fresh water: 4 weeks; sea-water: a little more than 6 weeks	LC50 (2 or 4 days): invertebrates: up to 0.4 ug/l; fish: up to 18 ug/l	no bioaccumulation	
Parathion-methyl	insecticide	(1973) USA estimate: 62,000 tons	soil: up to 4 weeks; fresh water: up to 4 weeks	LC50 (4 days): invertebrates: up to 2 ug/l; fish: up to 5 ug/l	no bioaccumulation	
Dimethoate	insecticide; acaricide		soil: up to 6 weeks; fresh water: half-life: 8 weeks	LC50 (2 or 4 days): invertebrates: up to 3 ug/l; fish: up to 6,000 ug/l		
Azinphos-methyl	insecticide		soil: more than one year; fresh water: half-life: 5 weeks	LC50 (2 or 4 days): invertebrates: up to 0.15 ug/l; fish: up to 10 ug/l		
Chlorfenvinphos	insecticide		soil: more than 7 months fresh water: more than one month	LC50 : fish: up to 1,500 ug/l		
Ethion	insecticide; acaricide		fresh water: half-life: 8 weeks	LC50 (2 or 4 days): invertebrates: up to 0.01 ug/l; fish up to 360 ug/l		

Table C. Principal organotin compounds

Substance	Use	Total input into the Mediterranean	Persistence	Toxicity	Bioaccumulation	Remarks
1	2	3	4	5	6	7
Tributyltin oxide	- bactericide and fungicide in paper industries, textiles of vegetal origin, antifouling paints, etc. - fight against bilharziasis - disinfectant - wood preservation		persists in fresh water for more than 8 months	LC50 - (48h) invertebrates: down to 2 ug/1 fish: down to 20 ug/1 algae: reduction of growth at 0.25 mg/1 death at 0.50 mg/1	probable	toxicity, acute: 28 ug/1 (in trout) 2 ug/1 (in water flies)
Fentin salts (Triphenyltin salt)	pesticide		persists in water for more than 9 months and in soil half-life = 6 months	LC50 (48h) invertebrates: down to 10 ug/1 fish: down to 14 ug/1	probable	

Table D. Mercury, cadmium and their derivatives

Substance	Use. Origin as marine pollutants	Total input into the oceans	Persistence	Toxicity	Bioaccumulation Concentration factor	Remarks
1	2	3	4	5	6	7
Mercury and its compounds	phytosanitary products, elecrode in chlore industry, electric industry, mercury vapour lamps, batteries, extraction of silver, catalytic agents in manufacture of acetaldehyde, vinyl chloride and of sulphanthraquinons, pharmacy. Municipal effluents	world oceans: from 4/5,000 t/y of which 3,500 tons from rivers; 3,600 t/y present in the atmosphere Mediterranean: 130 t/y from land-based sources	high in marine organisms (period of retention in molluscs and crustaceans from 400 to 1,000 days)	acute toxicity: organic compounds: hundredths of ug/l for juvenile forms and phytoplankton	direct concentration factor: from 100 to 1,000; bioaccumulation more than 1,000 in food chain	in metallic form, of little toxicity to man; but its organic compounds are very persistent, cumulative and toxic; hence high risks from eating contaminated products
Cadmium and its compounds	pigments in paints, ceramics glass; metallurgy (alloys), batteries, nuclear reactors, surface treatments. Municipal effluents		high in marine organisms and in man	acute toxicity: from 0.1 to 100 ug/l	high concentration factor, particularly in filter-feeders; possible bioaccumulation in food chain	no possibility of eliminating cadmium in man, although the toxicity of cadmium is only apparent in ingested doses bearing no relationship with the quantities currently found in molluscs; it seems necessary to keep the level of cadmium in the marine environment as low as possible because of its accumulation over the years

Table E. Carcinogenic compounds in the marine environment

Substance	Use. Origin as marine pollutants	Total input into the Mediterranean	Persistence	Toxicity	Bioaccumulation Concentration factor	Remarks
1	2	3	4	5	6	7
Benzidine	dyes and artificial rubber industries: USA production: several million tons		no elimination by treatment plants	carcinogenic to mouse, rat, hamster and dog.		occupational cancer (epidemiological studies)
3, 4 Benzofluoranthene	manufacturing impurity			some cases of carcinogenesis have been observed		concentration in European rivers: 0.01 - 0.2 ug/1
3, 4 Benzopyrene	industrial impurity coal industry, coking plants and paraffin treatment plants oils and waxes		photolysable; no biodegradation in three weeks in darkness (deep waters); biodegradation at the surface	mutagenic to mammals; carcinogenic to the nine species of mammals tested	concentration factor: 200; fish tend to metabolize and excrete the product	concentration in European rivers: 0.01 - 1 ug/1; fish sometimes contain small quantities of it
N-Nitrosodiethylamine			stable in water after 14 days in darkness; photolysable but actually persistent	degeneration of the liver in aquarium fish; carcinogenic to the ten species of mammals tested	no accumulation in plants	formation in *vivo* in man by the reaction between amines and nitrates
N-Nitrosodimethylamine			photolysable (ultraviolet); fresh water: more than four months	carcinogenic to the seven species of mammals tested		formation in *vivo* in man by the reaction between amines and nitrates
Diethylamine	in the effluents of several industries; a manufacturing medium			precursor of nitrosodiethylamine		concentration in European rivers: 10 ug/1; LD50 (rat): 540 mg/kg
Dimethylamine	(1970) USA production: 50 million tons, manufacturing medium			precursor of nitrosodiethylamine		concentration in European rivers: 10 ug/1; LD50 (rat): 700 mg/kg

Carcinogenesis in marine organisms has been studied very little -

Table F. Metals included in Annex II

Substance	Use. Origin as marine pollutants	Total input into the oceans	Persistence	Toxicity	Bioaccumulation Concentration factor	(1) Remarks
1	2	3	4	5	6	7
Zinc	Surface treatment, galvanization, pigments, artificial fibres, alloys, anodes. Municipal effluents	Mediterranean: 1,900 t/y (municipal effluents) 18,000 t/y (rivers)	Non-persistent	Acute toxicity: generally from 1 to 10 mg/l; juvenile forms most sensitive	Accumulation factor from 2,000 (fish) to 100,000 (oysters)	Synergy with Pb, Cu, Hg, Cd; not very toxic and not accumulable to man. Little risk to human health from contamination of the sea or of marine organisms
Copper	Alloys, electric apparatus, products for the protection of wood, paints, glass, wall-paper, building (roofs). Municipal effluents	(World oceans: 325,000 t/y rivers 2,000 t/y atmosphere)	Non-persistent	Acute toxicity: from some tens of ug/l for certain juvenile forms to some tens of mg/l for adults	Concentration factor from 100 to 1,000 in molluscs and polychetes; regulation mechanisms in crustaceans and fish	Not very toxic and not accumulable in man; little risk to human health from contamination of sea-water or of marine organisms
Nickel	Stainless steel, alloys, electronics, surface treatments, catalytic agent in hydrogenation reaction. Municipal effluents	(World oceans: 170,000 t/y rivers >5,000 t/y atmosphere)	Non-persistent	Acute toxicity: from some ppm (juvenile forms) to several hundred ppm	Concentration factor from 1,000 to 10,000 in algae, molluscs	Not accumulable in man; little risk from contaminated sea-water or sea-food.
Chrome	Stainless steel, cutting steel, refractory materials, tanneries, paints, pigments. Municipal effluents	(World oceans: 236,000 t/y rivers > 2,000 t/y atmosphere) Mediterranean: 500 t/y municipal effluents, 600 t/y industrial effluents, 1,600 t/y rivers	Non-persistent	Cr VI the most toxic. Acute toxicity: from 1 mg/l to some tens of mg/l	Concentration factor from 10,000 to 60,000 in mulluscs	Effects on man in case of prolonged exposure; little risk from contaminated sea-water or sea-food

Table F. (cont'd)

(2)

1	2	3	4	5	6	7
Lead	lead industry, petrol anti-knock, alloys, glass, munitions, batteries	(world ocean: from 110 to 180,000 t/y rivers 20,000 t/y atmosphere)	remains a very long time in sediments; the surface water content of lead would seem to have been on the increase recently	acute toxicity: from some mg/l to some tens of ug/l	concentration factor from 1,000 (fish) to 10,000 (invertebrates); very slow elimination	synergy with Zn and Hg: very slow elimination (possibility of chronic illness); frequent eating of molluscs in contaminated areas could create problems
Barium	paper, painting works dye works, synthetic rubber			acute toxicity: fresh water: from tens to hundreds of mg/l	fresh water: concentration factor from 100 to 10,000	
Beryllium	nuclear reactors, alloys with Cn, refactory materials, surface treatment, cetalytic agent	(world oceans: 5,600 t/y rivers 400 t/y atmosphere)		acute toxicity: fresh water: from 0.1 to some tens of mg/l according to the hardness of the water; toxicity in the sea would be lower	fresh water: 1,000	very toxic to people working with it, high persistence but few data on toxicity by ingestion
Bore	metallurgy, nuclear reactors			acute toxicity: fresh water: between 5 and 20 g/l; algae and marine phanerogams are the most sensitive		possible toxicity to man only with ingestion
Natural uranium (U_{238})	tracing, photography, special steel, porcelain, glass, nuclear industry		very persistent in the oceans	acute toxicity: fresh water: from some mg/l to some hundreds og mg/l		
Vanadium	alloys (genovanadium), pigments, photography, catalytic agent in organic chemistry	(world oceans: 312,000 t/y rivers 12,000 t/y atmosphere)		acute toxicity: fresh water: very low toxicity, decreasing with the hardness of the water; its toxicity is lower in the sea	10,000 for echinoderms	very toxic and present in man's daily food - little risk to human health from a possible contamination of the sea or sea-products
Selenium	glass, photoelectric cells, transformers, catalytic agent for the manufacture of plastic materials and rubber, dyes	(world oceans 8,000 t/y atmosphere)		acute toxicity: fresh water organisms: from 2 to 10 mg/l	an example of accumulation has been found in the fresh water food-chain	antagonistic to mercury; little risk from contaminated sea-water or sea-food

Table F. (cont'd)

1	2	3	4	5	6	7
Arsenic	Insecticide, wood preservative, herbicide, antifouling painting, textiles, paper, manifacture of mirrors, alloys with Pb, Cu, Sb	(World oceans: 7,200 t/y rivers more than 1,000 t/y atmosphere)		Acute toxicity: from 1 to 10 ug/l	Contradictory data on biomagnification. High concentration factor in molluscs	Certain arsenic inorganic compounds are very toxic and carcinogenic after prolonged exposure. Its organic compounds are less toxic and quickly eliminated. Crustaceans and molluscs being the main sources of arsenic in human food . Any contamination of fishing or aquiculture zones must be avoided
Antimonium	Alloys with lead (batteries), pigments, surface treatment, munitions, rubber, paints, glass, ceramics	(World oceans: 1,300 t/y rivers)		Acute toxicity: some tens of mg/l in freshwater fish	Concentration factor: from 10,000 to 100,000 in molluscs	Little ritention or accumulation in man; little risk from contaminated sea-water or sea-food
Molybdenum	Alloys, lubricaing oils, varnish for ceramics			Acute toxicity: from some hundred of mg/l to some g/l		
Titanium	White pigment, alloys, metallurgy			Acute toxicity: weak (hundreds of mg/l for freshwater fish, in the form of sulphate)		The effluents from titanium oxide factories can create more problems by their consumption of oxygen, their acidity and iron sulphate burden than by their concentration of titanium
Tin	Alloys and metallurgy, manufacture of organostannous and organostannic compounds	(World oceans: 2,000 t/y rivers 30,000 t/y atmosphere)				

Table F. (cont'd)

1	2	3	4	5	6	7
Cobalt	Alloys (refractory materials, high-speed steel, non-magnetic alloys), pigment Municipal effluents	(World oceans: 15,000 t/y rivers 700 t/y atmosphere)		Acute toxicity: (freshwater: not very toxic: between 16 mg/l to 5 g/l); few data on toxicity in sea-water: some tens of g/l to some hundreds of mg/l (contradictory data)	Between 100 and 10,000 for crustaceans. Possible transfer from phytoplankton to herbivores	Oligoelement of little toxicity to man; little risk to human health from possible pollution of the sea or marine organisms
Thallium	Raticides, pigment in fireworks			Acute toxicity: (freshwater: some tens of mg/l), possible chronic toxicity		Toxic to those using them
Silver	Coins and jewellery, electronics, photography, soldering	(World oceans: 70 t/y atmosphere 11,000 t/y rivers)		Acute toxicity: some ug/l	1,000 to 100,000 for algae, molluscs and fish	Not very toxic to man; little risk to human health from possible contamination of the sea or marine organisms

Table G. Biocides and their derivatives not listed in Annex I

Substance	Use	Total input into the oceans on a world scale	Persistence	Toxicity	Bioaccumulation Concentration factor	Remarks
1	2	3	4	5	6	7
Carbaryl (sevin) (carbamate)	contact and ingestion insecticide	(1972) in USA: 23 millions tons (consumption: 11 millions tons)	hydrolysed in alkaline medium; slow photo-decomposition; quickly biodegraded by micro-organisms; in soil it disappears after 2 weeks	LD50 (fish): 2 mg/l	not bioaccumulable	fairly soluble in water: 40 mg/l; LD50 (rat): 800 mg/kg anti-cholinesterasis action PDD: 0.01 mg/kg
Zectran (carbamate)	insecticide		hydrolysed in alkaline medium			LD50 (rat): 60 mg/kg
Carbofuran (carbamate)	insecticide by contact and ingestion	(1972) in USA: 2.7 million tons	in soil total degradation in 16 weeks	LD50 (fish): 0.2 mg/l	not bioaccumulable	LD50 (rat): 18 mg/kg soluble in water: 700 mg/l
Isolane (carbamate)	insecticide by contact, ingestion and inhalation					LD50 (rat): 10 mg/kg
Dimetilan (carbamate)	insecticide by ingestion		less biodegradable than the other carbamates; hydrolyses in alkaline medium			LD50 (rat): 50 mg/kg
Altrazin (triazin)	herbicide		soil: up to 6 years; hydrolysable in basic or acid medium	LD50 (fish): 10 - 20 mg/l	not bioaccumulable	LD50 (rat): 2,000 mg/kg; solubility (in water): 33 mg/l
Ametryn (triazin)	herbicide		soil: up to 3 months	LD50 (fish): 4 mg/l	not bioaccumulable	LD50 (rat): 1,400 mg/kg
Paraquat	herbicide			LD50 (fish): 5 - 50 mg/l		LD50 (rat): 160 mg/l
Diquat	herbicide		adsorption on sediments; photodecomposition; quick biodegradability	LD50: > 10 mg/l	not bioaccumulable	LD50 (rat): 230 mg/kg; very soluble in water

Table H. Organosilicon compounds

Substance	Use. Origin as marine pollutants	Total input into the Mediterranean	Persistence	Toxicity	Bioaccumulation	Remarks
1	2	3	4	5	6	7
Organosilicon compounds	silicon oils, elastomers, resins.		very persistent	acute toxicity: not toxic	not accumulated	not toxic to man in the only form in which they are spread (polydimethylsyloxanes); used principally in surgery and not toxic to aquatic life; insoluble in water

Table I. Cyanides and fluorides

Substance 1	Use. Origin as marine pollutants 2	Total input into the Mediterranean 3	Persistence 4	Toxicity 5	Bioaccumulation 6	Remarks 7
Cyanides	surface treatment, coking plants, gas-works, chemical plants, blast furnaces.		biodegradable, rapid chemical oxidation	fresh water: very toxic: some tens of ug/1		very toxic to man, but very limited effects in the sea; very little risk from a possible contamination of the sea or marine organisms, save in exceptional circumstances.
Fluorides	electrometallurgy, wood preservation, disinfection, insecticides, glass, enamels; effluents from manufacture of aluminum and phosphorus			fresh water: between 1 and 5 mg/1	very few data	only high quantities are noxious to man and mammals; no risk to human health from contamination of the sea or of marine organisms; important natural element of sea-water (1.3 mg/1)

Table J. Inorganic compounds of phosphorus

Substance	Origin as marine pollutants	Total input into the Mediterranean	Persistence	Toxicity	Bioaccumulation	Remarks
1	2	3	4	5	6	7
Inorganic compounds of phosphorus			elemental phosphorus very persistent	elemental phosphorus toxic		phosphates are normal constituents of sea-water: excessive amounts can provoke eutrophication (only if azotic sources are present in the environment); on the other hand it may be possible to add phosphates to the most deprived environments to aid fisheries and agriculture.

Table K. Substances having a deleterious effect on taste and smell in sea-food products

(1)

Substance	Use. Origin as marine pollutants	Total input into Mediterranean	Persistence	Toxicity	Bioaccumulation Concentration factor	Remarks
1	2	3	4	5	6	7
Acrolein	plastics industry		unstable and polymerizes	acute: LC50 less than 1 mg/l sublethal effects: less than 0.1 mg/l		disagreeable odour
Allyl alcohol	plastics and pharmaceutical industries			acute: 1-10 mg/l		pungent odour
Allyl chloride	dye industry; sites where such dyes are used			acute: 1-10 mg/l		irritating smell
Benzene	industries where it is used either as solvent or as intermediate			acute: 10-100 mg/l	not bioaccumulated by marine organisms	strong but not highly objectionable smell; floats on the sea
Carbon disulphide	chemical synthetic industries; sites where used as solvent		decomposes in sea by oxidation	acute: less than 1 mg/l	bioaccumulation observed	causes permanent damage to the nervous system; often impure; it has objectionable smell
Chlorobenzene	dyestuffs manufacture; fine chemicals production; sites where used as solvent		broken down by micro-organisms to HCl and phenol	acute: about 2.5 mg/l	rapidly accumulated by fish, largely in the liver	accumulated in sediments depending upon organic content; characteristic smell
Cresol	manufacture of disinfectants and synthetic resins; production of herbicides, and some other chemicals		biodegradable, the break-down products being less toxic than cresol	acute: 1-10 mg/l		liable to taint fish and shellfish at very low concentrations with consequent interference with marketing
Crotonaldehyde (methyl acrolein)	chemical synthetic industries; sites where used as solvent		biodegradable, the break-down products being less toxic than parent compound	acute: 1-10 mg/l	not accumulated	

Table K. (cont'd)

1	2	3	4	5	6	7
Isopropyl benzene (cumene)	synthetic plastics industry; sites where used as solvent		when released into the sea the bulk will be lost by evaporation but any that dissolved would be degraded	acute: 10-100 mg/l		practically insoluble in sea-water and volatile
O-Dichlorobenzene	dye industry; sites where used as solvent or paint-stripper		very little information on biodegradability in sea; can be metabolized and excreted by mammals	acute: (fish) 1 mg/l	accumulated and lost very rapidly (within one week)	highly toxic to fish; accumulated in sediment depending on organic content; the smell is penetrating but not unpleasant
Ethylene dibromide	chemical factories where used as intermediate; sites where used as anti-knock reagent in aviation fuels or as solvent			acute: 10-100 mg/l	short-term bioaccumulation	sweet odour; slightly soluble in sea-water; known as carcinogenic and mutagenic; solutions resulting from spillage at sea are unlikely to be hazardous to human health
Ethylene dichloride	plastics industry; sites where used as solvent; manufacture of paints and varnishes		breakdown products in the marine environment are likely to be less toxic than parent compound	acute: above 100 mg/l	short-term accumulation only	slightly soluble in sea-water; this substance cannot be detected in the marine environment by present analitical methods
Phenol	coal tar distillation; sites where used as chemical intermediate: pharmaceutical industry, production of herbicides		chemically stable; biodegradable, but the speed in the sea is not known; break-down products are likely to be less toxic than phenol	acute: 10-100 mg/l reacts with proteins but effect on marine life has not been closely studied		can be very objectionable as a contaminant of potential water supplies; can be tasted at conc. as low as 20 ug/l; significant hazard to marine life; tainting of fish and shellfish may occur at a very low concentrations
Phthalate esters	plastics and pharmaceutical industries; sites where used as solvent; present also in domestic sewage		hyrolysis 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	toxicity to marine life in general very high acute: 1-10 mg/l (for di-buthyl phthalate)	di-octyl and di-buthyl phthalates are accumulated by some invertebrates and fish by factors of 1,400 to 3,600 times	floats on the sea or sinks slowly; practically insoluble in water

Table K. (cont'd)

1	2	3	4	5	6	7
Styrene monomer (vinyl benzene)	plastics industry, production of artificial rubbers and resins		the monomer is unstable; polymerized material is very slowly degraded, but degradation products are not fully known	acute 10-100 mg/1		practically insoluble in sea-water; it would float on sea-water and would probably polymerize
Tetramethyl lead and tetraethyl lead	manufacture of these compounds; sites where used as anti-knock reagents in fuels; manufacture of organomercury fungicides and other pesticidal products			acute: 1 mg/1 (tetraethyl lead) no data available for tetramethyl lead	short-term bioaccumulation likely	slight but not unpleasant odours; practically insoluble in sea-water; harm through contact with polluted sea-water appears unlikely
Toluene diisocyanate	polyurethane production plants		if released to the marine environment would react with sea-water producing substances which are not harmful	acute: 1-10 mg/1		sharp pungent odour; it may be a solid or liquid (MP 20°c)
Trichlorobenzene	dye industry; sites where used as solvent		no information in break-down products	1.2.4 isomer is the most harmful: acute: 1 mg/1	no information	practically insoluble in water
Vinyl chloride	production of PVC		does not remain in the sea long enough to affect marine life			gas at normal conditions and liquid under pressure (transport); a health hazard in the marine environment is likely to occur only on exposure to concentration of gas which might occur in the immediate proximity of a major release