

6

1974

GESAMP VI/10

March 1974

ORIGINAL: ENGLISH

IMCO/FAO/UNESCO/WMO/WHO/IAEA/UN
JOINT GROUP OF EXPERTS ON THE SCIENTIFIC
ASPECTS OF MARINE POLLUTION
(GESAMP)

REPORT OF THE SIXTH SESSION

held at
WHO headquarters, Geneva
22-28 March 1974

N O T E S

1. GESAMP is an advisory body consisting of specialized experts nominated by the Sponsoring Agencies (IMCO, FAO, UNESCO, WMO, WHO, IAEA, UN). Its principal task is to provide scientific advice on marine pollution problems to the Sponsoring Agencies and to the Intergovernmental Oceanographic Commission (IOC).
2. This Report is available in English, French, Russian and Spanish from any of the Sponsoring Agencies.
3. The Report contains views expressed by experts acting in their individual capacities which may not necessarily correspond with the views of the Sponsoring Agencies.
4. Permission may be granted by any one of the Sponsoring Agencies for the Report to be wholly or partly reproduced in publications, provided that the source of the extract and the condition mentioned in 3 above are indicated.

Bibliographic Entry

IMCO/FAO/UNESCO/WMO/WHO/IAEA/UN Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) - Report of the Sixth Session, Geneva, 22-28 March 1974

C O N T E N T S

	<u>Page</u>
OPENING OF THE MEETING	1
HARMFUL SUBSTANCES IN THE MARINE ENVIRONMENT	1
IMPACT OF OIL ON THE MARINE ENVIRONMENT	4
SPECIFICATION OF PHYSICAL, CHEMICAL AND BIOLOGICAL PARAMETERS TO BE MONITORED IN AN EVOLVING MARINE POLLUTION MONITORING SYSTEM	4
INTERCHANGE OF POLLUTANTS BETWEEN ATMOSPHERE AND OCEANS	6
PRELIMINARY DISCUSSION OF BASIC INFORMATION REQUIRED FOR THE SELECTION OF SITES FOR THE DISPOSAL OF WASTE INTO THE SEA	7
OTHER MATTERS	7
Principles for Developing Coastal Water Quality Criteria	7
Pollution of the Ocean Originating on Land (POOL)	8
Scientific Aspects of Pollution Arising from the Exploration and Exploitation of the Sea-Bed	9
Membership of Working Groups	10
Availability of UNEP Funds	10
DATE AND PLACE OF NEXT SESSION	10
ELECTION OF CHAIRMAN AND VICE-CHAIRMAN FOR THE NEXT INTERSESSIONAL PERIOD AND FOR THE SEVENTH SESSION	10
CONSIDERATION AND APPROVAL OF THE REPORT	10

ANNEXES

- ANNEX I - Agenda
- ANNEX II - List of Documents
- ANNEX III - List of Participants
- ANNEX IV - Minutes of a preliminary meeting of the Working Group on the impact of
oil on the marine environment
- ANNEX V - Report of Working Group on the Scientific basis for disposal of waste
into the sea
- ANNEX VI - List of Working Groups

IMCO/FAO/UNESCO/WMO/WHO/IAEA/UN JOINT GROUP
OF EXPERTS ON THE SCIENTIFIC ASPECTS OF
MARINE POLLUTION

Report of the sixth session

(WHO headquarters, Geneva, 22-28 March 1974)

OPENING OF THE MEETING

1. The Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) held its sixth session at WHO headquarters, Geneva, from 22-28 March 1974. The Chairman of the Group, Dr. G. Berge, opened the session.
2. Dr. B. H. Dieterich, Director of the Division of Environmental Health of WHO, on behalf of the Director-General of WHO, welcomed the experts, the representatives of the sponsoring agencies and the observers from other organizations attending the session.
3. The Agenda for the sixth session, as adopted by the Group, is attached as Annex I. A list of the documents considered by the Group under each Agenda item and the list of information papers is shown in Annex II.
4. A list of participants, comprising the experts, the representatives of the sponsoring agencies and observers from other organizations is shown in Annex III. The Group noted that, owing to unforeseen circumstances, the following experts were unable to attend the session:

Dr. H. Thompson
Dr. H. A. Cole
Dr. T. Beasley

Dr. R. Fukai
Dr. Y. K. Strizhak

HARMFUL SUBSTANCES IN THE MARINE ENVIRONMENT

(a) Review of Harmful Substances

5. The Group considered the report of a working group which had met twice during the inter-sessional period under the chairmanship of Dr. H. A. Cole. It was noted that it had been possible to add sections on a number of metals in addition to those particularly specified at the fifth session of GESAMP. The report also included data on a number of organic chemicals and a revised section on radioactivity.
6. The Group commended Dr. Cole and the working group for a thorough and useful report and after the adoption of several amendments it was agreed that the updated and expanded sections should replace the appropriate sections of the existing review.
7. The Group discussed whether sections on other metals should be prepared and what should be done in relation to future findings from research currently being undertaken and concluded that although the Review now includes most of the substances presently important as marine pollutants, some updating machinery would be necessary.
8. The Group recommended the inclusion of a limited bibliography of major source materials. The Review should be published with the understanding that supplements of significant updated and/or additional material would be added in the future.
9. In citing the reference material, an attempt will be made to indicate which reference sources were used for particular types of data; this will probably have to be done on a general basis rather than in the manner usually adopted with a scientific paper.

10. The Group agreed that the introduction to the published version of the Review of Harmful Substances will need to take account of the existing documents, but with a number of additions, e.g. a list of all the experts who have been associated with the work, the background to the work and the statement that it is aimed at administrators and refers specifically to marine pollution. There will also be a reference to the much more detailed information available from WHO on the human health aspects of the harmful substances reviewed. In particular, the introduction will cover the fact that both text and tables are based on the assessment of data available to the experts at the time of preparation and therefore are produced in the light of current knowledge of the experts and their understanding of the current marine pollution situation. However, to enable certain questions relating to the effects of metals on human health to be resolved, the Group agreed to reconsider this particular section of the Review at its next session.

11. The Group noted that subject to the above, the task of the working group was essentially completed, nevertheless the United Nations Recommendation 88 from the Stockholm Conference on the Human Environment requires an annual examination of the Review of Harmful Substances. It was decided that this requirement would be fulfilled through the work of the new working group on The Evaluation of Hazards of Harmful Substances in the Marine Environment. Thus as new information becomes available or as other hazards become recognized, amendments or updated material will be prepared.

(b) Evaluation of Harmful Substances

12. The Group noted that for the purposes of Annex II of the International Convention for the Prevention of Pollution from Ships, 1973 (Regulations for the Control of Pollution by Noxious Liquid Substances in Bulk), the International Conference on Marine Pollution, 1973 had utilized the hazard profiles approved by GESAMP at its fourth and fifth sessions (GESAMP IV/19/Suppl.1), in order to categorize noxious substances according to their environmental hazards. Noting that numerous substances had been given provisional ratings because of insufficient available data and that many additional substances required evaluation, the Conference, by Resolution 14, recommended that IMCO should take appropriate steps:

(i) to evaluate the hazards of those substances for which further data were found necessary as well as new substances proposed to be carried in ships, in accordance with the rationale developed by GESAMP; and

(ii) to increase all the lists to cover all the substances known to be carried.

13. In this connexion, the Group was informed of the view expressed by the Marine Environment Protection Committee, at its first session (4-8 March 1974), that the work could best be achieved by using similar arrangements to those previously employed, i.e. an Ad Hoc Panel of IMCO and GESAMP Experts. While appreciating the excellent work carried out by the previous Panel, the Group nevertheless felt that it would not be feasible to continue to use this arrangement in the future, principally because of the increasing difficulties experienced by the experts concerned in obtaining the necessary data for the large number of substances carried.

14. During discussion it was pointed out that for many substances considerable time and resources were required to produce the authoritative data necessary for evaluating the hazards of substances in accordance with the rationale. This difficulty was particularly evident where laboratory work was necessary to assess such factors as toxicity effects on marine organisms. Noting that the 1973 Conference had invited Governments to pursue studies on the environmental hazards of harmful substances and to provide IMCO with available information, the Group agreed that the use of governmental experts or consultants might well be the most effective means of obtaining the necessary data.

15. The Group considered that for the submission of such data to IMCO, it would be appropriate to use the form annexed to Resolution 14 of the 1973 Conference but emphasized the importance of including references indicating the particular sources of the information supplied therein. It was the view of the Group that GESAMP's principal function would be to assess, when requested, the information received from all the various sources and to advise IMCO as to what particular data would be appropriate for evaluating the environmental hazards of each of the substances concerned in accordance with the GESAMP rationale.

16. To enable it to respond to requests from IMCO and also carry out such work as might arise with respect to the Review of Harmful Substances (agenda item 2), the Group decided to establish a working group on Evaluation of the Hazards of Harmful Substances in the Marine Environment (Annex VI).

17. In selecting the membership of the Working Group, the Group agreed to take into account the need to preserve a reasonable degree of continuity with the activities of former groups on these subjects and the importance of providing a balance of expertise particularly in the fields of toxicology, biology and chemistry.

(c) List of Substances to be Annexed to the Intervention Protocol

18. The Group was further informed of the action being taken in IMCO in implementation of resolution 26 of the 1973 Pollution Conference requesting the Organization to prepare, by 30 November 1974, a list of substances to be annexed to the Protocol Relating to Intervention on the High Seas in Cases of Marine Pollution by Substances Other Than Oil, 1973, as required by Articles I and III thereof. It was noted that, in carrying out this task, an ad hoc Working Group of the Marine Environment Protection Committee was making use of the hazard profiles of selected substances prepared by the Panel of IMCO and GESAMP experts (GESAMP IV/19/Suppl.1).

19. In this connexion, GESAMP was requested to supply any additional data that might be available with respect to particular substances for which the hazard ratings were at present provisional. In pursuing this task, the Group noted:

(a) that for some substances sufficient data appear to be already available to make or to complete the hazard assessment, in accordance with the rationale approved by GESAMP (GESAMP IV/19/Suppl.1). These are:

adiponitrile	pentachloroethane
chlorohydrins	pyrite residue
ethylene chlorohydrin	Simazine
fluosilicic acid	trimethylbenzene
latex	Warfarin

(b) that for other substances the assessment cannot be completed, as data are not yet available on the likelihood of tainting and/or bioaccumulation in marine organisms. These comprise:

acrylic latex	Chloronitrobenzenes
beryllium chloride	2-ethyl-3-propyl acrolein
brucine	2-methyl-5-ethyl pyridine
m-, o- chloroanilines	naphthenic acids
p- chloroaniline	β -propiolactone

(c) that for the remainder the assessment cannot be completed, as data are not yet available on the hazards of these substances to living marine resources. These are:

acrylic acid	p- chlorotoluene
allyl isothiocyanate	dibenzyl ether
brucine	dimethyl sulfate
chloroprene	pentachloroethane

In order to complete the assessment of those substances on lists (b) and (c), additional data are required. These data can only be obtained from fundamental laboratory work, and the Group noted that the Conference had already invited Governments to pursue such studies.

IMPACT OF OIL ON THE MARINE ENVIRONMENT

20. The FAO Technical Secretary of GESAMP informed the Group that the Working Group on the Impact of Oil on the Marine Environment which had been set up at the fifth session, could not undertake its work as funds requested from UNEP for this GESAMP Working Group were not received during the last intersessional working period.
21. In order to draw up a work programme for submission to, and approval by, the sixth session of GESAMP, a preliminary meeting was organized with financial support from IMCO for those members of the Group who had been designated at the fifth session.
22. The Group noted the progress made at the preliminary meeting and agreed upon the work programme and the time plan given in the minutes which are attached as Annex IV. The Group expressed the hope that funds from UNEP would be available in the near future so as to enable GESAMP to meet the request made by the Marine Environment Protection Committee of IMCO to accelerate the work on this subject.
23. The Group realized that a wide range of products is included within the definition of oil, as proposed by the Working Group, and considered that the diversity of effects of these products on living marine resources should be included in the discussion of the Group.
24. It was noted that problems associated with pollution by oil in tropical and polar regions differ in important ways from the more familiar problems of temperate areas, and agreed that they should be fully taken into account in the deliberations of the Working Group.
25. The Group further noted that the primary task of the Working Group was to consider those effects upon living marine resources where these are a matter of debate. It was not the intention of GESAMP that the Working Group should be concerned with other problems affecting the marine environment and its living resources where doubt does not exist.
26. The Group suggested that two further problems, for which at the present time there might not be common agreement upon the effect, should also be taken into account by the Working Group:
 - (i) The absorption of pesticides such as DDT, and metals, by oil films and layers on the sea surface and the effect this might have on marine resources,
 - (ii) Interference with gas exchange involving the transfer of carbon dioxide across the air/sea interface.

SPECIFICATION OF PHYSICAL, CHEMICAL AND BIOLOGICAL PARAMETERS TO BE MONITORED IN AN EVOLVING MARINE POLLUTION MONITORING SYSTEM

(a) Working Group on Parameters to be Monitored

27. GESAMP V formed a Working Group (No. 3) on this subject (less biological parameters) and at the fifth session the Chairman was asked to continue to develop the report in the intersessional period, with the inclusion in the Working Group of suitable biologists, at his discretion, with a view to presenting a final document to the sixth session of GESAMP. Experts were invited to let Dr Goldberg have their detailed views on this provisional report in the intersessional period.

28. United Nations Environment Programme financial assistance had been sought but was obtained too late for the Chairman of Working Group 3 to make use of it. The Working Group had, nevertheless, been unable to reach any positive conclusions on the specification of biological parameters. A new proposal was therefore put to the Group with a view to resolving the Working Group's problem. It consisted of expanding the present Working Group and redirecting it, without prejudice to its original obligations.

29. The Chairman of the Working Group doubted that the existing group could properly specify biological parameters. He reviewed the major difficulties in specifying biological parameters at our present stage of technical evolution. In response, several experts named specific parameters such as: primary productivity and standard microbiological determinations, for which the methodology was widely agreed; assessment of coastal, benthic invertebrate populations and fish populations, for which, however, there might still be some residual disagreement on methodology; and assessment of population of fish-eating birds, which would be comparatively easy to assess since they congregate at nesting sites. Bioaccumulation, properly evaluated in potential indicator organisms, was proposed as a valuable parameter.

30. Concern was expressed in a background paper by Dr. Geldreich (GESAMP VI/4/2) on the need to monitor the microbiological quality of marine waters for human health effects, marine organisms and ecosystem changes. Pathogenic organisms were felt to be pollutants not essentially different from chemical pollutants. Several major problems, such as poor initial dilution of sewage sludge or incorporation into tar balls or retention in the intestines of fish, were mentioned.

31. It was also generally recognized that rather different parameters might be required to be specified according to the monitoring system: global, regional and local. It was agreed that a Working Group consisting of two panels be established; one to specify parameters relating to concentrations, and one to specify those relating to effects.

32. The title of the Working Group shall be "Scientific Bases for the Determination of Concentrations and Effects of Marine Pollutants". The principal goal of the group is to provide a basis for the management of polluting materials in the marine environment that can jeopardize human health, the integrity of ecosystems and the amenities of the environment, by means of a monitoring scheme on a regional or global basis. The scientific base for monitoring procedures will be considered so that concentrations of pollutants and their effects upon living systems can be measured.

33. The terms of reference for the two panels were approved and are given in Annex VI.

(b) Scientific Workshops on Marine Monitoring

34. It was proposed that scientific workshops should be organized from time to time to document the extent and nature of the pollution of the oceans through the collation of data from national and multinational studies; to agree on techniques, specify procedures for intercalibration exercises, define media, and identify the specific pollutants to be monitored.

35. The participants in the first workshop should be scientists involved in the study of one or more pollutants in the marine environment from the following categories of substances: (1) oil; (2) radioactive nuclides; (3) halogenated hydrocarbons; and (4) heavy metals (mercury, lead, cadmium).

36. The scope of the workshop was thought by the Group to be too wide; some doubt was cast on the feasibility of arriving at mass balance statements, which in turn would compromise estimates of future levels of pollutants in the marine environment.

37. Particular concern was expressed over intercalibration as a fundamental obstacle to be overcome before meaningful estimates of pollutant levels on a regional or global scale could be made. Related to this was the problem of inadequate knowledge on background (natural) levels of many major pollutants. The proposed workshops were regarded as valuable means of assessing this problem, and problems of intercalibration were not considered to override the main purposes of these workshops.

38. The need to consider the degree of knowledge reached in monitoring the different media (waters, airs, sediments, organisms) was felt to pose a problem of time scale, but this was not regarded as insurmountable and was indeed a justification for holding the workshop to evaluate our knowledge of the various media.

39. The Group was informed of the IOC/WMO IGOSM Marine Pollution Monitoring Workshop to be held in the United States of America in May 1974, since this workshop was expected to specify some parameters and agree on some sampling techniques related to monitoring oil in the sea. It was pointed out also that three regional workshops were being organized by the IOC for the Mediterranean, Caribbean and Far Eastern Regions; these workshops would have certain elements in common with the proposed workshop and care would be taken to avoid unnecessary duplication.

40. It was emphasized that, although the proposal was for a workshop for scientists actually engaged in measuring pollutants, the concern of the developing countries to be involved should outweigh the fact that they might have fewer scientists active in this field.

41. The Group called upon the Intergovernmental Oceanographic Commission, as a joint specialized mechanism of the United Nations agencies concerned with marine pollution, to undertake this task. The Group was informed that every effort would be made to convene the workshop as early as possible in 1975.

INTERCHANGE OF POLLUTANTS BETWEEN ATMOSPHERE AND OCEANS

42. The Group was informed that the new WMO Executive Committee Panel of Experts on Atmospheric Aspects of Environmental Pollution will review, at its first session in May 1974, the WMO activities on the meteorological and hydrological aspects of environmental pollution of the atmosphere, land, inland waters and oceans. In considering the various aspects of the input of pollutants into the atmosphere, their fate and transport and the fallout and washout from the atmosphere, the Panel would no doubt welcome additional information on the processes which govern the sea/air interchange of pollutants and the knowledge still required on this subject.

43. The Group, in discussing this question, referred to its conclusion made at the fifth session, namely that the interchange of pollutants between the oceans and the atmosphere had an important role in the description of the mass-balance of pollution in the oceans. The Group felt that, in particular, assessments of the dry fallout and washout of pollutants from the atmosphere into the oceans should be encouraged. This is required particularly with regard to chemicals, while evidence should be sought for the fallout of other material as well, particularly bacteria. In making this conclusion, the Group was well aware of the restrictions imposed by the present state of methodology. It agreed that such questions as the computation of fluxes of atmospherically transported pollutants into the ocean, the type of pollutants which should be measured and the methodology to be used or developed are of an interdisciplinary nature and that it was essential that a review study of present knowledge in this field be arranged. Particular attention should be given to the fate of contaminants in the atmosphere under exposure to such effects as ultraviolet radiation.

44. It was decided that an ad hoc group be formed to study this question during the next intersessional period and to report back to GESAMP VII with some definite suggestions of approach. The ad hoc Group should comprise experts in meteorology, marine chemistry and physical oceanography. Arrangements for this ad hoc Group will be made by WMO as lead agency.

PRELIMINARY DISCUSSION OF BASIC INFORMATION REQUIRED FOR THE SELECTION OF SITES FOR THE DISPOSAL OF WASTE INTO THE SEA

45. The Working Group on the Scientific Basis for Disposal of Waste into the Sea, which was established at the fifth session of GESAMP, held its first meeting from 4-8 February 1974 at FAO Headquarters, Rome. A Summary Report was submitted to the sixth session for discussion. The Chairman of the Working Group, Dr. Kullenberg, introduced the paper and stressed that, in the group's opinion, this report from the first meeting should be taken as a preliminary one aimed only at receiving critical comments and guidance from the experts for the group's further work.

46. The Group recognized the interim nature of this report but nevertheless decided to include it in the Report of this GESAMP Session (Annex V) in order to inform the scientific community about the progress of the work. It was agreed that the report could also be circulated separately to selected scientists, suggested by the members of the Working Group, with a view to obtaining wider comment. It was agreed, however, that the preliminary character of the report should clearly be indicated pointing out that the conclusions made hitherto should not be used for decision making on dumping; WHO offered its collaboration in the further work of the working group.

47. The Group agreed that, as stated by the Working Group, the biological aspects are not covered appropriately in the preliminary report. It was suggested by some experts that biological aspects should be given more coverage than could be expected from the single biologist member. It was therefore agreed that the draft should be sent to some selected biologists seeking additional comments before submitting it to the seventh session of GESAMP.

48. Similarly, some experts felt that the paragraph 8.3 of the Preliminary Report dealing with health problems would need to be revised, at least, with regard to dumping in coastal waters. It was agreed that WHO should also provide the Working Group with appropriate documentation directly concerned with health problems in connexion with dumping activities and with specific reference to the selection of dumping sites. This documentation should be ready for distribution to the Working Group members for consideration before their second meeting, tentatively in November 1974.

49. It was agreed that all GESAMP experts who contributed substantially to the extensive discussion of the paper should submit their comments in writing to the Chairman of the Working Group immediately after this Session so that they can be circulated to the Working Group members and taken into consideration during the preparatory work for the second meeting of the Group.

OTHER MATTERS

(a) Principles for Developing Coastal Water Quality Criteria

50. The Group was informed that the Working Group on this subject, which had been envisaged at the fifth session of GESAMP, had not been established because of the inadequacy of funds.

51. The Group took note of Resolution 12 of the International Conference on Marine Pollution, 1973, concerning the need for establishing methods whereby the needs of the marine environment relative to water quality could be established, and noted also that the Marine Environment Protection Committee (MEPC) of IMCO had requested Governments to encourage studies on the matter and to submit available information to IMCO for transmission to GESAMP.

52. The Group further noted the need for developing coastal water quality criteria, in connexion with various international discussions on controlling the release of waste into the sea, particularly as reflected by the request to GESAMP made by the MEPC of IMCO to accelerate the current work of the Working Group on Principles for Developing Coastal Water Quality Criteria. The Group agreed upon a time plan for this Working Group as reported by the FAO Technical Secretary of GESAMP, bearing in mind that the terms of reference were already given in GESAMP V/10, Annex IV, and pointed out that the Working Group should take note of the comments contained in the Report of the fifth session of GESAMP on this topic.

(b) Pollution of the Ocean Originating on Land (POOL)

53. GESAMP was asked (GESAMP VI/8/2) to consider the terms of reference given by the International Coordination Group for Global Investigation of Pollution in the Marine Environment (ICG-GIPME) to an IOC ad hoc Group of Experts on Pollution of the Ocean Originating on Land (POOL), with a view to suggesting guidelines to the POOL group for undertaking their work. GESAMP was also invited to suggest candidates for this ad hoc Group in view of the difficulty being experienced by IOC in finding scientists familiar with the problem of production and use of important pollutants.

54. The Group suggested the following guidelines:

- (i) POOL should limit itself initially to a "test-case" pollutant such as DDT or PCB's. The experience gained in such a test-case would be a useful guide to dealing with other pollutants. DDT presents the advantage that the pattern of its use has not changed much over the last 10-15 years, so that the gathering of past as well as present data would be a valuable exercise. Nevertheless, the patterns of use of DDT were considered very important since mere production data may be relatively meaningless without knowledge of use.
- (ii) POOL should check with national groups that have attempted to assemble this sort of data, to learn of special difficulties or facilities in any particular nation.
- (iii) The IOC should be encouraged to seek the cooperation of its Member States in providing the desired information.
- (iv) POOL should approach chemical industry associations in a concerted manner so that individually they were aware of the widespread nature of the inquiry. A special difficulty was felt to exist in countries in which one company produced all the pollutant under study, since the production figures may be regarded as privileged information, and even where a small number produced all the pollutant in a given country questions of commercial competition were usually overriding. But each case or country should be treated on its merits.
- (v) The EEC was stated to be setting up a data collecting and referral mechanism to deal with production and use of pollutants, so that POOL is advised to explore that avenue.
- (vi) POOL should, through the IOC, encourage scientific associations to seek increased cooperation by industries and industrial associations in the release of appropriate data, under appropriate conditions, as an invaluable contribution to our knowledge of the environmental load in respect of the major pollutants.
- (vii) POOL should study indirect or inferential means of arriving at working estimates of global production of pollutants, not only as possible means of checking direct estimates, but as a "second-best" value, should direct values be unobtainable.

55. The UNEP representative was asked about the development of the International Referral System, the International Registry of Toxic Substances, and environmental statistics, and the Group was informed that progress was being made towards establishing firm sources of the type of data sought. POOL should keep itself informed on developments in the United Nations system as a possible source of global data.

Regarding membership the Group was not able to name candidates but did feel that the membership of POOL should include scientists and industrial statistics experts.

(c) Scientific Aspects of Pollution Arising from the Exploration and Exploitation of the Sea-Bed

56. Recognizing the increasing uses of the sea and the widespread interest in accelerated development of sea-bed resources, a GESAMP working group was proposed on the environmental impacts of the exploration and exploitation of the sea-bed resources as well as of other uses of the sea. The objectives are to determine the possible range of effects of certain activities in different regions, such as the Arctic and the tropics, and to assess the hazards to marine living resources, human health, amenities and the environment. In addition, the working group should determine the measures required to prevent and control pollution from such activities.

57. Without wishing to overly restrict the scope of the study, it was suggested that pollution arising from the following activities is considered of considerable importance and concern:

I. The exploration, assessment, production, transport and possibly the refinement of

- A. Petroleum (including natural gas)
- B. Manganese nodules
- C. Consolidated sedimentary deposits
 - sulfur potash
 - salt coal
- D. Unconsolidated superficial deposits
 - placer deposits of heavy metals and diamonds
 - sands and gravel
 - limestone shells
- E. Crystalline rock metallic deposits
 - copper nickel tin
 - lead gold mercury
 - zinc silver beryllium, etc.
- F. Other deposits
 - phosphorite
 - glauconite
 - fresh water (sub-sea-bed deposits)

II. The effects of other sea-bed activities, e.g.

- A. Dredging
- B. Offshore construction including platforms
- C. Artificial islands and reefs

58. The Group discussed the proposed study at length and agreed that it would be an important and ambitious undertaking. Reference was made to relevant work carried out by previous working groups of GESAMP on this subject and the need was expressed for a new approach coordinated with the ongoing working groups on the Impact of Oil on the Marine Environment and the Evaluation of Hazards of Harmful Substances in the Marine Environment.

59. The Group noted the importance of the Third United Nations Conference on the Law of the Sea but acknowledged that there would not be time to prepare a thorough and GESAMP-approved document for the June 1974 meeting. The group decided, however, that a working group should be established with a suggested list of initial priorities covering important activities for which data should be available.

60. A first report on the feasibility of carrying out the study plus a more thorough investigation of priority activities will be presented to GESAMP VII with the object of submitting an approved version to the Law of the Sea Conference at its second session in 1975. It was decided that the Conference would be informed of the study undertaken during its first session in June 1974. At the same time, the Group agreed that the objectives of the study should not be restricted entirely to the concerns of this Conference.

61. The Group nominated Dr. H. A. Cole as Chairman of the working group, subject to his acceptance, and the United Nations will act as lead agency. The composition and terms of reference of the Working Group are given in Annex VI.

(d) Membership of Working Groups

62. The Group reviewed the membership of both the existing and newly-established working groups in order to ensure an equitable distribution of the work involved, bearing in mind the types of expertise appropriate to each subject. A full list of the Working Groups, numbered and titled for easy reference, and including the names of the respective Chairmen and other GESAMP members allocated to each group, is shown in Annex VI. It was agreed that, where appropriate, additional non-GESAMP experts could be included by agreement among the Agencies concerned, the Chairman of GESAMP and the Chairman of the particular Working Group involved.

(e) Availability of UNEP Funds

63. Mr. Peter Thacher of UNEP joined the GESAMP VI session on its last day of deliberations, to review some of the latest developments in UNEP. He expressed an interest particularly in the scientific workshops. He further pointed out that funding for the first workshop would be considered by UNEP, even if it is planned for 1974. However, along with financial support to other working groups of GESAMP, the request for funding would have to be subjected to the established UNEP review process.

DATE AND PLACE OF NEXT SESSION

64. The Group was informed that the seventh session of GESAMP was expected to be held in Spring, 1975 at a place and date to be determined later.

ELECTION OF CHAIRMAN AND VICE-CHAIRMAN FOR THE NEXT INTERSESSIONAL PERIOD AND FOR THE SEVENTH SESSION

65. The Group unanimously re-elected Dr. G. Berge as Chairman and Professor A. I. Simonov as Vice-Chairman for the next intersessional period and for the seventh session.

CONSIDERATION AND APPROVAL OF THE REPORT

66. The present Report of the sixth session of the Group (GESAMP VI/10) was considered and approved by GESAMP on the last day of the session.

A N N E X E S

- I AGENDA
- II LIST OF DOCUMENTS
- III LIST OF PARTICIPANTS
- IV MINUTES OF A PRELIMINARY MEETING OF THE WORKING GROUP ON THE
IMPACT OF OIL ON THE MARINE ENVIRONMENT
- V REPORT OF WORKING GROUP ON THE SCIENTIFIC BASIS FOR DISPOSAL
OF WASTE INTO THE SEA
- VI LIST OF WORKING GROUPS

Annex I

AGENDA

Opening of the Meeting

1. Adoption of the Agenda
2. Further elaboration of the review of harmful substances
3. Impact of oil on the marine environment
4. Specification of physical, chemical and biological parameters to be monitored in an evolving marine pollution monitoring system
5. Interchange of pollutants between atmosphere and oceans
6. Preliminary discussion of basic information required for the selection of sites for the disposal of waste into the sea
7. Date and place of next session
8. Other matters
 - 8.1 Principles for developing coastal water quality criteria
 - 8.2 Pollution of the Ocean Originating on Land (POOL)
 - 8.3 Scientific aspects of pollution arising from the exploration and exploitation of the sea bed
 - 8.4 Membership of working groups
 - 8.5 Availability of UNEP funds
9. Election of Chairman and Vice-Chairman for the next intersessional period and for the seventh session
10. Consideration and approval of the Report of the Session

Annex II

LIST OF DOCUMENTS

No.	Agenda item	Author	Title
GESAMP VI/1	1	-	Provisional Agenda
" VI/2	2	Working Group	Review of Harmful Substances
" VI/3	3	Working Group	Impact of Oil on the Marine Environment
" VI/3/1	3	IMCO	Control of the Discharge of Oil
" VI/4	4	UNESCO	Specification of Physical, Chemical and Biological Parameters to be Monitored in an Evolving Marine Pollution Monitoring System
" VI/4/2	4	E. Geldreich	Monitoring Marine Waters for Microbiological Quality
" VI/5	5	WMO	Interchange of Pollutants between Atmosphere and Oceans
" VI/6	6	Working Group	Scientific Basis for Disposal of Waste into the Sea
" VI/8	8	IMCO	Hazard Evaluation of New Substances
" VI/8/1	8	IMCO	Development of Scientific Information on Water Quality Criteria
" VI/8/2	8	UNESCO	Pollution of the Ocean Originating on Land (POOL)
" VI/8/3	8	UN	Scientific Aspects of Pollution Arising from the Exploration and Exploitation of the Sea Bed
" VI/10	10	-	Report of the Sixth Session of GESAMP
" VI/INF.1		IMCO	Recent Activities of IMCO in the Field of Marine Pollution
" VI/INF.2		FAO	Summary Report of Activities of FAO in the Field of Marine Pollution

No.	Agenda item	Author	Title
GESAMP VI/INF.3		UNESCO	Recent Activities of UNESCO in the Field of Marine Pollution
" VI/INF.4		WMO	Recent Activities of the WMO in the Field of Marine Pollution
" VI/INF.5		WHO	Summary Report of WHO Activities during 1973
" VI/INF.6		IAEA	Recent Activities of IAEA in the Field of Marine Pollution
" VI/INF.7		UN	Recent Activities of the UN in the Field of Ocean Affairs

Annex III

LIST OF PARTICIPANTS

Members of GESAMP

Dr G. Berge (Chairman)
Institute of Marine Research
Nordnesparken 2
Bergen, Norway

Dr A.L. Downing
Binnie & Partners
Artillery House
Artillery Row
London SW1P 1RX, England

Dr E.E. Geldreich
Water Supply Research Laboratory
National Environmental Research Center - Cincinnati
US Environmental Protection Agency
4676 Columbia Parkway
Cincinnati, Ohio 45268
United States of America

Professor E.D. Goldberg
Scripps Institution of Oceanography
University of California
P.O. Box 1529
La Jolla, California 92037
United States of America

Dr C.S. Hegre
National Marine Water Quality Laboratory
Environmental Protection Agency
Narragansett, Rhode Island
United States of America

Dr P.G. Jeffery
Department of Trade and Industry
Warren Spring Laboratory
Gunnels Wood Road
Stevenage, Hertfordshire SG1 2BX, England

Dr R. Johannes
Department of Zoology
University of Georgia
Athens, Georgia
United States of America

Dr S. Kečkeš
"Rudjer Boskovic" Institute
Center for Marine Research
Rovinj, Yugoslavia

Dr G.E.B. Kullenberg
Institute of Physical Oceanography
Haraldsgade 6
2200 Copenhagen, Denmark

Dr L. Otto
Oceanography Section
Royal Netherlands Meteorological Institute
De Bilt, Netherlands

Dr J.E. Portmann
Ministry of Agriculture, Fisheries and Food
Fisheries Laboratory
Burnham-on-Crouch, Essex, England

Professor A.I. Simonov (Vice-Chairman)
Oceanographic Institute
6 Kropotkinsky Pereulok
Moscow G-34, U.S.S.R.

Dr J.B. Sprague
Department of Zoology
University of Guelph
Guelph, Ontario
Canada

Professor F. Valdez-Zamudio
Ministerio de Pesqueria
Ave. Santa Cruz 1390
Lima-18, Peru

Dr M. Waldichuk
Department of the Environment
Fisheries and Marine Service
Pacific Environment Institute
4160 Marine Drive
West Vancouver, B.C., Canada

Dr G. Weichart
Deutsches Hydrographisches Institut
Bernhard-Nocht-Strasse 78
2000 Hamburg 4, Federal Republic of Germany

Dr T. Yoshida
Tokyo University of Fisheries
Tokyo, Japan

SECRETARIAT AND REPRESENTATIVES OF THE UNITED NATIONS AND
SPECIALIZED AGENCIES

United Nations (UN)

Dr L. Neuman (Technical Secretary of GESAMP)
Office for Ocean Economics and Technology
United Nations
New York, N.Y., U.S.A.

Miss S. Kuwabara
UNEP European Liaison Office
Palais des Nations
1211 Geneva, Switzerland

Food and Agriculture Organization (FAO)

Dr G.H. Tomczak (Technical Secretary of GESAMP)
Fishery Resources and Environment Division
Food and Agriculture Organization
Via delle Terme di Caracalla
00 100 Rome, Italy

United Nations Educational Scientific and Cultural Organization
(UNESCO/IOC)

Dr R.C. Griffiths (Technical Secretary of GESAMP)
Intergovernmental Oceanographic Commission
UNESCO
Place de Fontenoy
Paris 75700, France

World Health Organization (WHO)

Mr R. Pavanello (Technical Secretary of GESAMP)
Division of Environmental Health
World Health Organization
1211 Geneva 27, Switzerland

Dr R. Helmer (Rapporteur)
Environmental Pollution Unit
World Health Organization
1211 Geneva 27, Switzerland

World Meteorological Organization (WMO)

Dr I. Zrajevskij (Technical Secretary of GESAMP)
World Meteorological Organization
Case postale No. 5
1211 Geneva 20, Switzerland

Dr G. Verploegh
Ocean Affairs Branch
World Meteorological Organization
Case postale No. 5
1211 Geneva 20, Switzerland

International Atomic Energy Agency (IAEA)

Professor Y. Nishiwaki (Technical Secretary of GESAMP)
Division of Nuclear Safety and Environmental Protection
International Atomic Energy Agency
P.O. Box 590
A-1011 Vienna, Austria

Inter-Governmental Maritime Consultative Organization (IMCO)

Mr Y. Sasamura (Administrative Secretary of GESAMP)
Marine Environment Division
Intergovernmental Maritime Consultative Organization
101-104 Piccadilly
London W1V 0AE, England

Mr S.L.D. Young
Marine Environment Division
Intergovernmental Maritime Consultative Organization
101-104 Piccadilly
London W1V 0AE, England

OBSERVERS FROM INTERNATIONAL ORGANIZATIONS

International Council for the Exploration of the Sea (ICES)

Dr J.E. Portmann
Ministry of Agriculture, Fisheries and Food
Fisheries Laboratory
Burnham-on-Crouch, Essex, England

Annex IV

MINUTES OF A PRELIMINARY MEETING OF THE WORKING GROUP
ON THE IMPACT OF OIL ON THE MARINE ENVIRONMENT

1. INTRODUCTION

1.1 The group held a preliminary meeting at WHO Headquarters, Geneva, on 20 and 21 March 1974. The following Experts participated:

Dr. M.G. Ehrhardt
Dr. P.G. Jeffery

Dr. R.E. Johannes
Dr. J.E. Portmann

The group received advice and assistance from the GESAMP Technical Secretaries of FAO and IMCO, Dr. G. Tomczak and Mr. S.L.D. Young, the latter acting as secretary for this meeting.

1.2 In the absence of the Chairman (Dr. H. Thompson), Dr. P.G. Jeffery acted as Chairman for the meeting. It was agreed that Dr. C.S. Hegre should attend the meeting as a personal observer acting on behalf of the Chairman.

1.3 It was noted that GESAMP, at its fifth session, indicated that experts from outside GESAMP should be appointed as members of the group, and it was agreed that:

Dr. E.M. Levy
Dr. O.G. Mironov

Dr. K. Okubo
Mr. K.H. Palmork

should be invited to join the group to assist with the task of studying the Impact of Oil on the Marine Environment.

2. SCOPE OF WORK

2.1 At the commencement of the meeting the group took note of the views expressed in the Report of the fifth session of GESAMP (GESAMP V/10, paragraph 44) together with suggestions put forward by the Chairman (Dr. H. Thompson). The group was also informed of the action taken by the International Conference on Marine Pollution convened by IMCO in October 1973 and subsequently at the first session of the Marine Environment Protection Committee of IMCO (GESAMP VI/3/1), with regard to oil pollution. Particular note was taken of the definition of "oil" contained in Annex I of the International Convention for the Prevention of Pollution from Ships, 1973 and the list of oils contained in Appendix I to Annex I of the Convention. In this connexion, the group noted Resolution 6 of the Conference calling upon IMCO to review at an early date and on a comprehensive basis, the environmental problems created by the discharge of all petroleum derived oils into the marine environment, with particular reference to the problems associated with the discharge of light refined oils.

2.2 Bearing all this information in mind, the group agreed that its terms of reference were primarily as stated in the Report of GESAMP at its fifth session, i.e.

"To consider the biological effects of oil on living marine resources in the light of recent scientific findings."

Nevertheless, the group recognized that certain physical and chemical effects do have a considerable influence on the biological effects and agreed that these should be taken into account in the discussions where appropriate.

The group further agreed that although there are other effects of oil on the marine environment, e.g. on diving birds and on beaches, these were well understood and would not be considered.

2.3 In order to define the scope of its present work the group agreed that it would be appropriate for the time being to consider the effects of the oils falling within the definition of oil as set out in Annex I of the 1973 IMCO Convention, i.e.

"'Oil' means petroleum in any form including crude oil, fuel oil, sludge, oil refuse and refined products (other than petrochemicals which are subject to the provision of Annex II of the Convention) and, without limiting the generality of the foregoing, include the substances listed in Appendix I to the Annex."

3. WORK PROGRAMME

3.1 In order to facilitate its work, particularly during the next intersessional period, the group agreed on the following Work Programme:

- A. Identify the effects which are of specific concern to environmental scientists arising from the impact of oil on the marine environment and its living resources.
- B. Identify the specific references, reviews, symposia, and other material which would provide a composite data base.
- C. Identify the significant assumptions and short-comings present in these studies. Identify results which could be taken as scientifically substantiated.
- D. Decide what data is unknown or unverified relative to the impact of oil on the marine environment.
- E. Look to its own or invited expertise to extrapolate predictions from existing data base as to what may reasonably be thought to be the impact of oil on the marine environment.
- F. Prepare a report relating production, distribution, use, disposal, physical-chemical properties, as well as biological effects of oil, to their impact on the marine environment.

3.2 As an initial step the group agreed that in preparation for its next session, evidence relating to the effects of oil as defined in paragraph 6, should be assembled on the following aspects which were considered to be the effects of specific concern to environmental scientists arising from the impact of oil on the marine environment and its living resources (paragraph 7A):

Tainting - accumulation of oil or oil components in marine products consumed or likely to be consumed by man, to levels causing taste or odour, rendering them less desirable as food.

Deoxygenation - effects of oil on the oxygen levels in water columns and sediments by interference with biological, physical or chemical activity including the transfer rates across the air/sea boundary.

Effects on microbial populations - stimulation or inhibition by oil of planktonic or benthic micro-organisms including primary producers and pathogens which result in altered biomass or species distribution.

Carcinogenesis - evidence relating to oil of:

- (i) accumulation of compounds known to be carcinogenic or mutagenic.
- (ii) the transfer of carcinogens along the food chain and the production of tumours in marine organisms and the consumers of such organisms.

Lethal effects - direct and immediate effects of oil including, but not limited to, toxicity, smothering and clogging.

Sub-lethal effects - chronic biological effects of oil (other than those covered by tainting, carcinogenesis, and microbial population effects listed above) including but not limited to chronic toxicity, and effects on behaviour, growth, reproduction, colonization and species distribution.

Heating effects - effects on marine organisms and substrates due to elevated temperature produced by absorption of solar radiation by oil films.

Routes into and within bio-systems - physical and chemical factors affecting the availability of oil to biological systems including, but not limited to, evaporation, microbiological degradation, chemical alteration, absorption and physical transport vertically and horizontally.

3.3 It was agreed that the task of identifying the specific references, reviews, symposia and other material from which the data base would be compiled should be undertaken for each topic of concern as identified above, and that individual members of the group should be asked to act as a "Lead Expert" for each topic. It should be the concern of each Lead Expert, with help from other experts inside or outside the working group as appropriate, to prepare a list of all relevant material to serve as the data base and to circulate copies of this list to all other members of the group no later than 30 June 1974. It should be the task of all members of the group to consider these lists and to report back to the Lead Expert, the existence of any new or additional data and to comment where appropriate on the material thus assembled.

3.4 After discussion within the group it was agreed to ask the following members of the group to act as Lead Experts for the individual topics of specific concern:

Tainting	Dr. K. Palmork
Deoxygenation	Dr. P.G. Jeffery
Effects on microbial populations	Dr. C.H. Thompson
Carcinogenesis	Dr. J.E. Portmann
Lethal effects	Dr. E.M. Levy
Sub-lethal effects	Dr. C.H. Thompson
Heating effects	Dr. R.E. Johannes
Routes into and within biosystems	Dr. M.G. Ehrhardt

3.5 The Lead Expert should be responsible also for the preparation of a preliminary draft report summarizing the topic of concern. In particular he should identify the significant assumptions and shortcomings of the studies, comment on the appropriateness of the methodology, identify the results that are substantiated and note what data are unverified and where the existing data are inadequate (Paragraph 7, C and D). These summaries should be circulated in draft form to all members of the group not later than 30 September 1974 to allow time for study and/or comment by all members of the group prior to the next meeting, tentatively scheduled for late October 1974 at FAO Headquarters, Rome.

P R E L I M I N A R Y R E P O R T

Annex V

WORKING GROUP ON THE SCIENTIFIC BASIS
FOR DISPOSAL OF WASTE INTO THE SEA

Preliminary Report and Conclusions of the First Meeting,
held at FAO Headquarters, Rome, 4-8 February 1974

Members of the Working Group:

Dr. G. Kullenberg (Chairman)
Dr. E. K. Duursma
Dr. B. V. Hamon
Dr. B. H. Ketchum
Dr. S.-A. Malmberg
Dr. J. E. Portmann
Professor A. I. Simonov
Dr. M. Waldichuk
Dr. G. F. Weichart
Dr. G. Tomczak (Technical Secretary)

NOTE

This report represents the preliminary conclusions of the Working Group. It does not necessarily reflect the views of GESAMP as a whole and does not take account of the comments passed at the sixth session of GESAMP. It is annexed to the report of this session not for the purpose of guiding administrators but with a view to soliciting comments from other scientists who, for this purpose, may contact the Chairman of the Working Group.

The Working Group met in Rome during 4-8 February 1974 under the Chairmanship of Dr. G. Kullenberg. The meeting was attended by the following members: Dr. E. K. Duursma, Dr. S.-A. Malmberg, Dr. J. E. Portmann, Dr. M. Waldichuk, Dr. G. F. Weichart. Unfortunately, Dr. B. Ketchum and Professor A. I. Simonov were unable to attend the meeting; the lack of input from a biologist was particularly regretted by the Working Group. Dr. B. V. Hamon being associated with problems of air-sea interaction will join the Group for intersessional work and the second session. The Group was welcomed by Dr. H. Kasahara, Director, FAO Fishery Resources and Environment Division; Dr. G. Tomczak (FAO) provided secretarial assistance to the Group.

The Working Group began its deliberations by a careful discussion of the terms of reference given to it by GESAMP V.

"With reference to Annex III of the London Convention for the prevention of marine pollution by dumping of wastes and other matter:

- (1) to carry out a critical review of our present knowledge of those aspects of dispersion and physical, chemical and biological processes relevant to the selection of sites for discontinuous injection of wastes into the marine environment in both deep and shallow waters;
- (2) to identify gaps in our present knowledge, focus attention on urgent research needs, and suggest research priorities."

1. Introduction

The Group considered that waste disposal at sea involves several disciplines, namely physical oceanography, chemistry, sedimentology and marine biology, all of which are interdependent and none of which can be considered in isolation. It was agreed that, although not specifically stated in the title, the Working Group was expected to discuss the factors which must be considered in the selection of sites for disposal of wastes at sea not in terms of specific examples but in general terms. It was further agreed that attention should be focused particularly on living resources of the sea and their exploitation. The Group interpreted this as meaning those species which are, or may be, exploited commercially and the food organisms on which they are directly or indirectly dependent, plus the need to avoid interference with fishing activity. It was recognized that, in many cases, the young stages were particularly vulnerable and also that certain areas of the marine environment, although not at present supporting commercial resources, were of potential interest and should also be protected. In addition, other interests, e.g. aquaculture and recreational interests, were recognized as being of importance.

The Working Group agreed that, at its first meeting, it should concentrate on an identification of these matters of importance in order to predict the behaviour and effect of materials when dumped at sea and that it should attempt to identify those areas where knowledge is reasonably precise and those areas in which knowledge is severely lacking. It was recognized that, in formulating judgements and policy outlines, the Group would be unable to provide a complete checklist for every situation and that always local information and conditions must be taken into consideration, not least of which would be the existing conditions and pollutant load in the area.

The Group noted that even in the field of marine dumping there is considerable experience which can be drawn upon and that this should be consulted before decisions relating to new proposals are considered and approved or rejected.

The Group noted that the critical pathway approach has been used with success in the field of radioactive disposal and agreed that this would be a useful line to follow for certain pollutants. They recognized, however, that the problems involved in non-radioactive waste disposal are more complex owing to the great variability in the most sensitive species to be considered, and also the different types of wastes and different modes of action.

The Group moved from this general discussion to more specific aspects related to waste disposal at sea using as a basis for its discussions various working papers prepared or submitted to it by the Working Group members (see Annex V, p. 19). It was agreed that discussion at the first meeting should concentrate on disposal of wastes from barges and tankers, since this was believed to be the normal situation, and to defer discussion on disposal of containerized wastes which must, according to the Dumping Conventions, be conducted in deep waters, which in general (though not always) will be of less importance in terms of marine resources. The Group drew upon the experience of its members in studies both in the laboratory and in waste disposal operations and a few examples are cited although in the interests of brevity many others have been omitted.

The Group wishes to emphasize that they were aware that due to the lack of biological input at the meeting the biological - and biochemical - implications have not been penetrated according to their merit.

The conclusions are given in Section 2.

2. Preliminary conclusions of the Working Group

(a) The Group considered that the disposal of waste at sea can be scientifically discussed without taking into account consideration of the justification of waste disposal. The Group did not discuss alternative disposal methods but agreed that these will always have to be

taken into account when choosing the best procedure. The sea has a receiving capacity for wastes, in particular, and very often only, because of its large volume. The self-cleaning and buffering capacity of the water is limited, while the seabed as a sink will only be effective for some materials.

(b) In considering the possibility of sea disposal, the physical conditions of the sea, the chemical and physical characteristics of the waste and the possible effects it might have on marine life in the area likely to be affected should all be taken into account. After careful consideration of the various aspects of these problems, the Group concluded that of these three subjects the physical conditions in the area are extremely vital since these will, to a large extent, determine the fate of the material. The rate of dispersion or aggregation in the area of disposal or the area of final deposition after transport, will be determined by currents, turbulent mixing, topography and the configuration of the coastline.

(c) It was agreed that dispersion after initial dilution can be relatively slow and in general it is therefore essential that maximum dilution is ensured on disposal.

(d) Under stratified conditions the thickness of the wind mixed layer is significant in determining the extent of dilution. Liquid wastes in particular, but also near-neutrally buoyant particles, are liable to be trapped at the layer of discontinuity, at least temporarily, and as a result dispersion is very much suppressed. As these layers of discontinuity are often sites where marine organisms are concentrated this may be an undesirable factor if the waste is toxic.

(e) Many substances commonly regarded as pollutants, e.g. metals, PCBs, etc. are strongly adsorbed on particulate matter - especially fine clay or organic materials - and are likely to be transported into areas of natural sedimentation of fine material, for example this would apply to an estuary.

(f) The Group noted that much more work was necessary on the subject of bioaccumulation, including tainting. More information is especially required on the mechanisms and rate of uptake and loss, the levels associated with death or harm to the animal in question and the accumulation factors to be expected. Only when this information is available can the safety factor for disposal of a bioaccumulatable substance be determined.

(g) Disposal of wastes, especially organic wastes should be avoided in areas of high productivity such as upwelling regions and continental margins since the oxygen demand is already high in such areas.

(h) Although the layer between 500 m and 1500 m in deep water areas is often one of high microbiological activity, disposal of waste in these areas should be avoided since the oxygen supply in such areas is also limited. Consequently degradable organic matter can probably be disposed of most safely in those coastal areas where oxygen is readily available. However, care should be taken to ensure that adequate dilution is achieved so as to avoid risk of acute toxicity.

(i) The various sites which might be suitable for waste disposal were considered by the Group to fall into four broad categories which, however, all require caution to a greater or lesser extent.

(i) Areas of great turbulence. Areas of tidal activity are often characterized by a high degree of turbulence and such areas offer great possibilities for natural dispersion. Care is, however, necessary to avoid conflict with local interests especially aesthetic and recreational, and also in order to predict where the waste might ultimately be deposited (in the case of a particulate material). In an inlet subject to even very strong tides deposition may be expected either along the bed or in the inner reaches of the inlet.

(ii) Confined basins. These will in many cases, to a greater or lesser extent, periodically approach anoxic conditions and be subject to periodic turnover. Such areas might sometimes be considered ideal for the disposal of inert wastes and also perhaps of those which are biodegradable. However, persistent and potentially bioaccumulatable substances should be avoided since ultimately they might be returned to the productive surface waters. It should be pointed out that the use of such areas is very much a matter of scale, and local considerations must be taken into account. It is unlikely, for example, that an area such as the Baltic Sea would be acceptable for such use whereas a fjord or inlet may well be.

(iii) Other areas of minimal turbulence or "quiescent" conditions. These areas are characterized by a distinctly limited capacity to receive wastes since dispersion and transport out of the area and renewal of oxygen supplies, etc. are all limited. The all important consideration in waste disposal in such areas is therefore how to achieve maximum possible initial dilution and careful control of the scale of operation. The more inert a substance, in general, the greater the acceptable scale of dumping but in this context the local existing or potential marine resource must be considered.

(iv) Abyssal plains. On the basis of present knowledge dumping in such areas is likely to present the minimum of risk to marine resources. Spread out (dispersion) is likely to be extensive in the water column unless dumping is of large or very heavy particles.

(j) Degradation of dissolved organic compounds in turbid waters favours decrease of concentrations, but some toxic substances have a greater persistence than non-toxic substances.

(k) Sewage-sludge or any other organic-containing material which, if it accumulates on the bottom, presents a potential risk of reduced oxygen concentrations in surface waters when stirred up.

(l) The sediments of the sea bottom in various areas are a potential sink for organic and heavy metal wastes owing to the sorption capacity of sedimentary particles. However, dissolved wastes will only effectively be scavenged to the bottom in areas where particulate material is regularly present in the water column. Otherwise dispersion in the water column is the main process. A drawback of scavenging is the accumulation in a certain area with risks of recycling for those substances that can be exchanged.

(m) In considering the three Annexes to both the London and Oslo Conventions the Group experienced some difficulty over phrases such as "bioaccumulated biodegradable" and in particular the exemption of Annex I substances as trace substances. Whilst they recognized that the intention of the exemption was to exclude those substances which were present in sewage sludge, dredging spoils and other wastes in an entirely fortuitous way they wish to point out the anomaly that these exemptions introduce. Namely, that a waste from a particular process, e.g. cadmium from cadmium plating cannot be dumped even though the total quantity per unit time be much less than that introduced in another exempt waste. This raised the question in the minds of the Group that perhaps a prohibition as currently prescribed in the Conventions was inappropriate. In any case it is clear that a suitable definition is required.

(n) The Group discussed the problem of turbidity introduced into the sea by such wastes as dredge spoils and sewage sludge. It was agreed that this would affect photosynthesis and ultimately primary production. While the effect of dumping on primary production, compared to other ecological effects, is probably small, this problem merits closer scientific examination. Questions need to be answered relative to effects of such turbidity on production during "bloom" and low production periods in clean and turbid waters, and under different conditions of disposal.

(o) The microbiological aspects of such wastes as sewage sludge have certain health implications. The Group agreed that these wastes would probably be released at points well removed from shellfish beds, fishing areas and recreational beaches. Nevertheless, the possible

movements of such materials from dumping sites to fishing and recreational areas cannot be ignored. The potential hazard of viruses particularly should be investigated more closely in this regard.

(p) The guiding principle will practically always be based on dispersion. When this condition can be fulfilled any self-cleaning or adsorption which occurs will serve to reduce the possibility of damage to marine resources.

(q) It was agreed that the following represent gaps in our present knowledge on dispersion (not according to priority):

Deep water dispersion (advection and mixing);

Gravitational settling velocity under natural conditions;

Depth penetration and vertical concentration distribution immediately after the dumping;

Bottom transportation mechanisms;

Trapping of waste particles at density interfaces: for which waste characteristic or waste type can this happen;

Predictive modelling.

3. Physical dispersion

Dispersion is here interpreted as the sum of the initial dilution and the subsequent spread. The technique of release and the physical properties of the waste determine the initial dilution which is often critical for the impact on the environment, and in general should be estimated in advance. Present experience shows that for wastes released from barges and tankers the initial dilution is in the range 1:100 to 1:500, rarely reaching 1:1000. By adjusting the technique of release the initial dilution can be increased to a considerable extent, and in many cases this should be aimed at.

Dispersion is determined by the characteristics of the waste and the environmental conditions at the site or in the area.

(a) Waste with a density close to that of sea water will be dispersed in the surface layer, i.e. the top 50 m of the sea. There we can reasonably well predict the rate of dilution as a function of the physical conditions: wind, waves, mixed layer thickness, vertical current and density distributions. The range of the relevant dispersion parameters is fairly well known. Under wind conditions of 4-5 m/sec, subsequent dilution in the range 1:10 and 1:30 over two to three hours can be expected, implying that even in the surface layer, where the turbulence is fairly well developed, the subsequent dispersion is very much slower than the initial dilution generated during the release operation.

(b) Waste with a density considerably higher than sea water will tend to sink, and in this case the development during the release and the subsequent dispersion must be considered in separate stages.

(i) The initial behaviour of waste heavier than the surrounding water, i.e. due to its buoyancy, may be modelled by treating the waste as a descending plume or as a falling cloud (like a thermal in the atmosphere); these examples assume a stationary vessel. By means of these models the depth of penetration in a neutral and a linear density stratification can be predicted as a function of the density difference, the released volume per unit time and the stratification. Calculations suggest that for dredge spoils and sewage sludge with the density range 1.05-1.40 tons/m³, the depths of penetration in the stratifications found in the top 500 m of the sea are in the range 50-500 m for a 3000 m³ release over an hour. However, field investigations on this point are absolutely necessary before a reliable prediction can be made.

The collapse of a falling plume or cloud of waste material in a pycnocline layer presents a situation on which there is virtually no information. This point requires much more theoretical as well as experimental study before any reliable prediction of the behaviour can be made. A field experiment with the proper design would yield much information.

The vertical concentration distribution in the contaminated water column immediately after a dumping operation has been observed in a few cases and provisional models can be formulated to describe the distribution analytically. However, again field investigations designed to yield this information by observations are required to test the relevance and accuracy of the models.

(ii) After initial loss of buoyancy and momentum the waste will spread horizontally and the contaminated water layers will slowly sink to their appropriate density level, which can be estimated from a knowledge of the contamination and the density distribution in the water column.

The remaining suspended particles will be subject to gravitational settling. The settling velocity has been estimated in a few cases and found to be of the order 1 m/hour, but the general applicability of this number is not known. A wide range of settling velocities may be expected, depending upon the types of particles present, and this point needs more study by observation. In many subsurface layers the vertical spread due to mixing is very slow and the spread due to settling can be important.

(iii) The subsequent dispersion due to turbulent mixing and advection can be reasonably well predicted as long as we are dealing with the top 100-200 m but for deep water layers this is not the case. We still know very little about the dispersion in deep water. From this point of view separate considerations should be given to deep and shallow waters.

(iv) Transport along or at the bottom can be inferred from observations in shallow waters (shelf areas), but is more difficult to predict in deep waters. Available information on deep sea, near-bottom currents suggest that resuspension will not take place except in certain areas. These may mainly be located at the lateral boundaries and be related, partly at least, to topographic features such as slopes, canyons and ridges.

The importance of the initial dilution was stressed. Clearly by proper design of the injection technique, the initial dilution can be considerably influenced. It should be increased as much as is practically possible. The density of the waste is very significant in this connexion, and material which will float or remain in suspension should not be dumped.

Since the available information on the depth penetration and gravitational settling is limited, it was felt that a relevant task is to design proper experiments. Experimental observations are required to test and develop predictive models which relate the penetration to the conditions at the site, the waste characteristics and the release technique. The fractionation of particulate matter and the separation from the solid and the liquid fraction, and the behaviour of liquid waste with special physical properties, is not fully understood, and comprehensive advice as to its proper handling cannot therefore be given.

Transport along the bottom was emphasized: in estuaries and river mouths the reaction (compensating) current can return the waste along the bottom: this will also occur in shallow water-upwelling regions. The oscillating currents in many areas will cause resuspension and fractionation due to differential settling. This implies that the fine grained part of the material may be transported most effectively. Several examples of very efficient bottom transport of dumped waste are known.

The possible trapping of almost neutrally buoyant material in pycnocline layers was discussed. This is likely to happen in many stratified areas. Since plankton and migrating animals are concentrated or oscillate through such a region this is of importance. In general the layered structure of the natural distribution of salinity, temperature and other properties will cause the waste to be distributed in a similar way. Internal layers can survive several days and this fact must be considered when selecting dumping sites.

The current distribution in many shelf areas is known and to a certain extent the current conditions are decisive for the selection of dumping sites. With the premise that we want dispersion of the material, the area of dumping must be characterized by strong currents. In this connexion it is worth stressing that the dispersion efficiency depends upon both the residual current and the oscillating current components. In many cases, the fluctuations are most important.

Areas which in general should be avoided, from a point of view of dispersion characteristics are: estuaries, upwelling regions where reaction (compensation) currents are present; ridges, special topographic features, e.g. slopes, shallow water trenches; areas with poor water exchange or weak flushing.

Required observations at the site from the point of view of dispersion:

- (1) vertical density distributions during different weather conditions and seasons
- (2) mixed layer depth on a seasonal basis
- (3) wind distribution
- (4) current conditions: vertical distribution, velocity range, directions, oscillations and residual; some information is necessary, the more the better
- (5) bottom conditions: sediments, topography (e.g. flat bottom, deepenings or trenches, ridges)
- (6) biological information (basic information on fishery resources and activities)
- (7) turbidity, i.e. the natural occurrence of particulate matter in the water column.

4. Characteristics of the waste

The characteristics fall into three categories, physical properties, chemical properties and biological properties. All three have a bearing on their effects on the marine environment. Under the category, physical properties, it was agreed that wastes in containers presented a rather special case and the group agreed to defer discussion on this until a later date.

If the behaviour of the waste after disposal is to be predicted with any accuracy it is necessary to know whether the waste is a liquid or solid, or a solid in suspension. It is also essential to have information about the density of the waste as a whole and of any solids it may contain, since this property will influence both initial dilution and subsequent dispersion under settlement. Settling velocity will be influenced by the shape of the particles and there is evidence that flocculated matter will settle more rapidly than individual small particles. Under stratified conditions particulate matter may be retained or have its dispersion suppressed at the layer of discontinuity.

Particulate material can influence the marine environment in several ways. If it settles in large amounts in a confined area then the benthic flora and fauna will probably be adversely affected. From a resource point of view, this need not necessarily be an adverse change although often it will be, especially if the solids are organic in which case

anoxic conditions are likely to become established. Although in some sea areas the suspended particle load is high, certain forms of a particular waste may clog gill surfaces of marine fish and crustacea and cause suffocation. In clear waters an increase in suspended matter can cause discolouration of the water with possible adverse effects on recreational interests. If a waste is relatively insoluble, and positively buoyant it will float and amenity interests will be affected. Floatable materials or those which remain suspended in the water for long periods should not be dumped at sea.

In general it is not possible to predict the full chemical nature of a waste from a knowledge of the raw materials used in the process and the method of production process, however, it is possible to obtain some clues. The need for comprehensive information should not be interpreted as a requirement for a standard analysis for an extensive list of chemical elements or compounds, such analyses should be tailored to the needs for each waste. Whenever a substance is used in a manufacturing process in large quantities it will be advisable to conduct analysis of the effluent for that substance, even if it is said by the producer to be absent, e.g. mercury in chlor-alkali effluents. Certain guidelines can be given. For example, sewage sludges should be analysed for total solids content, total particulate content, total organic content and specific gravity. Analysis for several trace metals, pesticide compounds and PCBs will provide useful information on persistent substances. Additional analyses may be required.

Present knowledge indicates that certain metals are particularly hazardous to marine life or via marine foods to man, and a local build up above normal concentrations is therefore likely to be undesirable.

For organic compounds it will be possible to determine the biochemical oxygen demand (BOD) from which the oxygen demand in the sea can be predicted. Besides this an oxygen demand will also be created by certain inorganic chemicals. This can be more important in the short-term since the demand is almost instantaneous. Certain chemical substances will react with components of sea water, e.g. acids and alkalis will be neutralized and certain metals will precipitate out - some examples are quoted in a separate section on this subject. Such behaviour can, of course, be predicted, provided suitable analyses of the wastes has been conducted. In the context of metal precipitation it should be pointed out that certain metals and organic substances are readily and strongly adsorbed on and subsequently absorbed into particulate matter. There is some evidence that in this form they are much less readily available to marine organisms, i.e. the risk of bioaccumulation or toxic effects is reduced. A notable exception to this is cadmium which remains reavailable while other metals become more firmly bound. Similar effects may also be created by the formation of organic complexes but this would be largely dependent upon the stability of that complex.

It should be noted that the valency state of an element is of importance when its effects on marine organisms are to be predicted, e.g. arsenic is less toxic in the pentavalent form than the trivalent form but chromium 6 is more toxic than chromium 3. Some compounds, of which the phenols and their chlorinated derivatives are the best known, can cause tainting of fish or shellfish and no wastes containing such materials should be dumped in the sea in such a way that tainting of marine products can result.

Even with a comprehensive knowledge of all these factors it is still difficult to predict with accuracy the effect of the waste on marine organisms, since in general the effect of interactions of the various chemicals will not be known. It is therefore always advisable to conduct a bioassay test using appropriate species when new substances or sites are selected for sea disposal. Several tests may be used but it is inadvisable to stipulate any single test since in every case it is necessary to tailor the test to the needs of the waste, the proposed conditions of discharge and the area of discharge. Often it will be possible to answer the requirements with a relatively simple test but for some wastes it may be necessary to conduct more extensive investigations. Such a need might be indicated by unusual or unexpected behaviour in the simple test. Extensive testing would, for example, be necessary if there were indications of bioaccumulation since then it would be necessary to establish whether this bioaccumulation was likely to result in harm to marine organisms.

The characteristics of the waste must also be studied in relation to other materials which might be disposed of in the same or nearby area. There are some preliminary indications that prediction of the effect of several wastes together is far from simple. As with individual materials combined in one waste, the effect of several wastes may be simply additive, more than additive or in some cases less than additive.

The previous work by GESAMP is relevant to the prediction of effects at least of single dumped materials. In particular the Review of Harmful Substances (see GESAMP V/10, Annex IV and to a lesser extent GESAMP IV/19/Suppl.1).

5. Specific examples of chemical interactions between wastes and sea water

Sea water has a considerable buffering capacity for acids and alkalis and the extent of pH change in sea water is limited. If 10% of the buffering capacity of sea water of salinity 35‰ are used for neutralization of an acid waste, the pH changes by less than 1.0 pH-units. This corresponds to the addition of, e.g. 10 g H₂SO₄ to 1 m³ of sea water. Nevertheless, elevation of pH can result if strongly caustic wastes such as kier liquors (from cotton industry) are dumped at sea. Although not normally serious in ecological terms this can lead to short-term precipitation of certain constituents of sea water, e.g. the hydroxide of magnesium. Conversely, the disposal of waste acid solutions can lead, on neutralization by sea water, to the precipitation of metal ions which were dissolved in the acid solution. One of the best known of these wastes is that from the older route of titanium dioxide production, which on neutralization by sea water produces a floccular precipitate of ferric hydroxide and titanium hydroxide. This example also illustrates the importance of a knowledge of the chemical nature of waste. In the original acid solution the iron is in the ferrous state, but in the sea it is oxidized immediately to the ferric state, thus exerting a chemical oxygen demand.

It should be kept in mind that freshly precipitated hydroxides can scavenge dissolved trace constituents (e.g. heavy metals) by coprecipitation. In the same way trace metals may be removed from the sea water by adsorption or ion exchange with suspended natural clay minerals.

Wastes with a high chemical oxygen demand (COD) and/or biochemical oxygen demand (BOD) can lead to deoxygenation of the water (examples are waste solvents such as alcohol, acetone or distillery effluents), or of the sediment. In this way sewage sludge, if it accumulates on the sea bed, can produce anoxic areas unsuitable for most forms of marine life.

Wastes containing large amounts of nutrients such as phosphate, nitrate and ammonia if not adequately dispersed will cause local enrichment of waters and eutrophication can result. In such circumstances blooms of algae may occur which on death can cause deoxygenation and odour problems. In certain areas, e.g. Oslofjord, eutrophication has been linked with the occurrence of toxic algae which can lead to paralytic shellfish poisoning.

Certain chemicals, of which the chlorophenols are probably the best known example, can cause tainting of the flesh of the fish and shellfish, rendering them unacceptable for human consumption. The concentrations required for this may be extremely low; for example, monochlorophenol taints oysters at concentrations in the water of 0.0001 ppm. It is therefore important to avoid disposal of such wastes to the sea and also of wastes containing compounds which might react to form tainting materials.

Certain chemicals (e.g. ammonia, chlorine, cyanide) are acutely toxic to marine life. In many cases they are rapidly rendered harmless by chemical or biological action. Cyanides are hydrolyzed leading to formic acid and ammonia. Chlorine is reduced to chloride which is a major constituent of sea water. The highly toxic organic phosphorus compounds are hydrolyzed in sea water with a half life ranging from a few days to several months. Colloidal elemental phosphorus is only very slowly oxidized in sea water and has been known to cause damage to marine resources. Barium which is present in some heat treatment salts is precipitated by the sulfate of the sea water as insoluble barium sulfate.

Many of the heavy metals are accumulated by marine organisms. The special risks posed to human health by mercury and cadmium are recognized by total prohibition of disposal (except as trace contaminants) under both Dumping Conventions; however, wastes containing other metals may be dumped but require special attention, for example, lead, zinc, copper and arsenic. Again the chemical state is important; in insoluble form and in some cases also in complexed form the acute toxicity of e.g. lead, zinc and copper is much reduced. In recent years, investigations have shown that, in the aquatic environment, mercury is transformed into organic mercury compounds, e.g. methyl mercury, which are by far more toxic than inorganic or metallic mercury. In anoxic areas of the sea where hydrogen sulfide occurs, many heavy metals can be eliminated from the sea water by formation of very insoluble metal sulfides. One exception is iron which as ferrous sulfide is more soluble in sea water than in the form of ferric hydroxide, the normal form under oxic conditions. In some cases, the precipitation of heavy metals as sulfides can be prevented by complexing agents present in sea water which form soluble metal complexes. For mercury sulfide, it was found that under anoxic conditions it is more soluble in sea water than it would be expected from the solubility product.

The incineration at sea of chlorinated hydrocarbons results in the formation of large amounts of gaseous hydrochloric acid. This reacts with atmospheric moisture to form droplets which precipitate usually within a short distance of the incineration vessel. The acid is readily neutralized by the sea water.

6. Processes related to bottom sediments

Although the sediments of the seabed of the major ocean basins have a large adsorption capacity for practically all kinds of waste material (being either metals or organic substances), this does not imply that the seabed will automatically be the sink for dumped wastes. Material in solution or suspension, on or above the seabed, has to migrate to and into the seabed in order to be removed and since this is a time dependent process, it has to compete with dispersion in the water column itself. For example, material dissolved in a 20 m layer above the sediment needs several days to be adsorbed to the sea water/seabed interface even when the turbulence is sufficient to supply the substances to the interface, while in a completely stagnant water layer the period is very much longer.

Where the wastes have a high affinity of the sediments, penetration into the seabed is very slow although the total uptake by the seabed might be high. This uptake is primarily in the thin surface layers of the sediment. Therefore, it is exposed to erosion and contact with the result that the material might be recycled to benthic flora and fauna.

In most natural cases, unless sediments are stirred up, little material is bound by the sediments of the seabed and in a dumping site most of the dissolved substances will become so dispersed within the water system that adsorption on bottom sediments will be extremely limited before reaching the bottom. This phenomenon is confirmed in dumping areas of, for example, $\text{FeSO}_4 - \text{H}_2\text{SO}_4$ wastes from titanium dioxide production where no increase of Fe in the bottom sediments can be detected. The same will apply, although to a lesser extent, for material leaking from drums lying on the seabed since the material will be in greater contact with the supernatant sea water than the seabed.

Wastes submerged inside the seabed would almost completely be removed and return to the supernatant sea water would be unlikely. The diffusion through the covering sediment layer is very slow. Most heavy metals, for example, will move only a few centimetres in some years. Dumping in an area where turbidity currents flow out might cause such a burying of wastes. Solid waste dumped on undisturbed sediments (out of areas with heavy turnover) will not in the technical sense be buried.

The question remains as to whether liquid wastes should preferably be disposed of in areas with high or low turbidity. In the presence of high turbidity, there is a scavenging effect by solid materials of substances from solution. In this way, toxic material is transferred from the water phase to the suspended matter, and subsequently, it is also accumulated on the bottom. However, with respect to repeated dumping, especially of materials

which are not rapidly degradable, the area will accumulate more and more material in the sediments which are frequently brought into suspension. This might return toxic material to the marine biota either through the water or by intake directly of suspended particles.

A phenomenon in favour of the immobilization is that many heavy metals, for example, are gradually more strongly bound by sedimentary particles (absorption inside crystal lattices) but exceptions exist, and cadmium is an example. This metal remains mobile and can be recycled.

The conclusion would be, that unless the suspended material disperses continuously over large areas dumping in turbid areas does not have many advantages over dumping in an area with low turbidity.

7. Processes as related to organic wastes

Since dissolved "decomposable" natural organic substances have residence times of several months to several years, in the open sea, it is to be expected that dissolved organic wastes will have a long residence time, especially when they are of a less digestible form for marine bacteria than the natural substances. Therefore, the fate of dissolved organic wastes can be inferred from the behaviour of the natural compounds.

Two different features can be distinguished: close to land the supply of natural dissolved organic matter is due to terrestrial material input and often productivity is greater than in the open sea. Thus the highest concentrations are found close to the coast. But, due to the turbidity, in late winter periods the lowest concentrations are observed, a phenomenon which can be explained by the abundance of microorganisms in coastal areas. Owing to the higher turbidities of the water, bacterial developments are favoured and thus organic decomposition is enhanced. Thus, dumping of organic wastes in coastal areas with high turbidity will also favour a rapid decomposition, at least when the compounds are degradable by bacteria. It follows, therefore, that in offshore water with little turbidity there will probably be little breakdown of the organic materials. Here bacterial action is low since the solid substrata necessary for bacterial activity is lacking.

This does not necessarily mean that dumping of dissolved organic material should be done preferably in coastal areas. It is clear that facets other than degradation are important. In particular some toxic compounds are resistant to degradation. With such materials, disposal in remote areas has preference over dilution and degradation in near-coastal areas. Nevertheless, it has to be taken into consideration that the persistence of organic substances, including the toxic substances will be great in sea water with low turbidity. The safest way for the estimation of the residual concentrations is to approximate them by physical dispersion calculations without taking degradation into consideration.

8. Dredge spoils and sewage sludge

8.1 Background information

In the United States of America, and probably on a worldwide basis also, the largest bulk of materials dumped into the sea is dredge spoils (80%) and sewage sludge (9%). The first consists of a heterogeneous aggregation of materials in a broad spectrum of sizes, ranging from sub-micron clay particles to pieces many centimetres in diameter, with possibly a large proportion of organic material. The second is a more uniform mixture of finer organic and inorganic material, with a relatively large proportion of water.

There is a considerable fund of experience in sea disposal of sludge from large coastal cities, e.g. from London in the United Kingdom where sludge does not appear to have accumulated and from New York in the United States of America, where it does.

8.2 Ecological effects

Two principal ecological problems arise from the disposal of dredge spoils and sewage sludge: (1) turbidity-reducing light penetration, and hence diminishing photosynthesis and primary productivity; and (2) alteration or total destruction of bottom habitats. The effect of turbidity from such dumping on primary production is not known. There is a need for investigation of these effects under different hydrographic conditions and water characteristics. The scales of these effects, both spatial and temporal, must be ascertained to provide some measure of ecological impact on the lower trophic levels relative to other effects. A number of basic questions need to be answered: (a) Is it preferable to dispose of such solid wastes in areas naturally turbid or in clear, relatively unproductive areas? (b) Should disposal be managed in such a way that the peak productivity periods of the year are avoided for dumping? (c) Can the dumping technique be designed in such a way, e.g. concentrated local turbidity or widespread light turbidity, to minimize productivity inhibition?

There is growing evidence that improperly controlled disposal of sewage sludge and dredge spoils can have adverse effects on benthic organisms and their habitats. Sludge deposition may exceed the assimilative capacity of the sediments, smothering bottom organisms already there and rendering their habitat unfavourable for recolonization. Decomposition of the sludge can deoxygenate both the sediments and the overlying water and lead to the formation of highly toxic hydrogen sulfide. Dredge spoils often contain decomposing organic material, which may still have a high biochemical oxygen demand (BOD) and/or contain high concentrations of hydrogen sulfide. They, too, can adversely modify benthic habitats.

8.3 Health problems

Other unfavourable characteristics of sewage sludge and dredge spoils from a pollutional point of view are: (1) heavy metals; (2) chlorinated hydrocarbon pesticides and PCBs; and (3) bacteria and viruses.

The degree of hazard from sludge-borne bacteria and viruses to shellfish resources is unknown. Viruses are particularly resistant to normal sterilization procedures, such as chlorination, and may be able to endure for some time the bacteriacidal effects of sea water. It is clear that microbiological research should be conducted on the problem for a better understanding of the behaviour of viruses associated with sewage sludge.

8.4 Environmental considerations in sea disposal

Experience to date in sea disposal of sewage sludge and dredge spoils indicates that the most favourable hydrographical conditions, which minimize ecological damage by sewage sludge and dredge spoils, are those providing the greatest degree of dispersion. Associated with these types of conditions are topographical features that prevent accumulation of these materials. Four characteristic areas might be considered for disposal of sewage sludge and dredge spoils:

- (1) confined anoxic basin;
- (2) turbulent, tide-swept channels and other well-mixed coastal waters;
- (3) quiescent coastal zones;
- (4) abyssal plains.

The confined anoxic basin is typified by the deep fjord system with a threshold sill which prevents regular flushing of the deep waters. Anoxic basins may also exist in open coastal waters, e.g. Santa Barbara Basin along the coast of California. The one feature favouring these basins for disposal of dredge spoils and sewage sludge is that the effects would be confined to a zone already abnormal in oxygen distribution from natural causes. It would be unwise to aggravate this character by introduction of persistent or bioaccumulative materials.

It should be recognized that these basins are flushed with irregular periodicity, ranging from one to 15 years, depending on the frequency of storm surges and other phenomena which introduce higher-density water to replace that already present in the system. Thus, the biological damage done during these catastrophic turnovers could be accentuated by the pollutional effects caused by sewage sludge and dredge spoils.

While it is not advocated that anoxic basins be chosen in preference to other coastal waters for dumping, they are to be preferred to shallow inlet zones only a few kilometres seaward of the dredged area, from which materials can be transported back to their source by the compensating subsurface counter current.

There are compelling arguments for disposal of sewage sludge and dredge spoils into turbulent, tide-swept channels and other such well-mixed coastal waters and several examples could be cited. One precautionary note which should be made is that areas of the continental edge and slope, which are now known to contribute to high production, should not be chosen for disposal even if dispersion is adequate in surface waters.

Quiescent coastal zones are obviously places to avoid for dumping of sewage sludge and dredge spoils. Neither turbulent mixing nor advective transport are satisfactory for rapid dispersion. While the New York Bight might not exactly typify a quiescent zone, in that it does display a certain degree of tidal action, the effects of sewage sludge in this coastal region are in sharp contrast with those in the outer Thames Estuary, suggesting that dispersive processes are inadequate.

Abyssal plains might be considered ideal for disposal of sewage sludge and dredge spoils, in that the dispersive processes in the upper mixed layer, great depths and slow rate of sinking would ensure widespread dispersion. However, economics largely predicate against this type of disposal which would usually require many days of steaming to reach such deep-sea oceanic areas.

9. Uses of the marine environment

9.1 Introduction

The uses of the oceans are manifold, such as transportation, fishing, recreation and mining, aquaculture, desalination, and waste disposal.

The problem is dealt with from a general regional oceanographic point of view, as the basic questions of physics, chemistry and biology are covered in the Working Group by scientists in these fields. A more complete discussion on the uses of the seas will be given at the next meeting.

9.2 Regional oceanography

In relation to waste disposal at sea it should be noted that the high productivity areas in the oceans are related to e.g. such physical conditions as cyclonic gyres, upwelling, lateral boundary currents, oceanic fronts. In addition high productivity areas are often found associated with submarine ridges, shelf areas, continental slopes, as well as specific physical characteristics in the water. All these conditions are more or less conducive to high nutrient and oxygen supplies and consequently to primary production and zooplankton concentrations, on which fish stocks and other marine life depend. The marine environment and its living resources, however, are sensitive to natural (e.g. climatic) environmental changes, and they have to be carefully protected against artificial changes.

Locations defined by distance and depth are by no means a satisfactory solution as regards ocean dumping. It is quite clear that ocean dumping sites have to be chosen with great care: e.g. dumping of certain materials should not be done in areas of high productivity.

Different criteria might be applicable for e.g. degradable and nondegradable substances, and also the degree of toxicity of the substances and turbidity might affect the selection of dumping sites.

Special attention must be paid to animal migrations. Migrating species, particularly anadromous fish, use their acute sense of smell in detecting odours (chemoreception) in coastal waters as a guide in homing on their native stream. Any interference with the natural odour characteristics of these waters by introduction of foreign materials can disrupt the fish's stream detection process. Dumped materials, particularly chemicals with strong odours, could conceivably mask natural odour characteristics of tributary streams and confuse migrating fish, possibly to the extent where they get lost and go unspawned.

Other uses, known as well as potential, for example aquaculture, mining and ocean cables have to be taken into account. Water quality in coastal aquaculture could be affected by dumping at some distance through transport by currents. All these aspects to the living resources and other uses of the sea will be considered further by the Group.

9.3 Relationships between marine conditions and living resources

The relationship between the global distribution of the maximum sea surface temperature anomalies and the highest values of primary production indicates an example of the connexion between the physical condition and the living resources in the world ocean. Among these areas are the ocean polar fronts and the boundary currents, off the western coasts of the continents and in the equatorial zone.

In the case of the North Atlantic, possible deep sea dumping areas, as defined in the Oslo Convention, are identical with some of the high productivity areas. Despite the fact that these ocean areas are some of the most thoroughly investigated areas of the world oceans, many details are still unknown. The connexion between the oceanographic conditions and the distribution of living organisms is, however, fairly well understood.

10. Outline of further work

The following aspects have been partially examined so far: dispersion, characteristics and transportation in the water, biological characteristics, chemical characteristics, topographical characteristics and other uses of the sea. In the light of the discussions which were summarized above, the Group agreed that attention will need to be given to a number of subjects in the future (see Annex III).

The Group discussed further work to be done by the members during the intersessional period and agreed that the success of the future meeting would depend upon the preparation of background documentation. Some responsibilities were tentatively assigned but it was agreed that before work is set in train the Group should await observations and advice from GESAMP at its sixth session. The Chairman will then write as appropriate to the various members requesting them to undertake certain tasks.

It was agreed that the Group should hold its next meeting in late November or early December. The exact dates to be fixed as soon as possible after the venue is confirmed.

SUBJECTS REQUIRING ATTENTION IN THE FUTURE

Dispersion:

Checking available information to fill the gaps identified and assignment of priority

Design of field experiment to obtain information on depth of penetration, vertical concentration distribution, turbidity generation, settling velocity, and subsequent dispersion in relation to the physical conditions

Turbidity and its influence on primary production

Bottom transport mechanisms and differential settling; initial dilution related to the method of disposal

Large-scale dispersion/transportation patterns

Biology and chemistry:

Bio-accumulation including tainting, bio-chemical interactions (review of literature)

Review of harmful substances and their degree of harmfulness, some definition of what is understood by trace amounts

Toxicity testing

Animal migration, both vertical and horizontal, and ability of ecological systems to withstand stress

Adhesive and cohesive properties of wastes under different conditions

Climatic variations, latitudinal changes and their relevance for waste disposal

Interaction between wastes

Uses:

Large-scale oceanographic features and their relevance in relation to dumping

Detailed consideration of the local uses in relation to dumping

Topography, its relation to current fisheries

In addition, consideration should be given to:

Dumping of containers and bulky materials

Relevance of air-sea interaction processes to the present problem

Review of experience on the effects of dumping and rationale adopted for dumping in various countries

Observations before the use of a site; monitoring or control during and after use.

Annex VI

LIST OF WORKING GROUPS

1. Evaluation of the Hazards of Harmful Substances in the Marine Environment

- Terms of reference: (a) To examine and evaluate available data and to provide such other advice as may be requested, particularly by IMCO, for evaluating the environmental hazards of harmful substances carried by ships, in accordance with the rationale approved by GESAMP for this purpose (GESAMP IV/19/Suppl.1); and
- (b) to examine annually, the Review of Harmful Substances in accordance with Recommendation 88 of the United Nations Conference on the Human Environment (Stockholm, 5-16 June 1972) in order to amend the Review if and when appropriate.

Chairman: Dr. P.G. Jeffery

Members: Dr. J.E. Portmann, Dr. J.B. Sprague, Dr. C.H. Thompson

Meetings: Annual meeting in connexion with GESAMP sessions

2. Principles for Developing Coastal Water Quality Criteria

- Terms of reference: To consider the desirability and feasibility of developing coastal water quality criteria for:
- (a) living marine resources
- (b) fishing activities
- (c) human health
- (d) amenity.

Chairman: Dr. M. Waldichuk

Members: Dr. A.L. Downing, Dr. E.E. Geldreich, Dr. C.S. Hegre,
Dr. S. Kečkeš, Dr. J.B. Sprague

Meetings: First meeting in autumn 1974, Rome

3. Scientific Bases for the Determination of Concentrations and Effects of Marine Pollutants

Terms of reference for the panel on levels:

- (a) chemical and microbiological pollutants to be monitored
- (b) associated chemical, biological and physical parameters of the system to be measured, including those necessary to permit an assessment of the chemical modifications of the marine environment
- (c) sampling sites, including waters, airs, sediments and organisms
- (d) sampling and storage procedures
- (e) sampling frequency
- (f) the formulation of scientific methods, models and mass balances
- (g) interlaboratory comparisons and preparation of standards.

Terms of reference for the panel on effects:

- (a) Effects on physical and chemical processes and properties
- (b) effects on marine communities feasible for monitoring
- (c) effects on biological resources
- (d) suitable organisms which can be used as pollution indicators or indicators of ecosystem changes
- (e) sites, sampling and storage procedures, frequency of monitoring the effects
- (f) formulation of scientific methods (models).

Chairman: Professor E.D. Goldberg

Panel on levels: Chairman: Professor E.D. Goldberg
Members: Dr. L. Otto
Professor A.I. Simonov

Panel on effects: Chairman: Dr. S. Kečkeš
Members: Dr. E.E. Geldreich
Dr. C.S. Hegre
Dr. T. Yoshida

Meetings: First meeting in 1974

4. Scientific Basis for Disposal of Waste into the Sea

- Terms of reference:
- (a) To carry out a critical review of our present knowledge of those aspects of dispersion and physical, chemical and biological processes relevant to the selection of sites for discontinuous injection of wastes into the marine environment in both deep and shallow waters.
 - (b) To identify gaps in our present knowledge, focus attention on urgent research needs, and suggest research priorities.

Chairman: Dr. G. Kullenberg

Members: Dr. J.E. Portmann, Professor A.I. Simonov, Dr. M. Waldichuk,
Dr. G.F. Weichart

Meetings: Second meeting in November 1974, Monaco

5. Impact of Oil on the Marine Environment

Terms of reference: To consider the biological effects of oil on living resources in the light of recent scientific findings.

Chairman: Dr. C.H. Thompson

Members: Dr. P.G. Jeffery, Dr. R. Johannes, Dr. J.E. Portmann

Meetings: First meeting in October 1974, Rome.

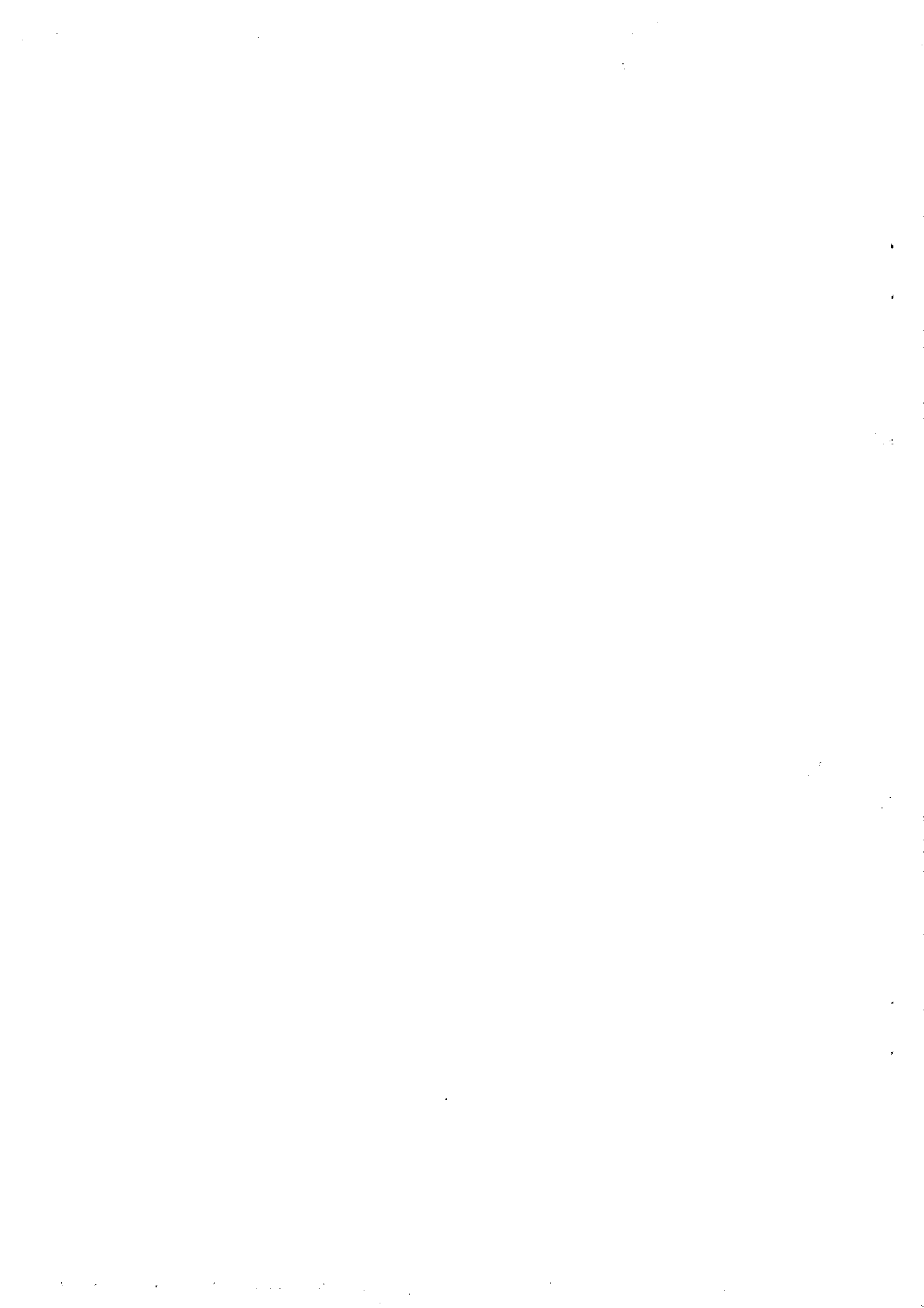
6. Scientific Aspects of Pollution Arising from the Exploration and Exploitation of the Sea Bed

- Terms of reference: (a) To identify the sources of information relevant to the scientific aspects of pollution, arising from present and future activities related to the exploration and exploitation of the sea bed. The suggested priorities for initial action are:
- (1) Petroleum (including natural gas)
 - (2) Manganese nodules
 - (3) Dredging for both mineral resources and construction projects, but excluding dredge spoil disposal
 - (4) Offshore construction (including platforms, artificial islands and reefs).
- (b) To collate and evaluate, where possible, all such existing information within time to present an assessment to GESAMP VII of current and potential marine pollution hazards from these activities and conflicts with other uses of the sea which may arise with the intention of obtaining approval for its submission to the Third United Nations Conference on the Law of the Sea at its second session projected for June 1975
- (c) To assess the feasibility of extending this information to meet future needs, such as measures to prevent and control marine pollution from these activities and to make proposals on the future action of GESAMP concerning this area.

Chairman: Dr. H.A. Cole

Members: Dr. A.L. Downing, Dr. G. Kullenberg, Professor F. Valdez-Zamudio

Meetings: First meeting in 1974.



GESAMP VI/10/Supp.1

26 September 1974

ORIGINAL: ENGLISH

IMCO/FAO/UNESCO/WMO/WHO/IAEA/UN
JOINT GROUP OF EXPERTS ON THE SCIENTIFIC
ASPECTS OF MARINE POLLUTION
(GESAMP)

SUPPLEMENT TO THE REPORT OF THE SIXTH SESSION

REVIEW OF HARMFUL SUBSTANCES¹

Provisional Version

¹ The views expressed in this review are those of experts acting in their individual capacities and may not necessarily correspond with the views of the Sponsoring Agencies.

N O T E S

1. GESAMP is an advisory body consisting of specialized experts nominated by the Sponsoring Agencies (IMCO, FAO, UNESCO, WMO, WHO, IAEA, UN). Its principal task is to provide scientific advice on marine pollution problems to the Sponsoring Agencies and to the Intergovernmental Oceanographic Commission (IOC).
2. This Report is available in English, French, Russian and Spanish from any of the Sponsoring Agencies.
3. The Report contains views expressed by experts acting in their individual capacities which may not necessarily correspond with the views of the Sponsoring Agencies.
4. Permission may be granted by any one of the Sponsoring Agencies for the Report to be wholly or partly reproduced in publications, provided that the source of the extract and the condition mentioned in 3 above are indicated.

Report prepared by an ad hoc working group under the Chairmanship of Dr H. A. Cole and formed by the following persons: Dr J. E. Portmann, Fisheries Laboratory, Ministry of Agriculture, England; Dr P. G. Jeffery, Department of Trade and Industry, England; Dr M. Sharratt, Senior Medical Officer (Toxicology), Department of Health and Social Security, England; Mr B. Okamura (Secretary), Senior Technical Officer, IMCO, London, England; and Dr S. Jensen.

This report has been considered by GESAMP VI and pertinent remarks on it are included in the report of the sixth session.

With respect to the human health aspects of some of the harmful substances reviewed, the WHO representative stated that certain statements made in the review on the effects of some substances on human health do not correspond to information available to WHO and would in his view be misleading. On the other hand, the group considered that both the text and tables satisfactorily reflect the assessment of data available to the experts and their understanding of the current marine pollution situation.

In view of the above divergence of views, the group agreed to reconsider the relevant section of the Review at its next session (London, 24-30 April 1975) in order to resolve the questions raised by the WHO representative.

INTRODUCTION

In accordance with a recommendation made at the fifth session of GESAMP, a working group was convened by the United Nations at IMCO headquarters, London on 3 and 4 January 1974, and again on 19 and 20 February 1974. Those present were: Dr H. A. Cole (Chairman), Dr J. E. Portmann, Dr P. G. Jeffery, Dr M. Sharratt, Mr B. Okamura (Secretary). Dr S. Jensen was unfortunately unable to attend. The instructions from the fifth session of GESAMP were examined and it was concluded that it would be advisable to have further consultations with selected industrial chemists before attempting to extend the section dealing with organic chemicals. The Chairman reported that the United Nations had agreed to provide the limited funds needed for such a meeting which had taken place on 18 February 1974. It was decided to proceed on the basis of the list of substances recommended for priority attention by the working group at its meeting prior to the fifth session of GESAMP.

At the first meeting, a standard format for the presentation of factual information regarding metals and their compounds was drawn up. This covered successively: the mode of occurrence and production of the metal; its principal uses; the ways in which it might reach the sea; its effects on marine life; hazards to man arising from consumption of seafood or exposure to the marine environment. The summaries which follow are based on the information available to the working group and the existing knowledge of levels in the marine environment in both natural and polluted situations. The information on mercury, cadmium, lead, copper and zinc prepared at earlier sessions was revised and extended and the assessments checked or amended as required. New material was prepared in provisional form relating to vanadium, nickel, chromium, selenium, arsenic, antimony, beryllium, cobalt, manganese and silver.

At the second meeting additional material relating to certain metals and metalloids was prepared and collated. A revised section on radioactivity was considered and approved. New material relating to some of the organic substances included in Annex II was available and it was agreed that this would be further studied with a view to completing the account of these organic substances during the sixth session of GESAMP.

The working group considered that, with the additional material on certain organic substances to be prepared at the sixth session, the review would include most of the polluting substances of major importance in the marine environment. Although it would be possible to extend the review by, for example, treating other metals or organic substances, the working group did not consider this to be an urgent task and recommended that consideration should now be given to the publication and wider dissemination of the material already prepared.

The working group wished to acknowledge the valuable assistance of IMCO in providing secretarial assistance and facilities for the meetings.

The sections which follow are intended to add to, or in the case of mercury, lead, copper, zinc, chromium, cadmium, arsenic and radioactivity, to replace those published as part of Annex IV to GESAMP V/10 including the ratings in Tables 1 and 2.

(It should be noted that where certain of the metals are concerned WHO is publishing/has published much more detailed reviews on human health aspects which should be consulted wherever detailed assessments of such risks are concerned.)

ANTIMONY

The overall 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 sulfides 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 1970 at about 65 000 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 sulfides 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 sulfide 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 1300 tons annually), or by fossil fuel burning. Normal levels in sea-water are reported to be of the order of 0.1-0.5 $\mu\text{g}/\text{l}$. Freshwater streams have been reported to contain about 2 $\mu\text{g}/\text{l}$.

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. Its actions are similar to those of arsenic but unlike arsenic it shows no tendency to be stored in tissues. Contact with polluted sea water and consumption of seafoods from polluted areas are unlikely to constitute a hazard.

ARSENIC

Arsenic is widely distributed in crustal rocks but at only a very small concentration - an overall 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 1000 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 µg/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 µg/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).

Inorganic arsenic compounds are highly toxic to man on acute or long-term administration, producing gastrointestinal, skin, liver and nerve tissue injuries, possibly by affecting enzymes containing sulphhydryl 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.

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% 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 6000 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 5600 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 µg/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 LC₅₀ 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.

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 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); in bearing metals; in fusible and other alloys; plating for corrosion inhibition and electrical contacts; in batteries and in nuclear reactors.

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 in association with zinc and lead. 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, 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, gastrointestinal tract and kidneys but such injury is unlikely to occur on contact with polluted sea-water or sea foods. Cadmium is virtually absent from the body at birth. Although only 5-10% 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.

CHROMIUM

Crustal rocks vary greatly in chromium content, from less than 1 ppm in some granites to almost 1% 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 has risen fairly steadily from 1.6 million tons in 1953 to 2.8 million tons in 1970.

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 1500 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 - 2000 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 µg/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 7-2400 mg/kg dry weight. In 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% 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 could occur in fish would be harmless to man.

COBALT

Cobalt is a dispersed element, most rocks containing from less than one 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 was 21.5 thousand tons in 1971, 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 of 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 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 its toxicity 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, being a component of vitamin B₁₂; the amount needed is contained in the diet which provides about 1 mg each week. It seems unlikely that polluted water or contaminated fish could increase the amount ingested to a level which might be a hazard to health is extremely small.

COPPER

Although not abundant, copper is widely distributed in crustal rocks with an overall 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 six million tons per annum, largely from sulfide 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 2000 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 worthwhile to recover the metal from such leachings.

World-wide carriage in ships is mainly as copper metal; smaller amounts are carried as concentrates (ca 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 1000 and 1500 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% 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 ca 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, roughly twice the probable daily requirement. 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.

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 slightly exceeds three million metric tons; production appears to have tended to stabilize during recent years following a steady rise during the fifties and sixties. The principal 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 3600 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% 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 is declining 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 sulfide 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 one 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% 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.

MANGANESE

Manganese is usually classed as a "minor" rather than a "trace" element in crustal rocks, ranging from 0.05-0.2%. Local concentrations occur in some sedimentary rocks and also in the form of accretions known as "manganese nodules" on the 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 four million tons in 1953 to seven million tons in 1966 and only slightly since.

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% 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 7000 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 6000 tons per year.

River discharges have been estimated to contribute globally both in solution and in particulate matter in total 2 200 000 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 high 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% 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 $0.005 \text{ mg}/\text{l}$. Certain species appear to have a striking ability to accumulate manganese e.g. scallops - concentration factor at 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 - $99 \text{ mg}/\text{kg}$ dry weight for Fucus sp.; 29 (two areas) for Porphyra; and 31 - 42 for Patella (soft parts). Values obtained for surf clams, Spisula solidissima, from off Delaware Bay ranged from 0.68 - $2.79 \text{ mg}/\text{kg}$ drained weight of shellfish in May/June 1967. Average values for the Northern Quahaug (Mercenaria mercenaria) are reported as 3 - $7 \text{ mg}/\text{kg}$.

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 who requires 3-9 mg each day. 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 present a health hazard.

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 9000 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 4-5000 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 3200 tons per annum. Input to the ocean by river discharges derived from the weathering of rocks has been estimated to be about 3500 tons.

Mercury is transported by sea, primarily as the metal in flasks or as formulated packaged products. Loss of the metal may or may not lead to leaching into the sea, since it has been reported that metallic mercury can accumulate in hollows in the sea bed and may become covered by sediment.

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 adsorbed 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% of Plumaria juveniles were killed by 0.044 mg/l methyl mercury (cf 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, 1000, 400 and 250-1000 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.

NICKEL

Crustal rocks vary greatly in nickel content, from a few ppm to about 0.5% 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% 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 has continued to rise, and amounted to 0.66 million tons in 1970. 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 3700 metric tons per annum of nickel, some of which will later reach the sea. For the North Sea, the annual contribution from the atmosphere from all sources has been estimated at 5000 metric tons per annum.

The "normal" content of nickel in open ocean sea-water is stated to be 2 µg/l. Waters of the United States eastern coast are said to show a five- to ten-fold 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 µg/l. North Sea values were slightly lower. Filtered shore-line samples from the North Sea yielded 0.1-6.0 µg/l. The English Channel and the western Irish Sea were very similar but the eastern Irish Sea, in an area receiving substantial industrial drainage and river discharges from mineralized areas, was approximately twice as high. Shore-line sea-water, from the same area, gave figures up to 9.8 µg/l of nickel. The suspended material from these shore-line areas in the Irish Sea yielded ca 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 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. The behaviour of nickel deposited in sludge seems to be very different from that of lead, copper and zinc.

Nickel is concentrated from sea-water by many marine organisms, e.g. oysters and clams, by a factor of ca 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 LC₅₀ 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 probable that nickel (in some form) is carcinogenic to those working in nickel refineries, there is no evidence that ordinary exposure to the low concentrations of nickel which occur in the marine environment constitutes a health hazard. The consumption of seafood is unlikely to be harmful.

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 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 1200 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 7200 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 of 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, of 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 from polluted areas would increase dietary selenium to a sufficient extent or for a sufficiently prolonged period to produce adverse effects on health.

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 sulfides, often complex sulfides 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 9000 tons in 1971, 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 $\mu\text{g}/\text{l}$. Stream water is said to contain 0.3 $\mu\text{g}/\text{l}$. 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 $\mu\text{g}/\text{l}$ respectively. The silver in the particulate fraction in these two sets of samples was 47 and 69% of the total. There is evidence that approximately half of the silver reaching the ocean from radioactive 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.

ZINC

Zinc occurs naturally as the sulfide 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 sulfide mineral and world production is rather more than five 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 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 7000 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 sulfate at a concentration of 0.125 mg/l is reported to reduce growth of a marine ciliate protozoan by 8.3%; 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 LC₅₀ (96 h) values 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 LC₅₀ 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 2000-100 000 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 1964-65. 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 tissues or produce chronic toxic effects.

VANADIUM

Vanadium is widely distributed in small amounts in both igneous and sedimentary rocks, with an overall 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 and has a biological function.

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 fresh water is low and decreases with increasing hardening of water. There seem to be no data for marine animals but toxicity is probably even lower.

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 $\mu\text{g/l}$ while coastal waters may contain 3-4 $\mu\text{g/l}$.

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 highly polluted with vanadium compounds. The normal diet provides man with about 2 mg of vanadium each day, an intake which greatly exceeds any exposure from consuming seafoods.

RADIOACTIVITY

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. Radioactive substances are naturally present in the marine environment, in solution, in crustal rocks and in sediments. There are two main sources of artificial radioactivity in the marine environment, fall-out from nuclear weapon testing and wastes from nuclear power production, including fuel processing.

Inputs of artificial radioactivity to the marine environment as a result of nuclear weapon testing are uncontrolled. At the rate of loss of this material due to radioactive decay, the global inventory 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 radioactive 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 overall 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. 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 radioactivity 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. In addition, several hundred nuclear power plants are expected to be in operation within the next 20 years. While the likelihood of a serious release occurring at any one plant in any one year is small, the likelihood of one or more serious incidents occurring somewhere in the world at some time in the future is much greater. Human error, equipment failure, sabotage, war and earthquakes are all potential causes of serious incidents. The indefinite prevention of this requires an exceptional level of social, political and geological stability.

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 (ca 22% in fresh water). 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.

ALLYL ALCOHOL

$\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{OH}$, 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.

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.

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.

ETHYLENE DIBROMIDE

$\text{CH}_2\text{Br}.\text{CH}_2\text{Br}$, 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 (ca 0.4%). It has an appreciable vapour pressure at normal atmospheric temperatures, but is not appreciably volatile (BP 132°C). It does not constitute a fire hazard; it was formerly used as a fire extinguisher, but this use has 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.

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 health.

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

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 drum-size containers.

They are heavy liquids (SG 1.99 and 1.66 respectively) virtually insoluble in water (0.03% for tetraethyl lead). They are not appreciably volatile (BP 110°C and ca 220°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 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, 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 re-use of these drums for other purposes would be highly hazardous to human health.

TABLE 1. MAJOR CATEGORIES OF MARINE POLLUTION

Category	Harm to living resources	Hazards to human health	Hindrance to maritime activities	Reduction of amenities
Mercury	++	++	-	-
Lead	(+)	(+)	-	-
Copper	+	-	-	-
Zinc	+	-	-	-
Cadmium	+	+	-	-
Silver	++	-	-	-
Antimony	(+)	-	-	-
Arsenic	(+)	?	-	-
Cobalt	-	-	-	-
Vanadium	-	-	-	-
Manganese	(+)	-	-	-
Nickel	-	-	-	-
Chromium	(+)	-	-	-
Selenium	?	-	-	-
Beryllium	(+)	-	-	-
Radioactive materials	-	+	-	-
Acrolein	++	+	-	+
Allyl alcohol	+	+	-	(+)
Allyl chloride	+	+	-	(+)
Ethylene dibromide	(+)	(+)	-	(+)
Tetramethyl lead	++	+	-	++
Tetraethyl lead	++	+	-	++

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

TABLE 2. RELATIVE IMPORTANCE OF THE DIFFERENT ROUTES BY WHICH POLLUTANTS ENTER THE SEA

Category of pollutant	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 dumping 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
Mercury	3	2	0	0	0	P	0	3
Lead	2	1	0	?	0	0	0	3
Copper	3	2	1	1	0	0	0	0
Zinc	3	2	0	1	0	0	0	1
Cadmium	3	0	0	0	0	0	0	1
Silver	2	0	0	0	0	0	0	0
Antimony	2	0	0	0	0	0	0	0
Arsenic	3	1	0	1	0	P	P	2
Cobalt	2	0	0	0	0	0	0	0
Vanadium	2	0	0	0	0	0	0	1
Manganese	3	1	0	?	0	0	0	1
Nickel	3	0	0	0	0	0	0	1
Chromium	3	0	0	1	0	0	0	0
Selenium	2	0	0	0	0	0	0	1
Beryllium	1	0	0	0	0	0	0	0
Radioactive materials	3	0	0	1	0	P	0	*
Acrolein	1	0	0	0	0	0	0	0
Allyl alcohol	1	0	0	0	0	0	0	0

TABLE 2. RELATIVE IMPORTANCE OF THE DIFFERENT ROUTES BY WHICH POLLUTANTS ENTER THE SEA (Continued)

Category of pollutant	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 dumping 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
Allyl chloride	1	0	0	0	0	0	0	0
Ethylene dibromide	2	0	1	0	0	0	0	1
Tetramethyl lead	2	0	0	0	0	P	0	?
Tetraethyl lead	2	0	0	0	0	P	0	?

Key to symbols: 3 important
2 significant
1 slight
? uncertain
0 negligible
P potentially important
* dependent on extent of weapon testing