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REPORT OF THE ICES ADVISORY COMMITTEE ON MARINE POLLUTION, 1983

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REPORT OF THE ADVISORY COMMITTEE ON MARINE POLLUTION, 1983

List of Members

Dr A D McIntyre

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Dr K Vagn Hansen

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Chairman, Marine Environmental Quality Committee

Chairman, Hydrography Committee

Chairman, Biological Oceanography Committee

Coopted Members

M Cl. Alzieu Dr (Ms) M C de Barros^{*)} Dr J M Bewers Dr L Brügmann Dr R H Cook Dr V Dethlefsen Prof. I Dundas Prof. G Kullenberg Dr J Lassig Dr M Parker Dr J E Portmann

Dr (Ms) Janet F Pawlak, ICES Environment Officer, Secretary to the Advisory Committee on Marine Pollution

*)Prevented from attending the meeting 30 May - 3 June 1983.

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INTRODUCTION

 The Advisory Committee on Marine Pollution (ACMP) was established by the International Council for the Exploration of the Sea with the task of formulating, on behalf of the Council, scientific advice on marine pollution and its effects on living resources to Member Governments and to regulatory Commissions. It is a firm procedure within the Council that reports of other subsidiary bodies concerned with pollution matters must pass the Advisory Committee on Marine Pollution.

2. The Advisory Committee on Marine Pollution consists of a number of scientists acting - when they meet as a committee - in their personal capacity as scientists, responsible only to the Council. The membership of the Committee is such that it covers a wide range of expertise related to studies of marine pollution. The members are not national representatives. The present membership of the Committee is found on page 1.

3. In its work, the ACMP considers, among other things, the results of work carried out in several ICES Working Groups (which also report to their respective Standing Committees during the annual Statutory Meetings). At the 1983 mid-term meeting, the ACMP considered the most recent reports of the following Working Groups:

Marine Chemistry Working Group (MCWG)

Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA)

ICES/SCOR Working Group on the Study of the Pollution of the Baltic Working Group on Marine Sediments in Relation to Pollution (WGMS) Working Group on Pollution-Related Studies in the Skagerrak and Kattegat Working Group on Baltic Seals.

4. During this meeting, the ACMP considered the 1983 programmes of work for ICES, as requested by the Oslo and Paris Commissions and by the Helsinki Commission. Information relevant to the 1983 work programme requested by the Oslo and Paris Commissions is given in paragraphs 60 to 76, while information concerning work requested by the Helsinki Commission is contained in paragraphs 78 to 81. In addition, many of the other sections of the Report are relevant to the work of these Commissions.

INTERCALIBRATION EXERCISES AND ANALYTICAL ISSUES

Trace Metals

Trace metals in seawater

5. The ICES Fifth Round Intercalibration for Trace Metals in Seawater (5/TM/SW) was conducted in Nantes, France, in September 1982. An administrative report of this experiment was forwarded to ICES just prior to the 1982 Statutory Meeting. The experiment comprised five components:

- 1) Intercomparison of filtration procedures for the collection of filtered samples of seawater for Cd, Cu, Ni, Zn, Fe, Mn, Pb and Co analysis.
- 2) The preparation of 100 replicate filtered seawater samples for distribution to and analysis by participating laboratories as part of an analytical intercalibration exercise for trace metals in coastal waters.

- 3) Intercomparison of sampling procedures for the collection of coastal water samples for mercury analysis.
- 4) The preparation of 100 replicate seawater samples for distribution to and analysis by participating laboratories as part of an analytical intercalibration exercise for mercury in coastal waters.
- 5) A training component in which sampling and analytical demonstrations were provided for visiting trainees.

6. It was noted that the results of the various components of the exercise will be described in three papers to be submitted to the 1983 Statutory Meeting. These papers will cover, respectively, component 1, component 2 and components 3 and 4. The results of the training component have already been reported in the administrative report of the intercalibration.

7. The ACMP noted that the preparation of these reports on the results of the Fifth Round Intercalibration for Trace Metals in Seawater will conclude the present series of intercalibration exercises on analysis of trace metals in seawater that was conceived in 1976. Future efforts on the topic should be devoted to (a) extending the range of analytes that can be reliably determined in filtered seawater samples, (b) considering the design and composition of quality control procedures based upon the preparation and distribution of uncompromised (blind) reference samples, and (c) giving greater attention to suspended particulate constituents of seawater.

8. During discussions on this topic, it was noted that there was an uncertainty regarding the integrity of the seawater samples for mercury analysis used in components 3 and 4 of 5/TM/SW, which has not yet been resolved. Thus, the offer for the conduct of a further intercalibration exercise as a repetition of component 4 of 5/TM/SW was welcomed, especially since the samples for this experiment would probably be obtained from a contaminated area. It appeared clear from the preliminary results of 5/TM/SW that the levels of metals in coastal waters in the Bay of Biscay are comparable with open-ocean values.

Trace metals in biological tissues

In preparation for the 1985 Baseline Study of Contaminants in Fish and Shell-9. fish, a two-phase programme for analytical quality control purposes has been designed by the Marine Chemistry Working Group (MCWG) and the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA). The first phase of this programme, entitled the Seventh Intercalibration Exercise on Trace Metals in Biological Tissues (7/TM/BT), will involve the preparation of four homogeneous tissue samples for use in an intercalibration exercise prior to this 1985 Baseline Study. Samples for this exercise will be distributed in the autumn of 1983. It is hoped to have results from this intercalibration available for the 1984 MCWG meeting in order to assess thoroughly the analytical capability of participating laboratories well in advance of field activities. The second phase of the intercalibration will comprise the preparation and distribution of uncompromised (i.e., blind) reference materials (four separate biological tissue samples). These samples will be included in routine operations by laboratories participating in the 1985 Baseline Study. The results of analyses of these samples will be used for quality control purposes during the baseline programme.

10. The ACMP generally accepted the philosophy proposed by the MCWG for long-term quality control of analytical results from laboratories through the use of uncompromised reference materials. It was realized that it would be unrealistic to expect laboratories to treat check samples in exactly the same way as the

routine analysis of unknowns. It could be anticipated that more care would be exercised with reference materials than with routinely analysed samples, but this should in no material way reduce the effectiveness of the quality control procedure proposed. The use of uncompromised reference samples should provide a means of extending quality control practice into the long-term, when the repeated conduct of intercalibrations would no longer be the most effective means of improving and maintaining data quality.

Organochlorines

11. The ACMP was informed that the results of the Fifth Intercalibration Exercise on Organochlorines in Biological Tissue (5/OC/BT) will be reported in a paper to the 1983 Statutory Meeting. Two alternative strategies have been contemplated by the Marine Chemistry Working Group (MCWG) as to whether, as recommended by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, the analysis of organochlorine residues should, or could, be included in the 1985 Baseline Study of Contaminants in Fish and Shellfish. If the results of 5/0C/BT indicate that there is sufficient intercomparability among laboratories to justify the inclusion of organochlorines in the baseline programme, homogeneous uncompromised reference materials could be prepared for use in quality control procedures. If, however, the results of 5/OC/BT show that the various analytical difficulties in the reliable measurement of organochlorines in biological tissues have remained unsolved, it would not be recommended that these analytes be included in the baseline study. It will be necessary to determine which of these situations applies once the results of 5/0C/BT have been made available.

12. The ACMP noted the general conviction on the part of MCWG that the previous approach to the determination of organochlorines in the marine environment needed to be revised, with emphasis placed upon the identification and quantification of single organochlorine compounds (e.g., individual PCB components) rather than placing reliance upon group analysis based upon comparisons with technical formulations of mixtures of such components. The MCWG foresaw considerable difficulty in the early resolution of existing analytical problems that need to be solved before being able to apply this new approach on a broad scale. However, every effort was being made to take advantage of activities in other organisations, such as the EEC Bureau of the Community on Reference Materials (BCR), in order to accelerate this process.

During the discussions on this topic, reference was made to current acti-13. vities taking place under the auspices of IOC/GEMSI (Group of Experts on Methods, Standards and Intercalibration) with regard to the measurement of organochlorines in seawater and the status of this work in view of the difficulties encountered in determining organochlorines at the higher concentrations found in biota. It was pointed out that the scientists involved in the IOC activities had, some time ago, concluded that quantification on the basis of technical formulations was unlikely to be satisfactory and had concentrated with some success on the individual component approach. Although it was premature to assess this work, because it would be discussed during the forthcoming GEMSI V meeting, it was felt that it fell into the realm of collaborative research activities between a very small number of laboratories and therefore was not strictly comparable with the work of ICES in cooperative monitoring programmes.

Hydrocarbons

14. The ACMP noted that the second intercalibration exercise on petroleum hydrocarbons in biological tissue (2/HC/BT) is being conducted under the Marine Chemistry Working Group. Four hundred samples of homogenized mussel (Mytilus edulis) tissue have been prepared. They will be freeze-dried, rechecked for homogeneity and distributed to laboratories requesting samples. This exercise will be combined with an intercalibration exercise on analysis of polycyclic aromatic hydrocarbons (PAHs) in biological tissues (designated 3/HC/BT), for which the intercalibration samples will consist of lobster extracts and aliphatic and aromatic standards. Samples for these two intercalibration exercises will be distributed during 1983.

15. Reference was made during the discussions to the conclusions of the Intercalibration Workshop on the Analysis of Hydrocarbons in Seawater, which had been held in Kiel in March 1981 under the auspices of the Baltic Marine Environment Protection (Helsinki) Commission (Report published as Baltic Sea Environment Proceedings No. 6 (1982)). The results of this Workshop confirmed that the measurement of the incidence and distribution of hydrocarbons of anthropogenic origin in sea water is possible using the solvent extraction/UV fluorescence procedure, which has previously been used during the IOC/MAPMOPP study, and further demonstrates that good intercomparability can be achieved using this method. These results could facilitate the inclusion of measurements of dissolved/dispersed petroleum hydrocarbons in sea water during the 1985 baseline study (see paragraphs 22-24, below).

ISSUES RELATED TO MONITORING

1981 Coordinated Monitoring Report

16. The ACMP reviewed the draft report of the 1981 results submitted for the Coordinated Monitoring Programme on contaminant concentrations in fish and shellfish. Data were included from Belgium, Denmark, England/Wales, the Federal Republic of Germany, Ireland and the Netherlands on the concentrations of certain trace metals and organochlorines in six species of fish and three species of shellfish. The report had been reviewed and approved by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, subject to the addition of relevant data which may be received subsequent to the Working Group meeting. No additional data had been received.

17. The ACMP noted that this is the final report in the series of reports prepared on the results of the Coordinated Monitoring Programme, finalizing eight years of work. Recalling the decision of the previous year, the ACMP agreed that this report should be published together with the 1980 Coordinated Monitoring Report and that this publication should also include an up-date of the Six-Year Review of the ICES Coordinated Monitoring Programmes, appropriately illustrated with graphs and charts. The ACMP further noted with approval that Dr J E Portmann, with the assistance of a small review group, will prepare a synthesis paper on the experience gained during the eight years of the Coordinated Monitoring Programme, assessing what has been learned from the Programme and the extent to which it has met its original aims. The ACMP looked forward to reviewing this paper at its 1984 meeting. In addition to this paper to be prepared by Dr Portmann, the ACMP considered that it would be worth taking a closer look at the full data set obtained during the eight years of monitoring to see what further interpretations can be made, but accepted that this would be most practical when the back data have been entered on the ICES computer files. 18. Having completed the Coordinated Monitoring Programme with the collection of 1981 results, the new Cooperative ICES Monitoring Studies Programme replaced it in 1982. This programme utilizes three separate procedures for the composition of samples of fish and shellfish, and the reporting of results, according to three separate aims of monitoring using fish and shellfish:

- the provision of a continuing assurance of the quality of marine foodstuffs with respect to human health (monitoring of commercial fish and shellfish species from commercial fishing areas, to be conducted every two years beginning in 1982),
- (2) the provision over a wide geographical area of an indication of the health of the marine environment in the entire ICES North Atlantic area (a baseline survey of contaminant concentrations in a small number of fish and shellfish species taken so as to cover as wide a geographical area as possible, to be carried out every five years beginning in 1985); and
- (3) the provision of an analysis of trends over time in pollutant concentrations in selected areas, especially in relation to the assessment of the efficacy of control measures (monitoring of one appropriate species of fish from a particular area according to a specific programme of sample composition and statistical analysis, to be carried out annually beginning in 1982).

It was noted that the preparation of detailed plans for the 1985 Baseline Survey of Contaminants in Fish and Shellfish under objective 2 is now well underway (see paragraphs 20 and 21, below).

The ACMP then reviewed the consideration by the WGMPNA of the need for the 19. continued involvement of ICES in contaminant monitoring programmes, in view of the fact that the Joint Monitoring Group of the Oslo and Paris Commissions had adopted for its more limited monitoring programme the protocols which the WGMPNA had developed for the ICES Cooperative Monitoring Studies Programme. The WGMPNA agreed that for the foreseeable future there is no likely replacement for the North Atlantic-wide programme of ICES. This programme covers a wider geographical area, a wider range of species and a wider range of contaminants than any other programme and is the sole provider of information for some contaminants and species. Some aspects of the programme (e.g., trend analysis) still require further research and the demands of this programme have led and are still leading to the development of new techniques for sampling, storage and analysis by MCWG. The ICES approach to evaluating the results is different from the approach used by the regulatory commissions and allows a flexibility in handling new problems which leads to further improvement in monitoring capabilities. Furthermore, the carrying out of the full sequence of work in the monitoring programme is essential to the formulation of the advice that ICES gives to the regulatory agencies. The ACMP agreed with these statements of the WGMPNA on the continued need for the ICES monitoring programme.

1985 Baseline Study of Contaminants in Fish and Shellfish

20. The ACMP considered the report from the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic and endorsed the view that the conduct of the baseline study in 1985 was both appropriate and desirable for three reasons. First, this type of study is one component of the three types of monitoring recognised by ICES, namely, objective 2 in the Cooperative ICES Monitoring Studies (see paragraph 18); second, analytical competence has advanced since the previous baseline study was carried out in 1975; and, third, it is desirable to conduct a study for the entire area of ICES interest at approximately the same time. In this context it was noted that scientists from the Baltic Sea countries were interested in taking part in the study, and that the Helsinki Commission had agreed to encourage participation by its member countries.

21. It was noted that the detailed proposals for the study include specification of a limited number of species of fish, all of which should be collected at two years of age and in prespawning condition. Mussels should also be collected before spawning and in a specified size range from as many coastal sites as practicable. A range of metals which should be analysed for by all laboratories has been agreed upon (namely, mercury, cadmium, lead, copper, zinc and arsenic) and an additional group may be included as optional extras. The ACMP noted that intercalibration and quality control measures were all in hand to allow the study on metals to proceed (see paragraph 9, above). For organochlorine compounds, the intercalibration position was less certain and, for the present, assumptions have to be made that the problems of agreement on methodology and results can be resolved. In the event that they cannot, it may be necessary to restrict analysis of organochlorine compounds to a few laboratories or to draw spatial comparisons with extreme caution. It was, however, noted that it may be possible, in the light of the intercalibration exercise on petroleum hydrocarbons and PAHs in biological tissues, to include analysis of these substances in the baseline programme. It was agreed that the WGMPNA should review the question of using seaweeds in monitoring studies but that it would not be appropriate to attempt to include seaweeds in the 1985 baseline study.

Baseline Study of Trace Metals in Coastal Waters in 1985

The ACMP noted that both the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic and the Marine Chemistry Working Group had considered the desirability of conducting a baseline study of trace metals in seawater in association with the planned 1985 Baseline Study of Contaminants in Fish and Shellfish. The WGMPNA had reaffirmed its previous (1982) recommendation that such measurements be carried out if practicable and suggested that, in addition to distributional assessments in coastal waters, attention be given to the end members for estuarine mixing. While a snap-shot picture of metal distributions in coastal waters would not provide any estimate of temporal variability, it might be useful as an indication of the overall ranges of concentrations likely to be encountered in the ICES area and might also be useful in the interpretation of the results of the concurrent baseline study for contaminants in biota. It was also pointed out that the simultaneous conduct of baseline measurements within coastal waters of the ICES area with the conduct of the planned IOC open-ocean baseline survey would enable the baseline coverage of the North Atlantic to be more comprehensive and cohesive.

23. It was noted that MCWG had subsequently considered whether it was feasible (in terms of sampling and analytical capability) to determine trace metals in seawater in the 1985 baseline study and, if so, whether their inclusion would be useful. The MCWG had concluded that it was indeed feasible to include measurements of Cd, Cu, Zn, Hg, Ni, Fe and Mn (and also possibly Al, Co, V, Mo, and Cr) in the baseline study. For these measurements to be most useful they should be made primarily in source regions in the coastal zones (i.e., near river mouths, dumping sites, and outfalls), in order to define extreme values of concentrations and to determine concentration gradients away from such sources. Such measurements, however, would need to be complemented by concurrently collected hydrographic, hydrologic and nutrient data. 24. Having considered these views of the two Working Groups, the ACMP agreed that a baseline study of trace metals in seawater should be carried out wherever it is determined to be possible and useful. Accordingly, appropriate plans should be prepared by a planning group for the baseline studies.

Trend Monitoring

Trends of contaminants in biota

25. The ACMP noted the various submissions on the question of trend monitoring of contaminant concentrations in marine organisms which had been made to the 1982 Statutory Meeting and the discussion which had taken place at the 1983 WGMPNA meeting. It was concluded that there now seemed to be considerable interest in the subject and that although some of the investigations were revealing new unforeseen problems, earlier issues were being resolved. It was now apparent that some of the concern expressed previously over the statistical packages to be used for analysing the data could probably be dismissed, and that agreement between results obtained was reasonably good for the software and hardware combinations so far tested. It also appeared that even data which had not been collected initially for the purpose of trend assessment might, with careful statistical treatment, be useful in that context.

26. An assessment of existing knowledge of the physiological behaviour of fish and shellfish in relation to the way organisms process (metabolize, distribute, excrete, etc.) the contaminants of greatest interest tended to confirm that the earlier assumptions on tissue types to be analyzed in trend monitoring were valid, although in the case of lead, chromium, and zinc, bone tissue might be a more appropriate matrix for trend monitoring purposes. (See Table 1). Examination of the currently proposed procedures for sampling and analysing fish for the purpose of observing trends in time at a particular site in the light of the new information suggests no need for any change at the present time, except, as mentioned earlier, that analysis of bone may be advisable for Cr, Pb, and Zn. It was noted that further investigations are currently underway in several countries and the whole question of the procedure to be followed will have to be kept under close and regular scrutiny. The continued interest of the Statistics Committee in this matter was noted with appreciation.

Table 1.	Appropriate	Fish	Tissues	for	Analysis	of	Contaminants	
	in Trend Mon	nitori	ing					

Contaminant Best organ		Residence time	Regulated/Co- regulated	Remarks
Hg	Muscle	>l yr	No	
Cđ	Liver	$>_{l year}^{l)}$	No?	
Pb	Bone? Liver?	?	?	
Cu			Yes	Widely-ranging fluctuations found
Zn	Bone?	>1 yr	No?	
Cr	Bone?	?	?	
As	Muscle	20-30 days	?	
Organo- chlorines	Muscle Liver Any fatty organ	>1 yr	No	* >

1) Measured in whole fish

<u>Note!</u> In considering the basic measurements which should be reported along with the concentration data so as to allow the important variables to be included in the MIR analysis, weight, length, and age are considered important in all cases (especially weight of organ/ total tissue analyzed), but fat content is also important especially for Cu, Zn, As, and organochlorines.

Trends of contaminants in sea water

27. The ACMP had a preliminary discussion on the feasibility of trend monitoring of contaminant levels in sea water. As in trend monitoring of contaminant levels in organisms and tissues, the main problem was to identify variability in determinand concentrations from time to time that was not covariant with matrix parameters, in this case the physical factors defining the water body. A study of this type has been carried out on the changing oxygen concentrations in the deeper waters of the Baltic Sea with the aim of distinguishing between anthropogenic and natural factors.

28. It was noted that to monitor trends in contaminant concentrations in sea water, three conditions have to be met: (1) the individual contaminants must be uniquely quantifiable; (2) the trend must be detectable above the existing variability which has both spatial and temporal components (the effects of the existing variability can be minimized by making measurements in a physical frame of reference); and (3) the response time of the study area has to match the objectives of the investigation (coastal waters have a relatively fast response to local anthropogenic injections whereas deep ocean waters have a slow response even to a more widespread anthropogenic emission). It was realized that few existing monitoring programmes meet these requirements, although measurements of winter nutrient levels at Station E 1 in the English Channel and of dissolved radioactive contaminants (Caesium) in the Irish Sea were noted as long-time data series collections that might be worthwhile investigating in this context.

Interim Reporting Format and ADP Handling of Data

29. The ACMP had before it the ICES Interim Reporting Format for Contaminants in Fish and Shellfish, which had been prepared by a sub-group of the Marine Data Management Working Group for reporting data to ICES in connection with the Cooperative ICES Monitoring Studies programme. This format has been proposed for use in the Baltic Monitoring Programme under the Helsinki Commission and is under consideration for use with data collected under the Joint Monitoring Programme of the Oslo and Paris Commissions.

30. The reporting format contains three types of forms: a Fish/Shellfish Contaminant Master, a Specimen Data Form, and a Tissue Data Form. The Fish/Shellfish Contaminant Master serves as the master record for the data obtained on one species from one station or area. It provides general information on the sample, its general biological characteristics (e.g., stock structure), and where the sample was obtained. The Specimen Data Form is the record for the data on the individual characteristics (length, weight, sex, age, etc.) of the organisms in the sample. The Tissue Data Form is used to record the concentrations of contaminants in each of the tissues analyzed from the organisms. Copies of the format description and of the forms can be obtained from the ICES Secretariat.

31. Noting that this format should be used for reporting data for the Cooperative ICES Monitoring Studies programme beginning with 1982 data, the ACMP encouraged the use of this format by all laboratories submitting monitoring results. It was felt that the introduction to the format should be amended to make it clear that the forms can be used for all types of relevant data and that if codes are missing for, e.g., sampling areas, species of organisms, or contaminants, appropriate codes can be devised on request to the ICES Environment Officer. Given the possibility of providing various types of additional information in plain language comments on each form, the ACMP felt that this opportunity should be particularly used for the provision of information on stock structure and related biological observations on the Fish/Shellfish Contaminant Master Form.

32. Finally, concerning codes for the analytical methods used to determine contaminants, it was agreed that each laboratory should devise its own threedigit numeric code and persons wishing to obtain information on the methods used should contact the laboratory from which the data originated.

BIOLOGICAL EFFECTS MONITORING STUDIES

Review of Techniques

 The ACMP continued its review of techniques identified by the ICES Workshop on Monitoring the Biological Effects of Pollution in the Sea (Beaufort, N.C., USA, 1979) with a view to eventually making recommendations about their application in monitoring programmes.

34. The use of measures of abundance and diversity of benthos to assess the effects of the dumping at sea of wastes that settle on the sea-bed is widespread; recently some countries have also been carrying out synoptic surveys over wider areas to establish bench-mark information. The ICES Working Group on Benthos Methodics is now addressing itself to the standardisation of methods for benthos assessment and is considering the possibility of a synoptic study of the North Sea.

35. Biochemical/physiological techniques are being more widely used and are proving in many cases highly sensitive (e.g., Mixed Function Oxidases) though sometimes complicated to apply (e.g., Adenylate Energy Charge (AEC) and ATP-ase activity measurements). A report is in preparation on the application of the AEC technique to oil contamination around rigs. Phytoplankton and primary productivity measurements will also be the subject of a review; these reviews will be considered by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic at its next meeting.

Implementation of the Biological Effects Monitoring Strategy

36. The first component of the strategy adopted by ACMP in 1982 (Coop. Res. Rep. 120, paragraph 41 and Annex 3) is that of identification of biological changes, to be followed later by assessment of their scale and significance and causes. The ACMP considered that this first phase could be implemented by including a biological component in the 1985 baseline studies of contaminant distributions, in addition to the pathobiological studies already commenced.

37. In addition to financial restrictions, the difficulties of learning new

techniques and of choosing between techniques have probably affected the willingness of laboratories to take part in biological effects studies up to now. Broad participation using a limited number of techniques to facilitate comparison from area to area will require that the techniques chosen are simple and inexpensive, and this will probably mean that they will be drawn mainly from bio-assay or physiology/biochemistry approaches. Planning for the selection of techniques is underway and the process should be completed in 1984. The ACMP considers that this initial cooperative effort will act as a spur to the wider application of biological effects techniques.

Fish Diseases and Pollution

38. While the approaches outlined in paragraphs 33-37 appear to offer increasingly improved possibilities for monitoring pollution using biological effects, the ACMP had earlier agreed that certain aspects of fish and shellfish pathology might be especially appropriate for inclusion in routine monitoring programmes. In consequence, ICES member countries have been collecting observations on a range of pathological conditions, including tumors, finrot and skeletal anomalies, with the object of recording the geographical distribution of these conditions in both clean and contaminated areas.

39. The ACMP noted the discussion of this subject in the 1983 report of WGMPNA. There were two aspects of the work that required particular attention. One was the identification of the pathological condition and the study of relevant etiological factors. The other was concerned with the distribution of contaminants and with the relevant environmental conditions. The first of these aspects requires the expertise found in the Working Group on Pathology and Disease of Marine Organisms, while the second was relevant to the activities of WGMPNA. The ACMP reiterated the need for these two working groups to interact on these topics.

40. In the meantime, the ACMP noted with approval that its suggestion for a workshop on methods to be used in fish disease surveys related to pollution had been taken up, and that a cruise has been arranged for January 1984 that would bring together experts in the study of disease and pollution. The workshop would study the problems of sampling methodology including optimal trawling time, fishing gear and the suite of observations that should be made, including the biological characteristics of the fish.

EFFECTS OF WASTE FROM THE TiO, INDUSTRY

41. The ACMP discussed the effects of wastes discharged to or dumped at sea from the TiO₂ industry. Two papers were presented. One, from Finland, gave an account of a disease condition of Baltic herring, affecting in particular the eye of the fish. This condition is associated with a significant increase in the iron content of tissues in affected fish, and is thought to be induced by the effluents from a TiO₂ factory. An extensive research project on this matter was initiated in 1982 involving investigations on the metal content of bottom sediments, benthos and plankton, and the biology of herring in the affected area the Bothnian Sea. Preliminary results will be available during 1983.

42. The second paper drew attention to other current studies on TiO₂ production wastes carried out by the Federal Republic of Germany, the Netherlands, Belgium and France. Final reports on these studies are either in preparation or are expected to be available within the next two years. In the light of these ongoing programmes, it was suggested that it would be premature to formulate any final advice without the information expected from these activities. The ACMP accepted that suggestion, particularly considering the conclusions of reports indicating the great variance in data from fish disease surveys, and agreed to keep the subject under close review. This review procedure should also take into account the pollution control and effluent reduction measures underway in various countries with regard to TiO₂ production wastes, as well as the effect of new control measures being proposed by the EEC.

PLANKTON BLOOMS

43. Taking into account the outcome of the successful Joint Session on Plankton Blooms at the 1982 Statutory Meeting, Dr Parker presented an updated version of his paper on exceptional plankton blooms and their implications for fisheries. After discussion and minor amendments the ACMP adopted this paper as an interim statement on current knowledge relevant to exceptional blooms. The paper is attached as Annex 1.

44. The ACMP noted that a special meeting on "Causes, Dynamics and Effects

of Exceptional Marine Blooms and Associated Events" will be convened by Dr Parker prior to the Statutory Meeting in 1984. A prospectus has been prepared for this meeting and will be circulated during 1983. The programme includes sessions on oceanographic and climatic factors, on ecophysiological and chemical factors (including pollution) and on the effects of blooms, including toxicity, and possible counter measures.

PROGRESS IN STUDIES OF CONTAMINANTS IN SEDIMENTS

The Potential Role of Sediments in Pollution Monitoring

45. The ACMP reviewed the report of the third meeting of the Working Group on Marine Sediments in Relation to Pollution (WGMS), noting that substantial progress had been made in the work of that Group. One major item accomplished by the WGMS was the provision of answers to common questions concerning the advantages and disadvantages in the use of sediments for contaminant monitoring purposes and the preparation of a paper on "The Potential Role of Sediments in Pollution Monitoring." The ACMP considered these issues in detail.

46. Concerning the question of the role of sediments in marine pollution monitoring studies, it was pointed out that most of the contaminants of interest are either fine-grained or attach themselves to fine sediment particles. Consequently, the use of sediments in a pollution monitoring context is likely to be most productive in areas where there is a high proportion of fine sediment on the bottom. If, in addition, the area is one of rapid deposition and is not biologically mixed, even more information can be gained on the history of contamination if dating techniques are applied. In a general sense, there is probably little point in attempting pollution monitoring in areas which are undergoing erosion unless the area happens to be one with a particular point source of contaminant input, e.g., from a dumping operation or from a pipeline. Areas of net erosion can usually be recognised initially by their bottom conditions (gravelly sand or hard mud and locally high tidal currents).

47. Where the sediment is either fine grained or contains a substantial proportion of fine grained material, there are a number of reasons why sediments should be considered as being particularly useful in a pollution monitoring context. The following paragraphs provide answers to some of the more commonly asked questions as to the advantage and limitations of sediments in monitoring studies and the paper on "The Role of Sediments in Pollution Monitoring" (which is attached as Annex 2 after amendment by ACMP) provides further details on these points plus details of a three tier approach to monitoring. The three tiers or levels take account of the different objectives of monitoring. The simplest level (Level 1) should be adequate to establish whether any gross changes are occurring at the site of interest. The second or intermediate approach will allow a more detailed assessment and the third approach includes dating to establish contaminant history and is intended to yield the maximum possible amounts of information. Simple decision trees are provided to assist in the selection of the most appropriate level of monitoring for the purpose required.

- 48. In discussing these levels, the ACMP noted that the Level 1 type of monitoring would be particularly applicable in dumping grounds or other areas receiving discharges of particulate or semi-solid wastes. In terms of Level 2 monitoring, it was noted that some idea of the history of the core could be obtained without using radiological dating methods by determining the concentrations of synthetic organic compounds, e.g., PCBs, in core sections back to pre-discharge times. The ACMP then noted the answers to some common questions regarding monitoring of contaminants in sediments, as follows:
- 1) In terms of whether there are any situations in which there is no point in collecting samples of sediments, either in relation to the type of pollutant inputs or because of sedimentological conditions, there is no need to monitor sediments when the contaminant of interest is predominantly in the dissolved form ($k_D < 10$ to 100) and does not associate closely with sediment particles. There are, however, few contaminants that do not associate with sediments. In terms of areas, one does not need to monitor in areas of erosion or in areas with old sediment outcroppings. Additionally, monitoring in sandy areas is generally not very useful.
- 2) Apart from any exceptions which might be identified under the preceding question, methods are available for the analysis of most contaminants of interest in sediments. The same core can be analysed both for metals and for some organic contaminants if the core is carefully subsampled for each type of analysis that is to be conducted.
- 3) In general, the best fraction of the sediment to analyse is the fine-grain fraction, defined in marine sedimentology as the fraction less than 63 µm; 63 µm has been chosen as the dividing point because it is the boundary for the sand/silt classification. Particles above this size tend to behave differently from particles below; e.g., particles above this size limit will tend to precipitate more easily, while smaller particles will be transported more easily. However, if a contaminant is associated with a larger size fraction, then this larger fraction should be analysed. It should be noted that when one wishes to compare data from different areas, samples should be compared on the basis of normalization of texture and grain size composition. In comparing between areas, the organic carbon concentrations at each site must also be taken into account as grain size does not fully account for the scavenging effects of organic matter on trace metals.
- 4) The question of whether any particular chemical extraction techniques should be recommended for particular metals or organics is under active study. Intercalibration exercises will be held to investigate the various techniques, but at present the Working Group was not in a position to recommend any particular techniques.

In this connection, it was noted that there is general agreement that hydrofluoric acid digestion will give as total a digestion as possible so as to determine total trace metal (except chromium) concentrations in sediments. This total digestion is needed to know total concentrations of trace metals and to be able to compare techniques. HF digestion is not carried out in a number of laboratories, however, owing to the fact that it is considered dangerous.

5) Assuming similar analytical procedures, the results of analysis of sediments collected from one area can usefully be compared with results for the same area collected at a different time when the sediment samples have been fully characterized so that one can distinguish changes in the amount of the fine fraction and in the concentrations of contaminants. A sound statistical basis is an absolute necessity for attempting to make comparisons.

- 6) Assuming that the analytical procedures used are comparable and that there are no inter- or intra-laboratory analytical anomalies, comparisons can be made of the results of analyses of sediment samples taken from different areas, provided due account is taken of the relative background concentrations. Thus, in order to be able to achieve good, valid comparisons, cores should be taken to determine the baseline concentration of the contaminant of interest and the change from the baseline to the present concentration of that contaminant. One can then compare the concentration over background concentrations in the core. A more complex comparison can be obtained if sedimentation rates are measured and fluxes determined. It would not normally be valid to compare only total or selective leachate concentrations on a direct concentration recorded basis.
- 7) The question of to what extent the concentrations of a particular contaminant found in a sediment can be considered to represent the fraction potentially available to organisms living in or on the sediment in question is still a matter for research. Resolution of this question will depend on finding a statistical correlation based on studies of concentrations of contaminants in biota, water and sediments in an area and will be different for different organisms.

49. Having considered this information and that contained in the paper on the role of sediments in pollution monitoring attached as Annex 2, the ACMP noted with approval the progress already achieved by the Working Group on Marine Sediments in Relation to Pollution and looked forward to reviewing the results of its future work.

Progress in the Pilot Sediment Studies in the German Bight and in the Skagerrak

50. The ACMP reviewed the progress in the conduct of two pilot studies of contaminants in sediments which are being carried out under the Working Group on Marine Sediments in Relation to Pollution. With regard to the Pilot Sediment Study in the German Bight, it was noted that a number of sediment cores were collected in the study area in October 1982 and additional cores were taken in May 1983. The analysis of these cores will probably be completed by the end of 1983, so preliminary reports on the results can probably be reviewed in 1984. Concerning the Pilot Sediment Study in the Skagerrak, samples of sea water and suspended particulate matter have been collected in the different water masses in the Skagerrak and the analysis of these samples is nearly completed. Although several sediment cores have been taken, the ACMP took note of the difficulties which have been encountered in obtaining funding for the collection of cores in the study and hoped that a solution to this problem will be forthcoming shortly.

Progress in the Pilot Study of Sediments in the Baltic Sea

51. The ACMP then considered progress in the Pilot Sediment Study in the Baltic Sea, which is being carried out under the ICES/SCOR Working Group on the Study of the Pollution of the Baltic. This study aims to investigate sediment processes in relation to contaminants and has the following three objectives:

- determining the history of pollutants in dated sediment samples and monitoring the pollution component of recent sediments in terms of the rate of sedimentation,
- (2) determining the role of sediments as a final sink for substances with regard to materials balances, and
- (3) determining the role of sediments as a source of materials to the water column, taking account of changing redox conditions.

52. An intercalibration exercise has been designed with the problems of analysis of Baltic Sea sediments in mind. The intercalibration samples will consist

of (1) two dry reference sediment samples, and (2) a wet sediment core for which every second slice will be subjected to sediment and geochemical analyses, while the remaining slices should be dated using radiochemical and other methods. The samples for this intercalibration exercise will be distributed in summer 1983.

REGIONAL ASSESSMENTS OF THE HEALTH OF THE MARINE ENVIRONMENT

53. The ACMP recalled that at its recent meetings it had discussed the importance of conducting assessments of the health of the marine environment on a regional basis and had requested the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA) to (1) develop a general format for the conduct of assessments in the ICES area, and (2) consider the best way to carry out such regional assessments. In response to the first of these requests, a sub-group of WGMPNA had developed a set of guidelines for the preparation of regional assessments of the marine environment (contained in ICES Document C.M. 1982/E:22); these guidelines had been discussed and accepted by the appropriate Standing Committees at the 1982 Statutory Meeting. On the basis of these discussions, the Council had approved a resolution (C.Res.1982/4:10) that regional assessments should be conducted on the health of the various coastal areas of the North Atlantic.

54. The ACMP had before it the guidelines in Doc. C.M.1982/E:22. These guidelines describe the format of and the procedures for preparing assessments that might enable the quality of individual regions of the marine environment to be appraised and compared with that of other areas. According to these guidelines, each assessment should contain a succinct summary or overview of the existing knowledge of the physical, chemical and biological conditions of an area and a multi-disciplinary assessment of the kinds and degrees of anthropogenic effects on the environment. By using this format, it is intended that a uniformity can be achieved in the assessments of the various areas that will promote intercomparisons to be made of the relative extents of anthropogenic disturbances.

55. The ACMP agreed that these guidelines should be annexed to its report, with appropriate modifications. The guidelines are attached as Annex 3. The ACMP agreed that the guidelines should be widely adopted so as to ensure that assessments from different areas would be comprehensive and comparable. As a test of their suitability, it was suggested that they should be applied first to a small number of examples and for this purpose the Firth of Forth, the German Bight, the Kattegat / Skagerrak, and the New York Bight were felt to be particularly appropriate.

REVIEWS ON MARINE CONTAMINANTS

56. In recent years, the ACMP has considered a number of overviews on the transport and cycling in the marine environment of substances that have been widely recognized as causing pollution in particular situations, e.g., PCBs, mercury, lead and cadmium. Following on from that tradition the ACMP expects, over the next few years, to consider reviews on substances which currently are the cause of some concern on grounds of their occurrence and/or toxicity. At this meeting, the ACMP considered two reviews which have been prepared by members of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic. These reviews have been discussed and approved by that Working Group and also briefly considered by the Marine Chemistry Working Group. After discussion by the ACMP, these two reviews were approved for annexation to this report (Annexes 4 and 5).

57. One of these reports reviewed the available information on Toxaphene di-

stribution in the environment and its toxicity. This report, attached as Annex 4, concludes that toxaphene has probably been used on a greater scale in North America than any other organochlorine pesticide. The ACMP noted that most of the papers that report the finding of components of toxaphene (the technical material contains a wide range of compounds) refer to samples collected on the western side of the Atlantic. It considered, however, that this might well be an artifact as most European laboratories have not looked for toxaphene on the grounds that they did not expect to find it. The few laboratories which in recent years have looked for this substance do appear to find components of toxaphene in environmental samples. The ACMP therefore endorsed the concern expressed in the review that more work should be done to establish the extent of contamination of the marine environment by toxaphene. It was noted that the WGMPNA has recommended the inclusion of toxaphene in the Baseline Study of Contaminants in Fish and Shellfish, although it was recognized that a number of analytical problems in the determination of toxaphene must first be solved.

58. The second review concerned Hexachlorobutadiene (HCBD); it is attached as Annex 5. This review concludes that HCBD poses much less of a threat to the marine environment than many other chlorinated compounds. It does not appear to be particularly persistent or toxic and is normally only encountered in the marine environment in association with high concentrations of Hexachlorobenzene (HCB) close to point sources of input. The ACMP endorsed the view that wide-scale investigations into the occurrence, fate and effects of HCBD are not justified at the present time and that HCBD need not be determined, except where unusually high concentrations of HCB are encountered.

59. The ACMP noted that a number of other reviews are in the course of preparation through the collaborative activities of the two working groups, WGMPNA and MCWG. It gave preliminary consideration to one such review on polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans and noted that this could be expanded in the light of information which has recently become available.

PROGRESS IN THE WORK REQUESTED BY THE OSLO AND PARIS COMMISSIONS

60. The ACMP considered the 1983 programme of work which ICES has been requested to perform by the Oslo and Paris Commissions, on the recommendation of their subsidiary bodies, and noted the progress in this work as reported in the following paragraphs. Several of the items have been dealt with in other parts of this report, or in the 1982 ACMP Report (published as Coop. Res. Rep. No. 120 (1983)), and so are merely referenced.

Specimen Banking

61. This subject was covered in the 1982 ACMP Report (in paragraphs 52-57 and 67 and in Annex 4). The consideration of this topic has thus been completed.

Transport of Lead in the Marine Environment

62. The overview on lead in the marine environment has been published as Annex 5 to the 1982 ACMP Report, with accompanying comments in paragraphs 59-60

and 68 of that report, thus fulfilling the request for information on this subject.

Trend Monitoring

63. This topic is under continuing review by the ACMP; the most recent major information and guidance on the use of marine organisms in monitoring trends in contaminant concentrations was given in the 1982 ACMP Report (paragraphs 22 and 25). The results of the further consideration of this topic at the 1983 midterm ACMP meeting are contained in paragraphs 25-26, above. In addition, the ACMP gave preliminary consideration to the issue of monitoring trends in contaminants in sea water, as recorded in paragraphs 27-28, above.

Biological Effects Studies

64. The ACMP has continued its review of potentially useful techniques for monitoring the biological effects of pollution. The results of this review are contained in paragraphs 33-40, above.

Methods for the Assessment of River Inputs

65. A set of guidelines to be followed in assessing gross riverine discharges of trace metals and organohalogens to the marine environment is contained in Annex 6 to the 1982 ACMP Report, with accompanying comments in paragraphs 61-65 of that report.

66. In terms of the assessment of the <u>net</u> input of contaminants from a river to the marine environment, this is considerably more difficult to carry out owing to the complexity of the effects of coastal zone processes on the fate of the contaminants discharged from rivers. Further work on the methods that could be used to assess net riverine inputs will be carried out in association with the Symposium on Contaminant Fluxes Through the Coastal Zone, which will be held in Nantes, France on 14-16 May 1984, and the Workshop immediately following the Symposium.

Outcome of the Fifth Round Intercalibration on Trace Metals in Sea Water

67. The ACMP consideration of this intercalibration exercise is contained in paragraphs 5 to 8, above. It was anticipated that the final reports on the results of this intercalibration will be available in early 1984.

Progress in Studies of Contaminants in Sediments

68. The ACMP consideration of this subject is contained in paragraphs 45-52, above, and a paper on the role of sediments in marine pollution monitoring is attached as Annex 2.

Feasibility of Conducting an Intercalibration Exercise on Analyses of Hydrocarbons in Sea Water

69. The ACMP noted that this subject is under consideration in the Marine Chemistry Working Group. Although no plans for such an intercalibration exercise have yet been developed owing to the technical difficulties involved in terms of the samples to be used, it was hoped that some progress would be made by next year.

Method to Calculate PCB Concentrations

70. Work on this subject is currently underway in the Marine Chemistry Working Group (see paragraphs 11 and 12, above).

ADP Handling of Monitoring Data

71. The Interim Reporting Format for Contaminants in Fish and Shellfish, discussed in paragraphs 29 to 32, above, has been developed and transmitted to the Oslo and Paris Commissions for consideration for use in the Joint Monitoring Programme. Work on the development of reporting formats for contaminants in sea water and in sediments will begin in the latter half of 1983.

General Rationale for Intercalibration Exercises

72. This subject was considered at the 1982 meeting of ACMP; the general ra-

tionale for the intercalibration programme is contained in paragraphs 12 to 18 of the 1982 ACMP Report and an assessment of the status of intercalibrations is contained in Annex 1 to that report. While updating of this information will be carried out when appropriate, the ACMP felt that the information provided in its 1982 report fulfilled the request of the Commissions.

Effects of Disposal of TiO2 Wastes at Sea

73. Having noted that several major studies on this subject are currently being carried out (see paragraphs 41 and 42, above), the ACMP agreed to await the results of these studies before attempting to formulate further advice on the discharge of wastes from the TiO₂ industry at sea.

Evaluation of "Special Care" Methods of Capping Contaminated Dredged Spoil Dumping Sites

74. The results of the ACMP consideration of this subject are contained in paragraphs 99 and 100, below, and in Annex 7. The ACMP agreed that the provision of this information fulfills the request on this subject.

Atmospheric Deposition of Contaminants to the Sea

75. Some information on this subject is contained in paragraphs 96 to 98, below. The ACMP expected that some further information would be available for review at its 1984 mid-term meeting.

Unusual Phytoplankton Blooms

76. An interim statement on current knowledge relevant to exceptional plankton blooms is contained in Annex 1 (see also paragraphs 43 and 44, above). Further information will be available after the Special Meeting on Causes, Dynamics and Effects of Exceptional Marine Blooms and Associated Events has been held in connection with the 1984 Statutory Meeting.

1984 Work Programme

77. The ACMP noted that there are two new items in the 1984 Work Programme: (1) to keep under review the question of any new contaminants that might be relevant to the interests of JMG, and (2) to assess the importance of the bio-availability of organohalogen compounds dumped in the Oslo Convention area. Concerning the request for information on new contaminants, the ACMP agreed that the review on Toxaphene contained in Annex 4 and the review on Hexachlorobutadiene contained in Annex 5 should be the first two submissions to the Oslo and Paris Commissions with respect to this request. In terms of the second request, the Working Group on Marine Sediments in Relation to Pollution was requested to begin consideration of this subject.

RESPONSE TO REQUESTS FROM THE HELSINKI COMMISSION

- 78. The ACMP took note of the current requests from the Baltic Marine Environment Protection Commission (Helsinki Commission):
- (1) to develop a reporting format for contaminants in biota;
- (2) to prepare a species code list for phytoplankton; and
- (3) to assess continuously the condition of the seal populations in the Baltic Sea, particularly in view of the strong indications that the serious decline in the reproductive rate of the seals in the Baltic Sea Area is due to pollution.

79. With regard to the first request, the ACMP noted that the ICES Interim Reporting Format for Contaminants in Fish and Shellfish has been prepared (see paragraphs 29 to 32, above) and forwarded to the Helsinki Commission in fulfillment of this request.

80. Concerning the second request, a species code list for phytoplankton in the Baltic Sea is under development using the eight-letter mnemonic RUBIN code system. This RUBIN code list is expected to be completed in the second half of 1983. This code list for phytoplankton will complement the RUBIN Code List 01 for Baltic Invertebrates, which was transmitted to the Helsinki Commission in 1982 for use in the Baltic Monitoring Programme. The ACMP noted that, while the original request was for species code lists using the 12-digit U.S. National Oceanographic Data Center (NODC) Taxonomic Code System, difficulties had been experienced in obtaining the codes according to this system owing to the large number of species for which codes must be assigned.

81. Finally, concerning the request for an assessment of the condition of Baltic seal populations, the ACMP noted that a draft report on this subject was available and that advice will be forthcoming after full consideration of that report (see paragraph 82, below).

BALTIC SEALS

82. The ACMP took note of the draft report of the Working Group on Baltic Seals, which has been established to assess the condition of seals in the Baltic Sea Area in response to a request by the Helsinki Commission and the International Baltic Sea Fisheries Commission. This report provided information on changes in seal population size and distribution during this century, estimates of the current size of populations and factors affecting it, and predicted future changes in the size of Baltic seal populations. The ACMP noted that the report will be considered by the relevant Committees during the 1983 Statutory Meeting and agreed to consider it more fully after that time.

PROGRESS IN THE STUDY OF THE BALTIC SEA

83. The 1983 meeting of the ICES/SCOR Working Group on the Study of the Pollution of the Baltic was preceded by a Workshop on Patchiness Experiments in the Baltic Sea. The Workshop had been initiated by the Working Group because the patchiness problem, i.e., the inhomogeneous distribution of properties, has been one of the central areas of study of the Working Group. The Workshop was convened under the auspices of ICES in cooperation with the Baltic Marine Biologists. The results of the Workshop and the other deliberations by the Working Group are summarized below.

Workshop on Patchiness Experiments in the Baltic Sea

84. The 16 presentations given at the Workshop covered the results of studies of physical, chemical and biological patchiness relating to most parts of the open Baltic Sea which had been carried out by all countries bordering the area. The studies demonstrated the frequent occurrence of inhomogeneous distributions of properties over a wide range of space and time scales, from several tens of kilometres to several tens of metres and from an order of days to an order of hours, respectively. The patchiness in the Baltic Sea constitutes not only an important scientific problem (involving studies of generation and dissipation mechanisms; interactions between physical-chemical-biological processes, scales, role for the ecosystem as a whole or parts thereof), but is also of great significance in relation to understanding the anthropogenic impact on the Baltic Sea environment, and to the design of monitoring programmes and the interpretation of their results. The Workshop proposed, and the Working Group agreed to, the establishment of a study group with representatives from all Baltic Sea countries and from all relevant scientific disciplines. This study group should a) coordinate work on patchiness in the Baltic Sea on a national level, b) serve as a center for information on results of patchiness studies, and c) plan a joint patchiness study for the Baltic Sea. The long-term aims of this joint work include three major components:

1) to compile statistics on the occurrence of patchiness;

- 2) to gain an understanding of the mechanisms and processes of generation and dissipation; and
- 3) to determine the significance of patchiness in relation to
 - (i) the ecosystem of the Baltic Sea, including fish;
 - (ii) pollution, pollution monitoring, and effects of and on fisheries.

The overall scientific aim should be to determine the importance of physical, chemical and biological control mechanisms on offshore ecosystem dynamics and production in the Baltic Sea.

Other Cooperative Studies in the Baltic

Sediment studies

85. The ICES/SCOR Working Group on the Study of the Pollution of the Baltic is also coordinating a pilot study of sediments in the Baltic Sea, including an intercomparison exercise on analytical methods to be used in the study. The plans for this pilot study and intercomparison exercise were considered and reported in paragraphs 51 and 52, above. It was noted that, according to these plans, the pilot study will be carried out in 1985.

1985 Baseline Survey of Contaminants in Fish and Shellfish

86. The Working Group also noted that the Helsinki Commission, at its meeting in February 1982, had endorsed the conduct of the baseline survey in the Baltic Sea. The plans for the survey had been developed intersessionally, with analysis of the following contaminants being mandatory: (1) metals: mercury, copper, zinc, cadmium, lead, arsenic; and (2) organochlorine compounds: HCH, HCB, dieldrin, PCBs, op and pp DDT, DDE and DDD. The species which had been chosen include cod, herring, flounder, plaice and mussels (Mytilus edulis). (See also paragraphs 20 and 21, above). From the participants in the Working Group, it was clearly indicated that all countries around the Baltic Sea will participate in the study and the Working Group emphasised the importance of participation.

Biogeochemical cycling and budgets or mass balances

87. Some intersessional work had been initiated which had identified several

gaps and open questions in relation to the estimation of biogeochemical cycles or the development of mass balances, including (1) the magnitude of the atmospheric input of substances, (2) the concentrations of substances in the surface microlayer of the sea, and (3) the quantities of trace metals discharged into the Baltic Sea via rivers. It had also been difficult to obtain numbers on the total amounts of certain substances in the Baltic Sea because of the difficulty of calculating the amounts in the different components of the system (biota, water, sediments). The Working Group agreed that work on this general problem should continue intersessionally.

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Biological effects studies

88. The ICES/SCOR Working Group on the Study of the Pollution of the Baltic had attempted intersessionally to establish an exchange of information among Baltic scientists working within this field with a view to stimulate their work on a cooperative basis. It was noted that meeting activities in the form of workshops were being planned both under the auspices of ICES and the Helsinki Commission. The Working Group urged Baltic Sea scientists to participate in these activities.

General Pollution Studies

Input studies

89. Gaps had been identified in the knowledge of quantities of inputs to the Baltic Sea from land and atmosphere as regards single substances and it was strongly emphasised that more precise input information is required for single components (substances). It was noted that recent studies suggest that considerable amounts of inputs of nutrients to the sea area derive both from land and from the atmosphere. Input quantities presented at the Working Group meeting were about an order of magnitude larger than quantities reported around 1970. The Working Group emphasised that integrated information on inputs of given contaminants to sub-areas of the Baltic Sea, with an explanation of how the data have been obtained, are required for further work on cycling and mass balances of substances within the marine environment. It was also emphasised that diffuse inputs (land and atmosphere) must be ascertained.

Monitoring - Scientific considerations

90. The on-going Baltic Sea monitoring programme is currently being reviewed by the Helsinki Commission. The ICES/SCOR Working Group on the Study of the Pollution of the Baltic felt that there is a need for a continued discussion of the scientific basis for the programme in terms of the location of stations, frequency of sampling and parameters being studied.

91. The Working Group also felt that there is a need for a long-term series of observations to be made at several representative stations in the Baltic Sea. It may also be necessary to gain more information on the physical conditions around monitoring stations at the time of sampling, in order to facilitate interpretation of observations carried out at low frequencies at separate points. In addition, it was emphasized that special studies are needed to broaden the understanding of the conditions in the Baltic Sea and to support the interpretation of

the monitoring data. The Working Group agreed to initiate intersessional work on these and other aspects related to the scientific basis for monitoring programmes.

New contaminants

92. The Working Group noted the review paper on toxaphene in the marine environment (contained in Annex 4). In considering other possible new contaminants, reference was made to discharges from oil refineries and it was agreed that studies should be done to identify substances in these discharges and determine their toxicities. A new class of surface active substances was also mentioned, which may require studies in relation to their use in the marine environment.

93. The ACMP took note of these activities and developments and endorsed the

programme of the Working Group. Concerning the work on the scientific considerations for monitoring, the ACMP noted the value of this work not merely in terms of the Baltic Sea but in terms of the development of the general scientific basis for monitoring. The ACMP noted that similar reviews of the monitoring programme in the North Atlantic are carried out on a continuous basis by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic.

OIL SPILL COMBATTING

94. Following preliminary discussions in 1982 on the implications of the development of concentrated oil dispersants and the application of these products to oil spills by aerial spraying, the ACMP considered a review of the recent developments on oil spill combatting which included information on these subjects. The review is not intended to cover all eventualities or side-effects of an oil spill combatting activity, but it does provide a brief summary of the developments which are now available for use. An important change over the last ten years has been the considerable improvement in the understanding of how oil spills behave, how oil degrades and what its effects will be whether treated or left alone. It is now recognised that there are many situations when the best option is to let nature take its course. Attempts at mitigation by man will often cause more damage to marine organisms in the short-term and will not usually significantly affect the long-term result of an oil spill. However, a wide-spectrum of response actions are now possible and the ACMP concluded that the review contained a useful summary of these actions and thus should be appended to its report (Annex 6).

95. In the course of the discussion, concern was expressed over the possible effects of long-term low-concentration releases of oil from rivers, harbours

and oil exploitation activities, and it was agreed that this matter should be considered in more depth at a future meeting.

ATMOSPHERIC DEPOSITION TO THE OCEAN

96. The ACMP noted that, while atmospheric deposition is now recognised as a significant avenue for the introduction of many categories of contaminants to the ocean, there are few data on organic compounds in the marine atmosphere. More importantly, the routes whereby these organic compounds enter the oceans are poorly understood. Nonetheless, the amounts actually entering marine waters can be roughly estimated using the limited amount of data available.

97. With regard to petroleum hydrocarbons, the compounds for which a significant data base exists are the <u>n</u>-alkanes. Estimates of the deposition of n-alkanes to the world oceans have recently been made for "representative" parts of the oceans.¹⁾ Considering several routes of deposition (rain scavenging, dry deposition of particulates, and direct vapour exchange of gaseous <u>n</u>-alkanes), Duce and Gagosian estimate that rain scavenging of particulate <u>n</u>-alkanes appears to be the primary pathway. The total input of <u>n</u>-alkanes is <u>estimated</u> to be 0.04 to 0.4 x 10^{12} g/yr, a maximum of 10-15% of the 3.3 x 10^{12} g/yr of total petroleum hydrocarbons which are thought to be entering the world oceans.

98. More precise estimates of the atmospheric input of contaminants (both organic and inorganic) to the oceans cannot be made until additional information is available on the atmospheric abundance and inputs of other types of substances. The ACMP accordingly recommended that additional information on this subject be gathered, and that research and review papers be presented to the Statutory Meetings in 1983 and 1984.

 Duce, R.A. and Gagosian, R.B., 1982. The Input of Atmospheric n-C₁₀ to n-C₃₀ Alkanes to the Ocean. J. Geophys. Res. 87: 7192-7200.

CAPPING OF DUMPED CONTAMINATED SOLID WASTES

99. This subject was discussed at length on the basis of the paper, "Information on Capping of Contaminated Dredged Material", which is attached as Annex 7 to this report. The ACMP agreed that capping, as a special care measure, was technically feasible. Current activities ongoing in this field in Japan, the United States, and certain European nations were noted, but it was considered that further studies are required. The ACMP suggested that continuing results from ongoing experiments should be reported to appropriate Committees at the Statutory Meetings. This is especially true for data that results from studies designed to assess (1) how the capping materials stay in place with time, and especially following major storms or unusual hydrographic events; (2) leakage of contaminants from solid wastes through the capping materials; and (3) various sediment types as the most effective capping materials.

100. The ACMP also considered that the criteria for selecting sites for dumping in the context of these special care procedures would be different from those for the more routine dumping operations.

ANNEX 1

EXCEPTIONAL MARINE BLOOMS AND THEIR IMPLICATIONS FOR FISHERIES

Miles Parker Department of Fisheries and Forestry Fisheries Research Centre Abbotstown, Castleknock Co. Dublin, Ireland

1. INTRODUCTION

As used here the term 'exceptional marine blooms' refers to those outbursts of growth of certain types of plankton (particularly Dinoflagellates, but also certain Cyanophytes, Haptophytes, Diatoms and Ciliates <u>inter alia</u>) which result in visible effects at the sea surface or in dramatic effects such as fish kills. On a small scale, abnormal blooms are probably common and not much noticed. Interest has developed in recent years because of the apparent increased frequency and scale of effects of plankton blooms in North Atlantic and neighbouring waters. This note provides a brief summary of the types of problems which blooms give rise to, current thinking on their causation and the requirements of the fishery manager with respect to information and control. This review limits itself to a discussion of the types of blooms observed in the North Atlantic (north of Gibraltar to the east and Cape Hatteras to the west), though it draws on experience from elsewhere in the world.

2. EFFECTS OF PLANKTON BLOOMS

Blooms may affect fisheries either indirectly, by rendering fish products toxic or unpallatable and thus unmarketable, or directly by killing fish and shellfish.

Within the ICES area the closure of shellfisheries due to the risk of Para-2.1 lytic Shellfish Poisoning (PSP) incidents causes considerable local economic losses. PSP results from ingestion by man of shellfish which have accumulated the toxins (saxitoxin and others) produced by the dinoflagellate referred to generally as Gonyaulax tamarensis or G. excavata or its more toxic resting cysts; (in one case in Spain, Gymnodinium mochimaensis appears to have been the causative organism). While within the ICES area, outbreaks of PSP, or high levels of toxin have been recorded in shellfish in certain areas from Spain to Norway (particularly in fjords, rias, estuaries and docklands), there appear currently to be two major foci, one on the east coast of Britain (Firth of Forth to Humber Estuary approximately) and one on the East coast of North America (Bay of Fundy to Cape Cod). Even within these focal areas, the degree of toxicity varies from site to site and from year to year and there is evidence to suggest an overall increase in extent and severity in recent years. The presence of resting cysts in the sediments is an important indicator of likely PSP problems. Controls are usually applied by regular monitoring in the season of shellfishing in affected areas and closure of the fishery when levels exceed 80 µg toxins per 100 g shellfish flesh. Toxin levels are measured using a standard mouse bioassay; chemical techniques are as yet too complex and costly for routine use. Most countries in the ICES area have carried out surveys for the presence of the toxins and have identified affected areas; this approach provides the only protection currently available. Such surveys should be repeated frequently in affected areas and at,

e.g., 2-5 year intervals even in areas apparently free of PSP since conditions have been noted to change in this respect (e.g., there has been a southward progression down the Gulf of Maine in the areas affected).

- 2.2 Within the area under consideration, Neurotoxic Shellfish Poisoning (resulting from Ptychodiscus brevis, (Gymnodinium breve)) blooms and Ciguatera fish poisoning (caused by Gambierdiscus toxicus) are not known. Some other dinoflagellates have been tentatively associated with gastrointestinal disturbance, but the evidence is circumstantial; species include members of the genera Prorocentrum and Dinophysis. While it would be of interest to know whether these or any other dinoflagellates pose any sort of threat to human health, no economically or epidemiologically serious problems appear to have arisen so far with the exception of a recent outbreak of Diarrhetic Shellfish Poisoning in the Netherlands associated with some Dinophysis species. There was a tendency in the older literature to treat all blooming (red tide) species as toxic, so that older lists of toxic organisms include Noctiluca and Polykrikos; however, there appears to be no evidence of toxicity in these genera in the North Atlantic. The common North Atlantic species Gonyaulax polyedra is apparently identical to a toxic species in California, but has caused no known problems in the Atlantic.
- 2.3 In addition to direct effects on public health, blooming organisms may disrupt the fish trade by tainting fish products (as has been the case with blue-green algal blooms in the Baltic Sea) and by interfering with catching operations. Many blooms produce mucillage (e.g., Phaeocystis) or simply produce cells in such density as to have a clogging effect (e.g., the needlelike diatom Nitzchia is recorded as forming aggregates under bloom conditions), which may clog driftnets or render them highly visible under water. It is probable that many fish will avoid blooms, particularly those which produce much mucillage or irritant materials (e.g., Phaeocystis secretes acrylic acid); such effects may locally disrupt coastal drift net fishing in particular. Finally, in terms of the trade in fish, the dramatic visible effects of blooms, especially if associated in any way with fish kills, have a powerful effect on the opinion of the fish-buying public. It is essential that fishery authorities be prepared to make unemotional information available to the public at short notice.
- 2.4 While public health problems are primarily the result of the consumption of contaminated shellfish, blooms may also cause fish kills, either through the direct action of toxins produced by the bloom, or through a reduction in dissolved oxygen during bloom decay. G. excavata toxins have been shown to be accumulated through the food chain to herring, sand-lance and menhaden in the wild, resulting in kills; more serious effects may lie with the impact on planktivorous fish larvae. Other dinoflagellates are known to produce ichthyotoxins, including Gymnodinium veneficum and Amphidinium carteri, both known from the North Atlantic. Ichthyotoxins are also produced by other organisms, e.g., certain Haptophyte species. In the eastern North Atlantic, the most serious problems are caused by the dinoflagellate Gyrodinium aureolum which has caused fish kills in Spain, France, England, Ireland, Scotland, Norway and in the North Sea, though for no obvious reason, not in North America where it was first discovered. It is also implicated in deaths of littoral (rocky and muddy shore) and soft-bottom sub-littoral marine invertebrates. G. aureolum has become a major cause for concern to fish farmers, having caused several kills at sea-cage salmonid rearing installations. Mixed blooms of various flagellates including the dinoflagellate Katodinium and various Haptophytes were also implicated in two kills of caged fish in Scotland. Since conditions of calm and shelter suitable for rearing caged fish are also suitable for bloom development this is probably a continuing problem. Indeed, the presence of cages as a source of nutrients may serve locally to exacerbate blooms that have developed elsewhere. The

ciliate <u>Mesodinium rubrum</u>, which blooms not uncommonly in coastal waters throughout this area, has been observed to bloom at cages and may be taking advantage of local nutrient sources. Finally, toxins or other by-products of <u>G. aureolum and Phaeocystis are implicated in poor molluscan larval</u> settlement and poor spat growth.

- 2.5 Fish kills due to ichthyotoxins have tended to be rather local in the North Atlantic. However, kills due to oxygen deficiency resulting from the decay of the blooms may be on a larger scale. Small local 'Jubilees' (where healthy fish are driven onshore ahead of unfavourable water conditions) may be due to blooms or local oxygen deficits. On a larger scale, oxygen deficits associated particularly with the decay of <u>Ceratium</u> spp. blooms have resulted in fish kills over wide areas in the North Sea, off the Swedish west coast and in the middle Atlantic Bight off North America. Not only fish but also benthic shellfish are affected; one figure puts the damage by the 1976 <u>Ceratium</u> bloom-related low dissolved oxygen event in the New York Bight at over a half billion dollars, when all costs are taken into consideration.
- 2.6 It should be noted that most blooms cause no discernable damage. Extensive blooms of species such as <u>Noctiluca</u> have occurred in the North Atlantic without any obvious effects and small scale visible coastal blooms of various dinoflagellates, diatoms and <u>M. rubrum</u> are not uncommon and are not recorded as having deleterious effects. <u>Ceratium tripos</u> has regularly bloomed in large numbers in the New York Bight (and elsewhere) without giving rise to the effects recorded there in 1976. <u>G. aureolum</u> apparently blooms all along the Celtic Sea coastal tidal rising front, from Oessant via Land's End to Fastnet and only causes problems in a few areas, notably those where there are caged salmonid installations. By contrast, the appearance of blooms could be a useful indicator of oceanographic events and phenology, and the collecting of such observations should be encouraged.

3. CAUSES

The recent upsurge in reported bloom incidence has been attributed to three causes. These are, firstly, an increase in observers, secondly, increased pollution providing nutrient sources, and, thirdly, long term changes in oceanographic conditions.

- While it is true that there are more research vessels at sea, there have 3.1 always been many observers among fishermen, to whom the surface effects of blooms could be useful indicators, especially in herring fishing. There have been, as well, trained observers at sea since the middle of the last century, many of them working in areas now noted for bloom incidence. It is difficult to see how these observers could have missed large-scale events (for example, Marie Lebour (author of a major key work on dinoflagellates) worked at Plymouth in an area now notable for Gyrodinium aureolum blooms. While the organism was only identified in the U.S. in 1957 by Hulbert, it is still difficult to imagine how Lebour could have missed it had it been there). Records of PSP outbreaks in Britain show a rather patchy distribution in time, with none being recorded between 1910 and 1958. While it is true that much of the new interest derives from the effects of blooms on new activities (mariculture), there is some evidence to suggest that the problems are genuinely more prevalent currently than in previous years.
- 3.2 The possibility that hypertrophication of coastal waters due to inputs of nutrients, particularly from sewage and certain industrial wastes, may have been responsible for an increase in blooms has been considered but has not proved to be a fully satisfactory hypothesis. Certain local events, particu-

larly in enclosed inshore waters, can be related to hypertrophication (e.g., in the Oslo Fjord, in blooms occurring in docks, in certain events in the inner New York Bight and at the New York Bight Apex Sludge Dumping Ground), but this hypothesis does not provide all the answers. Firstly, it seems possible that the major nutrients (N and P) are not the limiting factors in dinoflagellate blooms, which may develop in nutrient-poor waters, though other micro-nutrients, growth factors or vitamins, which could be provided by sewage, may be of more importance than has hitherto been considered. In many cases, dinoflagellates apparently require that the water has previously been 'conditioned' by other species (e.g., diatoms), so it may be that the effect of hypertrophication on these components of the plankton needs further study. In general, the role of nutrients and micro-nutrients in bloom development is not well understood and by no means have all the factors been identified. Finally, the very extensiveness of many blooms points against single sources of origin such as a dumping or discharge operation. While the added source of nutrients (as from discharges or salmonid cages) seems likely to exacerbate the situation, it is less likely to be the root cause. Nonetheless, control over such sources could help to ensure that anomalous natural events do not become disasters. Moreover, the role of diffuse sources is not well understood.

3.3 Blooms have long been associated with particular oceanographic features such as upwelling, stratification and, more recently, estuarine and coastal frontal systems, and with climatic factors resulting in increased land runoff or high insulation. The primacy of the correct physical (oceanographic/ climatological) conditions for bloom development is becoming well established. Biological and chemical aspects seem secondary, though nonetheless important; correct biological conditions may not occur even when correct physical conditions are available.

Changes in bloom incidence may be related to large-scale long-term physical changes in water masses which themselves are related to climatic changes. For example, the long time scale changes observed in the western English Channel and known as the Russel Cycle have resulted in a variety of major biological changes on an approximately forty-year time scale; the apparent increase in bloom frequency in the Celtic Sea may be associated with such changes.

ANNEX 2

THE POTENTIAL ROLE OF SEDIMENTS IN POLLUTION MONITORING

1. INTRODUCTION - ROLES FOR SEDIMENTS

- 1.1 Sediments and suspended solids are important sinks for marine contaminants and potential sources of contaminants for marine organisms. Where metals are concerned, anthropogenic inputs become highly associated with bottom sediments and suspended particles. Some of the metal is relatively weakly bound and thus potentially available for uptake, at least in the long-term. Chlorinated hydrocarbons and other organic contaminants are probably more strongly absorbed and there has been less study on desorption processes except in a few cases, such as for Kepone. Microbial biotransformation of metal speciation occurs primarily in sediments or in association with particles, making this source particularly important in the transfer of, for example, mercury or lead to the food chain. In general, however, much basic research requiring substantial investment of specialists and equipment is required, both on adsorption/desorption processes in sediments and on biological uptake mechanisms, before the transfer processes can be satisfactorily modelled.
- 1.2 Given the important role of sediments as a repository of contaminants and source of food for biota, it is appropriate for monitoring programmes concerned with the protection of biota to include measurements of contaminant levels in sediments. The long-term stability and integrating effects of sediments make them an effective indicator of potential impact on biota, regardless of the relative importance of the sediments themselves or the dissolved phase as the direct source. (By contrast, short-term variability of dissolved and suspended components renders them less suitable for use in monitoring.)
- 1.3 Quality standards for sediments would need to be derived from the ultimate critical impact of the contaminants, e.g., on human health or the biota. Currently, it is not possible to back-calculate from the data on lethal and sub-lethal effects to a suitable sediment standard, not only because of our inability to model the transfer processes, but also because of a lack of toxicological data on the various affected components of the ecosystem. Thus, while the idea is valuable, it is not currently possible to set standards on the basis of toxicity and transfer processes.

2. ADVANTAGES AND DISADVANTAGES IN THE USE OF SEDIMENTS FOR CONTAMINANT MONITORING PURPOSES

2.1 Sediments

2.1.1 Several properties make sediments an essential component of multi-media investigations, including monitoring programmes, except in the cases of contaminants that are not susceptible to sediment associations and in the cases of sediments that are relic rather than recent. Bottom marine sediments are valuable matrices for use in monitoring programmes for several reasons: they integrate contaminant inputs over time; they are stationary relative to biota and water; in many cases they are easier to sample and analyse than either biota or water; and they constitute a reservoir and food source for certain marine organisms. Thus, it is generally easier to obtain adequate samples of sediments than of marine organisms, including infauna, and sediments offer the most suitable matrix in which to examine spatial and temporal gradients in contaminant concentrations, particularly in areas of strong physical gradients and considerable biological heterogeneity.

- 2.1.2 There are, however, certain factors which tend to limit the suitability of sediments in pollution monitoring activities. Sediments are one step further removed from man in most exposure pathways. Furthermore, while they are very suitable for assessing contaminant distributions, both on small and large scales, and temporal trends, it is far more difficult to determine what role sedimentary contaminants might play in effects on marine organisms and man because of the unknown nature of contaminant phases that are "available" to organisms. Sediments in erosional or complex erosional-depositional environments are either unsuitable for monitoring purposes or can only be used following detailed sedimentological, biological and geochemical investigations. Even the use of sediments in continuously depositorial environments is complicated by biological mixing (bioturbation) processes which limit the resolution of sedimentary measurements.
- 2.1.3 Finally, some contaminants do not concentrate in sediments and, even in cases where they do, the concentrations are not as large as those found in marine biota.
- 2.2 Suspended Particulate Matter
- 2.2.1 There would generally be much less value in the repeated monitoring of suspended particulate matter (SPM) because it is very mobile and changes rapidly in space and time.
- 2.2.2 Nonetheless, studies of suspended particulate matter are very important when conducting investigations in contexts other than monitoring. Suspended particles act as scavengers of trace components in seawater and generally have the highest concentrations in the system apart from biota. The study of suspended particulate matter can provide useful information on response times and on the pathways of transport of pollutants in coastal and estuarine environments. During the initial stages of a discharge, the response of the system will be easier to monitor using suspended particulate matter than bottom sediment because negligible deposition will have occurred in the short time elapsed. Similarly, suspended sediments can also be useful in studying the possible build-up of contaminant concentrations in the water column in nearshore areas over sand beds.

3. A GRADUATED APPROACH TO SEDIMENT MONITORING

- 3.1 General
- 3.1.1 Different problems dictate different approaches and levels of sophistication in monitoring. Monitoring in this context involves the repeated sampling of sediments to establish a trend. The trend may be temporal, the change in concentration at a point (or points) with time, or spatial, the spatial gradient in contaminant concentrations above some critical level within an area. Some areas receive contaminants from several sources and have done so for many years. Other areas are subject to pipeline discharges or dumping from a single source. In the latter case, it is relatively clear that monitoring should deal with the material being introduced; sampling should seek to establish its spatial spread in terms of grain size and chemistry, and repeated sampling should establish its dispersal and the build-up of concentration at the disposal site. This is a special case of the more general one of monitoring an area that is gradually being contaminated. How should that be dealt with?

- 3.1.2 The first decisions should involve the aims of the monitoring programme, the identification of the contaminant of interest, the extent of its sediment association, and the potential impact on biota in and on the sediments. When these decisions have been made for an area in question, an investigation of the area should be made to determine whether and how to monitor.
- 3.1.3 For any study of marine sediments in relation to contamination, there is a basic minimum of information about the deposit and its composition that is necessary. That information requires determination of:
 - 1. Grain size, $\% < 63 \ \mu m$
 - 2. Carbonate content
 - 3. Organic carbon content
 - 4. Aluminium and/or iron content
 - 5. The contaminant of concern
 - 6. Sample description.
- 3.1.4 A comprehensive survey in terms of marine pollution monitoring could not be conducted over a time frame of less than 5 years; such a long-term survey is necessary in order to understand the conditions so that the data can be properly interpreted. Furthermore, before work on contaminants can begin in an area at the most complete level of study, a survey of the deposition rate on a spatial basis is needed. Important information will be obtained already during the early phases of such studies, so consumers of the information need not expect to wait 5 or 6 years before they obtain some advice on the implications of sediment monitoring.
- 3.1.5 We suggest three levels of sampling and analysis appropriate to differing requirements. The first is the simplest, least expensive and least informative. The third should allow a complete assessment of the contaminant concentrations and budget for an area. The sampling is likely to be more rationally based than the simplest system and thus may ultimately be more cost-effective.

3.2 Level I, Simple: Grab Sampling of Surface Sediment

3.2.1 The samples taken by grab may be relatively undisturbed if care is taken in grab deployment, but in soft muds one cannot be certain that the upper half centimetre or so has not been washed away. Prior to doing any regional survey, the statistical variances associated with sampling need to be established, if comparison between surveys is desired. The basic parameters listed above are determined, making possible some investigation of contaminant concentration in relation to size and scavengers (organic C and Fe). The measurement of total contaminant concentration in surface sediments may be sufficient to relate to an absolute standard for decision-making purposes. However, there are several drawbacks to this sort of sampling and basic analysis. Without dated samples one cannot know the deposition rate and so not know either the time trend of contamination at the site, or whether a pre-industrial baseline concentration can be defined there. One does not have any basis for assessing the importance of biological mixing, although visual inspection of the sediment should reveal whether it is laminated or burrowed. However, the sample length will be insufficient to show the depth of biological mixing. Because of the uncertainty of knowing whether the surface has been recovered, there is a greater uncertainty in comparing successive surveys than if the surface is known to be undisturbed. This is more important for laminated deposits than for burrow-mixed ones as in the latter case a temporal change in pollutant input should show up throughout the mixed layer. However, not knowing the deposition rate makes for greater uncertainty about the reality of timetrends.

- 3.2.2 A decision-tree for use with results from Levels I and II is given as Figure 1 and is discussed under Level II.
- 3.3 Level II, Intermediate: Box-core Sampling of Surface Sediment
- 3.3.1 The greater quality of carefully taken box- or Kasten-cores allows (a) greater confidence in comparing the results of successive surveys because the surface is more reliably sampled, and (b) examination of the stratigraphy of the upper 0.2 to 2 m of the deposit. This examination may be simply visual or slabs may be X-rayed. The depth and intensity of biological mixing can be qualitatively assessed in this way. Several sub-samples can be taken from a box core and the small scale variability of the deposit can be determined. This level stops short of radiochemical determinations and therefore information is assumed not to be available to give deposition rate or to parameterise biological mixing. However, in cases where monitoring is dictated by statutory requirements this may be the most cost-effective option. In addition, the box core can be archived and if subsequently a need arises for down-core measurements for determining sedimentation or biological mixing rates, they can be made on preserved material. Additionally, it must be remembered that even if the Level III complete approach is adopted, the detailed down-core determinations need only be made on the first survey. Subsequent resurveys may be to a Level II standard.
- 3.3.2 The information gathered in surveys of the simple and intermediate levels must be acted on systematically. Figure 1 presents a simple decision tree for deciding whether and how to monitor a given area. The following are comments on the principal components of that decision tree.
 - a) Sediment-contaminant associations

There are few contaminants that do not associate strongly with sediments. Examples are Technetium and Lindane. It may be possible to compile a list of such weakly associated chemicals. In most cases sediments should be considered as potential monitoring devices; exceptions occur when the contaminant is present in soluble form and is known to behave conservatively in seawater.

b) Basis of decision to monitor

The decision to include sediments as monitoring devices will be based on the objectives of the pollution study. There may be obvious reasons for their inclusion, such as legal requirements, or the decision may have to be based on quality standards. There may be a legal requirement to carry out a monitoring programme. In the U.K., for example, monitoring is required for the control and licensing of waste disposal at dumping sites under the Dumping at Sea Act 1974 and the control and licensing of liquid radioactive effluent disposal under the Radioactive Substances Act 1960. In other cases, the demand for public information may dictate the conduct of a monitoring exercise. There may be other circumstances when a decision to monitor is made either as a safeguard to detect the operational failure of an industrial process or disposal operation, or to provide reassurance that there is no accumulation of contaminants in such circumstances.

c) Point-source inputs

In normal circumstances monitoring will be desirable in the vicinity of major point-source inputs, whether or not there is a legal obligation to do so. Examples include major sewer outfalls and pipe-line discharges of industrial wastes.

d) Contaminant concentration

Monitoring may also be required if it is considered that levels of contaminants are significantly elevated above a reference concentration. The reference value may represent the natural background level in the area in question and can be defined as a <u>baseline</u> value. In other circumstances, the reference value may represent the pre-existing concentration which indicates the situation prior to the current disposal practice or pollution investigation. This may have a different value from the natural background and can be defined as a benchmark value.

As contaminant levels are usually much higher in finer-grained sediments, it is appropriate to apply measurements to the fine-grained size fraction. This not only simplifies the analytical treatment, but also introduces a level of uniformity within the monitoring scheme allowing comparison of benchmark or baseline values with levels in the monitored samples. Problems associated with variable sediment composition are largely removed by adopting this approach. It is convenient to separate particles at the sand/silt size classification boundary ($63 \ \mu m$). Particles above and below this size tend to have different properties and behave differently. It is also a practical limit for separation by sieving. However, it should be confirmed that the contaminant does reside in the < $63 \ \mu m$ fraction and, if not, in which fraction it does lie. This size fraction should then be used for the monitoring exercises.

The main difficulty arises in attempting to set the concentration level of the contaminant, above the baseline or benchmark value, upon which the decision to monitor sediments is based. For substances which exist naturally in the marine environment, a contaminant may be considered significant (i.e., should be monitored) if it is found at concentrations of 1.5 - 2 times baseline or benchmark levels.

This approach is not applicable to substances introduced for the first time into the marine environment as a result of man's activities (e.g., PCBs). Quality standards for these substances will be set according to the toxicity and persistence of individual contaminants and in some cases may be comparable with the detection limits of current analytical techniques.

e) Erosional areas

Without radiochemical data areas of erosion may be identified by the presence of strong tidal currents, rough topography and outcrop of layers seen on a shallow seismic reflection profile (e.g., with a 3.5 kHz profiler). Areas not obviously erosional must be presumed depositional though possibly at very slow rates. Good surface samples ought to be taken for monitoring in this case. If the area is one of erosion and the sediment is burrow-mottled, then the contaminant is presumably introduced by burrowing organisms and a homogenised sample of the biologicallymixed layer may be used for monitoring. If the sediment in an erosional area is laminated, the situation is clearly complex and monitoring at Level II should only be conducted after further examination of the area.

3.4 Level III, Complete: Box-core Sampling with down-core Radiochemistry

3.4.1 The sampling methods at this level are the same as those at Level II but with the significant addition of radiochemical, or other, measurements to determine the rate of deposition and apparent diffusivity K_B due to biological mixing. The radionuclides most commonly used for the rate of deposition are the naturally occurring ²¹⁰Pb and ²³⁴Th and the man-made radionuclides ¹³⁷Cs and ²³⁹, ²⁴⁰Pu. The first two radionuclides may be used in determinations of K_B and the man-made radionuclides in assessing the depth of mixing in burrowed sediments. It is the objective of this work to determine contaminant budgets, and to understand the rate and mechanism of contaminant build-up in the sediment reservoir. This should also involve specification of <u>sources</u> and their magnitude, <u>pathways</u> and their relative importance, and <u>sinks</u> with their accumulation rates.

3.4.2 Muddy and sandy areas pose different problems. A more comprehensive decision tree than that in Figure 1 can be used for the former (see Figure 2), but sandy areas cannot always be neglected.

3.4.3 Muddy areas (sediments contain > 20% of < 63 μ m)

A systematic consideration of those aspects of the sediment necessary to arrive at a decision as to whether or not the sediments of an area should be monitored is here set out in the form of a decision tree (Figure 2). The parameters used are grain size, accumulation rate, contaminant concentrations and biological mixing rate.

Our general recommendation is that sediments with > 20% of < $63 \mu m$ material are sufficiently muddy to carry an appreciable contaminant load and are likely to be sufficiently homogeneous to minimise within-sample variability. There may be local requirements to use sediments with less mud than this (e.g., the discharge of highly contaminated mud into a sandy area).

The criteria to set for deposition rate depend on the desired frequency of monitoring. If frequent monitoring is desired, there must be a rapid deposition rate; for less frequent monitoring there can be a slower deposition rate. As an operational criterion, a deposition rate of 1 cm/yr would permit annual monitoring of an area. Thus, the relationship $f = R^{-1}$, where f is sampling frequency in years and R is rate of deposition in cm yr⁻¹, may be used. With this criterion, a 0.5 cm yr⁻¹ deposition rate would permit sampling every second year, while a 1 mm yr⁻¹ deposition rate would allow sampling every ten years. For a one-shot health check of an area the deposition rate does not matter. However, when very precise sampling is carried out using a box-corer, very little surface sample material is lost, and the basic criterion can be changed to permit annual sampling with a deposition rate of 0.5 cm/yr. In this case, the relationship 2 f = R⁻¹ can be used.

If the contaminant budgets and accumulation rates are known, more complex criteria can be used, for example:

- (a) the required time interval for statistically significant trends to be detected if the rate of input remains fairly constant,
- (b) the expected time interval for statistically significant trends to be detected if the rate of input were to alter appreciably,
- (c) an arbitrary time interval chosen for logistic reasons.

The necessity of determining the deposition rate at the top of the decision tree can present a significant stumbling block when beginning to decide where and whether to monitor. One method of screening samples is to use Xradiography to see which cores have the least amount of bioturbation or the thinnest bioturbation zone. This is particularly useful as a screening technique when a large number of cores have been taken on a grid and one wants to determine quickly which cores are likely to be the most promising in terms of deposition rate versus sediment mixing.

Contaminant concentration is clearly a major factor. However, it is not necessary to set criteria in cases where a study of an area is being con-

ducted prior to the introduction of contaminants, as monitoring will have to be carried out regardless of contaminant concentrations. For areas which have already been exposed to contaminants, we are not yet in a position to propose numbers. In general, if the concentration of a contaminant is more than twice the background level, taking due account of, and normalising for, variations due to biogeochemical processes within the sediments, then monitoring should take place.

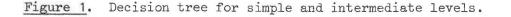
Contaminants can enter the sediment column by either advection (net deposition) or biologically-induced diffusion. In most situations both processes act, though in laminated deposits diffusion is negligible. Early work using a single radionuclide (often ²¹⁰Pb) characterized the diffusion by a single value of diffusivity. It is now recognised that the intensity of biological mixing decreases downwards and a depth-dependent diffusivity is necessary. This may be achieved by numerical modelling (Olsen et al., J Geophys. Res., 86, 11010-8) constrained by estimates of diffusivity based on the profiles of several radionuclides; those with short half-lifes for sediment near the surface and longer half-life radionuclides deeper down, e.g. ²³⁴Th (24 days), ²¹⁰Pb (22 years), ¹⁴C (5600 years). From such an approach, good estimates of both biological diffusivity and deposition rate may be obtained. Deposition rates obtained with only one radionuclide may well be in error by a factor of two. This means that a contaminant may be incorporated into the sediment column even in cases where there is only a slow net accumulation rate of other sedimentary components. In order for there to be a high rate of build-up of the contaminant in the sediment column in such a case, there must be a high rate of biological mixing (bioturbation) and thus a high apparent diffusivity, KB. With a high value of KB, annual monitoring might be sustainable in an area of low R (rate of deposition). The time scale of mixing is given by L^2/K_B , where L is the thickness of the mixed layer and K_B is the mixing rate (in cm² sec⁻¹). For a mixed layer of 10 cm thickness and a K_B of 10⁻⁶ cm² sec⁻¹, the mixing time would be about three years. Values of Kg much lower than this would indicate a bio-mixing time too low to sustain a monitoring programme, in the absence of an adequately high sediment accumulation rate.

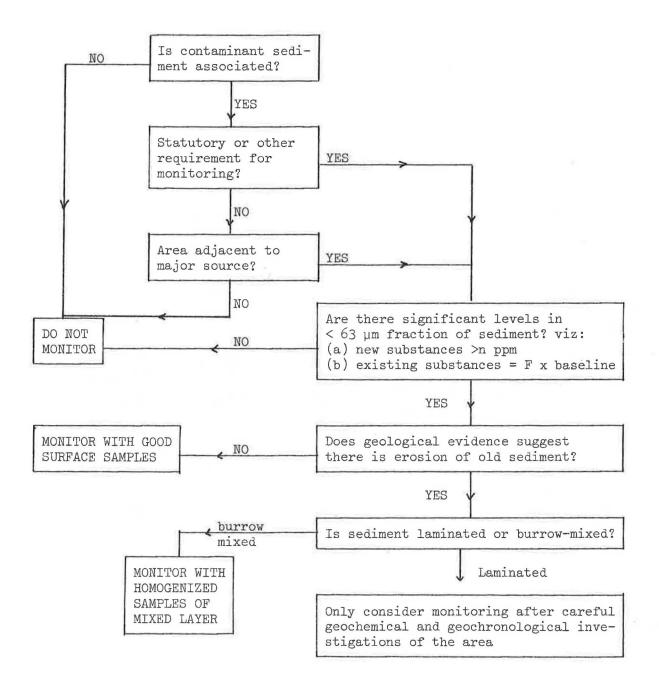
Thus, in areas where there is not a high deposition rate, but where it can be shown that contaminants are accumulating due to their biological working into the sediments, a determination of the mixing time is needed. A combination of diffusivity and mixed layer depth should give a mixing time appropriate for the sampling frequency desired, i.e., a mixing time of one year is necessary for annual sampling, and a mixing time of 5 years will permit sampling every fifth year. The most reliable way of obtaining these mixing times is by measurement of radionuclides of different half-lifes, coupled with numerical modelling.

It is clear that in order to avoid these complexities, regions of rapidly accumulating laminated bottom sediments with little or no burrowing infauna are best. However, such regions are not common in nearshore waters. In most areas the detailed down-core sedimentological, chemical and radiochemical work will only need to be done once, on the first survey. Thereafter the surface or the mixed layer will be determined for monitoring.

3.4.4 Sandy and gravelly areas

Sandy areas are not normally suitable for monitoring, unless it is necessary to assess the impact of a point source, for example, in the case of dumping grounds. In that case, a decision tree for sands is not really appropriate in terms of deposition rate, because one is more concerned with the horizontal spreading and increasing concentration of dumped materials. Another case in which it could be useful to monitor in sandy areas is when the contaminant deposited is in the form of particles of similar size to sand, e.g., mining wastes. Another type of area of interest is a sandy coastal area, and also some deeper areas, where there is some very fine particulate matter (but < 20% < $63~\mu$ m) which attracts diatoms on the surface and appears to be able to incorporate contaminants. An increase in the proportion of mud to the deposits due to dumping may also constitute a disturbance of sandy areas. For the biota of a sandy bottom, mud itself is a contaminant and monitoring the change in texture is a simple task. However, as noted above, other than in areas of direct dumping, monitoring of sandy bottoms is generally less suitable.





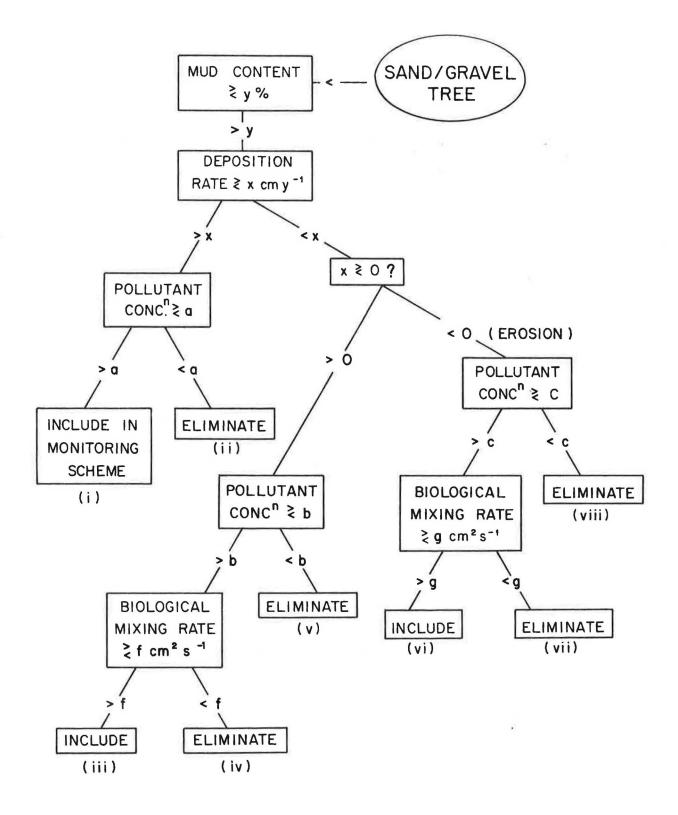


Figure 2. Decision tree for muds.

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ANNEX 3

GUIDELINES FOR THE PREPARATION OF REGIONAL ENVIRONMENTAL ASSESSMENTS*

by

J M Bewers¹, A Jensen², A D McIntyre³, M M Parker⁴, J B Pearce⁵ and J E Portmann⁶

ABSTRACT

This paper proposes a mechanism for the preparation of environmental assessments for regional areas within the ICES sphere of interest. It describes both the format of, and the procedures for preparing, assessments that might enable the quality of individual regional environments to be appraised and compared with that of other areas.

¹Bedford Institute of Oceanography, Dartmouth, Nova Scotia B2Y 4A2, Canada.
²Marine Pollution Laboratory, Kavalérgaarden 6, 2920 Charlottenlund, Denmark.
³Marine Laboratory, P.O.Box 101, Victoria Road, Aberdeen AB9 8DB, Scotland.
⁴Fisheries Research Centre, Abbotstown, Castleknock, Co. Dublin, Ireland.
⁵Sandy Hook Laboratory, NMFS/NOAA, Box 428, Highlands, N.J. 07732, U.S.A.
⁶Fisheries Laboratory, Remembrance Avenue, Burnham-on-Crouch, Essex CMO 8HA, England.

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INTRODUCTION

The need for, and methods of preparing, regional environmental assessments for individual coastal or marginal sea regions within the ICES geographical area was discussed during the 1982 meeting of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA). This discussion arose during consideration of the Assessment of the Effects of Pollution on the Natural Resources of the Baltic Sea (Melvasalo et al., 1981) carried out jointly by the Interim Baltic Marine Environment Protection (Helsinki) Commission and ICES. It was thought timely to consider the preparation of similar reviews for other areas so that a more comprehensive picture of the state of contamination and/or pollution within the whole ICES area might be gained. As a consequence of these discussions during the WGMPNA meeting, a small sub-group was established to prepare a relevant contribution for the 1982 Statutory Meeting. This paper is the result of intersessional work by this sub-group, which comprises the authors, and is intended to stimulate discussion during the Statutory Meeting. It should be read in conjunction with section 7 of the Report of the 1982 meeting of the WGMPNA (ICES Doc. C.M. 1982/E:3). The proposals contained in this paper require for their implementation the participation of hydrographers, marine chemists and marine biologists.

PURPOSE AND SCOPE

This paper is intended to provide a framework for the preparation of environmental assessments of coastal and regional sea areas. Each assessment is intended to comprise a review of the kinds and degrees of anthropogenic disturbances to the area set in the context of existing knowledge of physical, chemical and biological conditions. One objective of these reviews would be to state succinctly how contaminated the subject regions are, and indicate the degree to which existing or potential changes resulting from anthropogenic activities, could have been, or can be, predicted. The framework for the preparation of such assessments has been devised to enable this to be accomplished, as well as to delineate deficiencies in knowledge that restrict the comprehensiveness of each review. Furthermore, the framework is intended to facilitate the preparation of intercomparable environmental assessments so that the relative extent of anthropogenic disturbances in different areas can be readily appreciated. Emphasis has, therefore, been placed upon obtaining uniformity amongst the assessments of individual areas to simplify the task of making such intercomparisons.

Both the authors, and the WGMPNA, have also considered the nature of the audience for regional assessments of this type within ICES. In the first instance, it is expected that the audience would be the Working Group itself and ACMP. Both of these groups could use the assessments to make informed judgements about the nature and extent of anthropogenic influences, to draw comparisons between different regions, and also to determine where additional information needs to be acquired (i.e., where existing information is deficient). Perhaps the most valuable aspect of the assessments might be to enable these groups to provide warning of potential adverse consequences that might ensue from the existing or future deterioration of the physical, chemical or biological conditions in an area. It seems clear that there exists some conviction among the WGMPNA that regional environmental assessments are needed to assist in such prognoses. It is also expected that the documents should be understandable to a wider audience, including regulatory commissions, administrators and the general public, so that a more diverse appreciation of the environmental status of various regions bordering the North Atlantic might be gained. Finally, it should be stressed that, if the value of the proposed assessments is established, other agencies might wish to use the same approach for the preparation of assessments for regions outside the ICES sphere of interest.

APPROACH

It has been assumed that the briefer the assessment, the easier will be the task of assimilating the information contained within it and of giving emphasis to the most serious environmental disturbances. Environmental assessments have been, or are being, prepared for the Baltic Sea, the Skagerrak/Kattegat area, the German Bight, and several areas along the eastern coast of North America, such as the New York Bight. Indeed, as indicated in the introduction to this paper, the review of the Baltic Sea (Melvasalo et al., 1981) was the primary stimulation to the WGMPNA in considering the desirability of preparing similar reviews for other ICES areas. However, the magnitude of effort devoted to the review of the Baltic Sea was very large and it is not considered reasonable to expect comparable levels of effort to be devoted to the review of each of the other candidate sub-areas. Furthermore, although these various reviews are generally very valuable for gauging the prevailing state and extent of anthropogenic disturbances in regional areas, they tend to be rather voluminous and this makes them difficult to digest and complicates the process of drawing comparisons between different regions. For these reasons, the authors have chosen to stress brevity in the approach to the preparation of regional assessments. The experience gained through the GESAMP 'Health of the Oceans' review, in which an executive summary of 8 pages was prepared, would suggest that brevity may be achieved without compromising the value and objectives of such assessments. The authors therefore propose that the individual assessments be about 20 pages (7,000 words) in length. Expansive background material, which may be produced as part of the preparatory process and to which reference may be required for making

detailed comparisons, could be published independently, or as a collection of background documents, much as was done in the case of the 'Health of the Oceans' review.

Another condition that the authors have accepted in formulating a procedure for the preparation of regional environmental assessments is uniformity of presentation. They have tried to deduce a format which would be universally applicable, and which would simplify both the drafting and assimilation of the documents and, ultimately, comparisons between different regions. Finally, since the main types of marine information needed for the preparation of an assessment are physical (hydrographic), chemical and biological (including fisheries-related material), it is believed that a disciplinary approach would greatly simplify the initial stages of the preparatory process. It is, therefore, proposed that, while the assessments should contain a multi-disciplinary summary, the main bodies of the documents should be prepared from individual disciplinary perspectives.

The disciplinary sections should therefore be prepared by scientists closely involved in the particular discipline within the regional area concerned. Involvement of specialists from laboratories that do not normally report to ICES would ensure full coverage of disciplines that are often under-represented in ICES fora. It would have the added advantage of wider acceptability by potential users of the reviews who are not familiar with ICES committees.

PROCEDURE AND FORMAT

The main body of an assessment should comprise self-contained disciplinary sections. Each such section should contain two parts with an aggregate length of approximately 6 pages (2,000 words). The larger of these would constitute a summary, or overview, of the existing disciplinary knowledge of the area concerned. This should be gleaned from existing information in the literature rather than requiring a large data-gathering exercise which might itself consume significant effort. Emphasis should be placed upon obtaining information summaries from scientists closely involved in the discipline and regional area of interest. The other part of the disciplinary sections should attempt to describe the extent to which the area has been, or might be, affected by anthropogenic activities in their broadest sense. Thus, anthropogenic influences that should be considered should not be restricted to contaminant inputs and their impacts, but should include physical modifications (such as freshwater regulation and the extraction of resources) to the region and their consequences. This section should conclude with an evaluation of the degree to which evidence of the effects of anthropogenic activities has been acquired and where additional information is needed to detect such effects. Some attention should also be paid to judging the quality of the data upon which the disciplinary information is based and reference should be made to unresolved aspects of the prevailing conditions in the region concerned.

Once the disciplinary sections have been prepared, using these guidelines, some attempt must be made to summarise the conditions in the region and assess, from a multidisciplinary perspective, the ways and extent to which the region has been affected by anthropogenic activities. This summary would constitute a synopsis of the conclusions reached in the disciplinary sections, but every effort should be made to relate the disciplinary sections to one another and to weigh their relative importance in striking an overall balance between the disciplines. The summary should ultimately form the basis for initial intercomparisons of the environmental conditions and severity of anthropogenic effects in different regions. The disciplinary sections would provide greater detail for these intercomparisons, whilst the background documents, published separately and cited in the assessment, would provide even greater detail, if needed.

The layout, or format, of the assessments would therefore be as follows:

1	Summary	(2-3 pages/700-900 words)
2.1	General circulation and physical oceanography	(3 pages/1 000 words)
2.2	Extent of anthropogenic modifications to the	
	physical oceanography	(2 pages/700 words)

3.1	Incidence and distributions of potential conta- minants and general marine chemistry	(4	pages/1 400 words)
3.2	Modifications to chemical fluxes and extent of contamination	(2	pages/700 words)
4.1	General biology and fisheries of the area	(5	pages/1 700 words)
4.2	Biological trends and/or disturbances due to anthro- pogenic activity (including exploitation of fishe- ries resources)	(3	pages/1 000 words)
5.	References	(1	page)

The total length of the document would then be 22-23 pages, or about 7 500 words. The authors have purposely suggested that the physical oceanographic section be somewhat shorter, and the marine biological section somewhat longer, than the average section length because of the relative diversities of the information involved in these disciplines. Summary tables and figures might be included in addition to the text, because they may simplify the intercomparisons of different regions. The sole justification for increased length of an assessment should be the ability to present more detailed conclusions as to the nature and extent of anthropogenic disturbances. Additional tabular material might comprise mass-balances for particular contaminants or summaries of trends in species diversity, year-class success or contamination of biological organisms. Reference should only be made to detailed compendia of information and other literature that provide greater detail and amplification of the contents of the assessment. If a comprehensive bibliography is considered valuable, this should be published independently and merely referenced.

The authors fully appreciate that their argument for brevity greatly restricts the detail that can be provided in the assessments. Furthermore, it may result in the document being more controversial than it would be otherwise. However, the need to resolve controversy, in order to prepare the disciplinary sections may well prove to be a great advantage in putting together a concise, reasoned and widely-accepted description of prevailing conditions. Overall, it is strongly felt that brevity will demand the preparation of an easily comprehensible and relatively straightforward document that will greatly simplify subsequent intercomparisons of the extent to which regional areas have been affected by anthropogenic activities.

REFERENCES

- ICES, 1982. Report of Eighth Meeting of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic. ICES C.M. 1982/E:3.
- GESAMP, 1982. The Review of the Health of the Oceans. Reports and Studies GESAMP No. 15.
- Melvasalo, T., Pawlak, J., Grasshoff, K., Thorell, L., and Tsiban, A. (Eds.) 1981. Assessment of the Effects of Pollution on the Natural Resources of the Baltic Sea, 1980. Baltic Sea Environment Proceedings No. 5B.

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ANNEX 4

TOXAPHENE

A Review

by

J F Uthe

Fisheries and Environmental Sciences Halifax, Nova Scotia, B3J 2S7 Canada

and

L Reutergårdh The National Swedish Environment Protection Board Wallenberg Laboratory, Special Analytical Laboratory University of Stockholm, S-106 91 Stockholm Sweden

ABSTRACT

This paper reviews and describes the distribution of toxaphene (polychlorinated camphene, PCC, Camphechlor "Hercules 3956") in the marine environment in the light of the limited data that are available. In addition to the general toxicology of toxaphene, the implications and public health aspects of the occurrence of toxaphene in the aquatic environment are discussed.

INTRODUCTION

Toxaphene is the tradename for a chlorinated pesticide introduced in the mid-1940s by Hercules Chemical Inc. Toxaphene (polychlorinated diterpenes, polychlorinated camphenes, PCC, Camphechlor, Polychlorocamphene, Strobane) is produced by chlorination of camphenes produced by isomerization of a-pinene. This synthetic method results in a complex mixture of at least 670 camphene compounds with a total chlorine content of 67-69% weight and 6 to 10 chlorine atoms per molecule (Casida et al., 1974; Jansson, 1982). Based on a bornane structure, there are 13 824 theoretical isomers of toxaphene with from one to eighteen chlorine atoms, only a few of which have been synthesized. About 25% of the total peak area found on analysis by capillary gas chromatography (electron capture detection) can be accounted for by identified toxaphene components (Saleh and Casida, 1979). The most toxic component of toxaphene isolated to date is 2,2,5-endo-6-exo-8,9,9,10octachlorobornane (Saleh and Casida, 1979). Since its introduction, toxaphene has been the most heavily used insecticide in the U.S.A.; annual toxaphene production in the United States has been approximately 50 million kg (U.S.EPA, 1978). Some other countries with known applications of toxaphene or similar products (1977 data) were Mexico (1.8 million kg), India (0.4 million kg), Czechoslovakia (0.03 million kg), Hungary (0.3 million kg), and Poland (0.15 million kg). The U.S.A. production estimates should be compared with the peak production in the U.S.A. of DDT of 63 million kg in 1968 (Bevenue, 1976). Toxaphene that has been manufactured by the major American producer (Hercules) has been extremely consistent from batch to batch between 1949 and 1975 and is easily differentiated from toxaphene produced by other manufacturers and from radiolabelled toxaphene (Saleh and Casida, 1979). In addition to its use on cotton and vegetable crops and in livestock dips, some toxaphene has been used as a piscicide in freshwater lakes (Pollock and Kilgore, 1978; Terriere et al., 1966). Toxaphene residues in wildlife from remote, unpolluted areas were found by Jansson <u>et al</u>. (1979) in fish, sea birds and seals. Ballschmiter and Zell (1980) and Zell and Ballschmiter (1980) reported toxaphene residues in tissues of fish captured in widely separated and apparently pristine areas of the world. Toxaphene residues have also recently been reported in fish from the western part of the North Atlantic by Zitko (1980) and Musial and Uthe (1983).

The multiplicity of components in toxaphene and the general lack of pure analytical standards and good analytical methods to separate these compounds from other chlorinated hydrocarbons makes the accurate measurement of toxaphene difficult (Barthel <u>et al.</u>, 1969; Widequist <u>et al.</u>, 1982). For example, the presence of relatively high levels of toxaphene in a herring oil used in an interlaboratory comparative exercise on the analysis of PCBs and other organochlorines was reported by certain participating laboratories but not by others (Uthe and Musial, 1982). These difficulties can partially be solved using chemical-ionization mass spectrometry (Jansson and Widequist, 1983; Ribick <u>et al.</u>, 1982).

Toxaphene has been the subject of a number of review articles (Durkin <u>et al.</u>, 1980; Casida and Saleh, 1978; Pollock and Kilgore, 1978). Ambient water quality criteria have been established in the U.S.A. (U.S.EPA, 1978). In freshwater the guideline limit is 0.007 µg/l as a 24-hour average with a 0.46 µg/l maximum. The corresponding limits for seawater are 0.019 µg/l and 0.12 µg/l, respectively. Due to the carcinogenic nature of toxaphene, a drinking water guideline of 0.00047 to 0.0000047 µg/l has been suggested at an interim target risk level of 10^{-5} to 10^{-7} .

Environmental Aspects of Toxaphene

The relatively high volatility of toxaphene results in appreciable atmospheric concentrations both during the post-application period and following spring tilling, especially in those agricultural areas where toxaphene is used (Arthur et al., 1976). The potential long-range aerial transport of toxaphene to the marine environment was demonstrated through detection of ng/m^3 levels in air over both Bermuda and the open ocean (Bidleman and Olney, 1975). Levels of toxaphene ranged from the detection limit (0.02 ng/m^3) to 5.2 ng/m³, with mean seasonal air concentrations over Bermuda of $0.5 - 2.8 \text{ ng/m}^3$. Toxaphene levels were at least twice as high as PCB levels and ten times higher than other organochlorine pesticide levels. Toxaphene was also detected in air samples at various North American sites including areas far removed from application, e.g., the Northwest Territories of Canada (Bidleman et al., 1976). Bidleman and Christensen (1979) studied atmospheric removal processes for a number of organochlorines over a high salinity marsh in South Carolina, U.S.A. The mean aerial concentration of toxaphene was 1.7±2.4 ng/kg air, while the rainwater mean was 159±133 ng/kg rain. Rainwater concentrations of toxaphene exceeded those of all other organochlorines studied. Dry deposition rates of toxaphene ranged from 21 to 512 ng/m²/day. Sundström (1981) reported 3-6 ng toxaphene/liter in rainwater collected in August-September 1980, 100 km south of Stockholm, Sweden in spite of the fact that toxaphene-containing products have not been registered in Sweden since 1956. Only 5 600 kg toxaphene had been sold on the Swedish market prior to 1956.

Toxaphene has not been reported in routine studies of surface waters in the U.S.A. The relatively high detection limit for toxaphene probably precluded its detection (Mattraw, 1975; Schafer <u>et al.</u>, 1969). Toxaphene residues have been detected in surface and ground waters near manufacturing plants and high usage areas (Reimold and Durant, 1973; Nicholson <u>et al.</u>, 1966), but it is adsorbed on suspended matter and sediments.

Photolysis of toxaphene in air has apparently not been systematically studied. Wolfe and co-workers (1976) concluded that sunlight photolysis of toxaphene in pure water was very slow. Weber and Rosenberg (1980) found that micro-organisms in estuarine sediments could slowly metabolize toxaphene under both aerobic and anaerobic conditions, but could not use it as a carbon source since the overall concentration of toxaphene-like material did not decrease over the 21-day term of the experiment. A change in the polarity and an increase in water solubility of toxaphene components following incubation with sediment was observed by Williams and Bidleman (1978). Investigators generally report that toxaphene residues in environmental compartments give altered chromatograms compared with toxaphene itself (Durkin <u>et al</u>., 1980). Toxaphene has been shown to persist in freshwater lake waters and sediments up to 9 years after treatment (Hughes, 1970).

Toxaphene is accumulated by aquatic biota (Terriere et al., 1966), bacteria, fungi and green algae (Paris et al., 1975), plankton (Johnson, 1966) and by organisms from higher trophic levels. Toxaphene has been detected in zooplankton samples from the Chesapeake Bay (Munson, 1976). Salt marsh (grasses) accumulated toxaphene levels as high as 36.3 mg/kg. Fish and saltwater invertebrates accumulated high levels of toxaphene from water, e.g., maximum bioconcentration factors of 32,800 for oysters (Crassostrea virginica) (Lowe et al., 1971) and 27,900 and 29,500 for larval and juvenile longnose killifish (Fundulus) (Schimmel et al., 1977). After 12 weeks in clean water, toxaphene levels in exposed oysters were only 10% of maximum levels (Lowe et al., 1971). Jansson et al. (1979) reported levels of toxaphene residues in Baltic Sea organisms as follows: herring (Clupea harengus) 13 mg/kg muscle lipid; guillemot (Uria aalge) 17 mg/kg egg lipid; and grey seal (Halichoerus grypus) 11 mg/kg blubber. In contrast to DDT and PCB, toxaphene did not biomagnify. A freshwater fish, Arctic char (Salvelinus fontinalis), had 9 mg/kg muscle lipid. On a lipid weight basis, toxaphene residues in Alpine char (Salvelinus alpinus) were 124 ng/g, 68 ng/g in Antarctic cod (Dissostichus) liver and 72 ng/g in sperm whale oil (Ballschmiter and Zell, 1980). Musial and Uthe (1982) estimated toxaphene levels of 4.4 and 12 mg/kg in two herring (Clupea harengus harengus) oil samples, and 2.4 mg/kg in cod (Gadus morhua) liver from the northwestern Atlantic. They did not detect toxaphene in scallop (Placopecten magellanicus) from Georges Bank. Widequist et al. (1982) found toxaphene concentrations of 5.2 - 7.9 mg/kg lipid in guillemot muscle. Another herring-feeding species, the ringed seal (Pusa hispida) had 6 - 12 mg toxaphene/kg blubber in pooled samples. Pooled eggs from osprey (Pandion haliactus) and marsh harrier (Circus aeroginosus) had mean toxaphene residues of 3.7 and 5.2 mg/kg fat, respectively.

The above information implies that widespread contamination of the marine environment by toxaphene is occurring. This, along with the observation that fish eliminate toxaphene from their bodies (Mayer <u>et al.</u>, 1975; Lowe <u>et al.</u>, 1971), indicates that these marine species are being consistently exposed to toxaphene. All components of toxaphene are not eliminated at the same rate. Rather, there appears to be selective elimination of lower molecular weight components with formation and storage of more polar material (Pollock and Kilgore, 1980; Saleh <u>et al.</u>, 1979). Biessman <u>et al.</u> (1983) found that the Japanese quail tended to eliminate higher molecular weight components. It must be emphasized that the problems in analyzing toxaphene make quantitative studies of the pesticide in biota, particularly at low levels of contamination, difficult.

Some work has been done with radiolabelled toxaphene. Casida and Saleh (1978) have studied the metabolism of a number of purified or partially purified toxaphene components in a number of species of mammals, houseflies and chickens. Dehydrochlorination occurred, apparently mainly in the liver, since liver and feces contained metabolites while fatty tissues did not. Biessman et al. (1983) found high concentrations of ¹⁴C in bone marrow of Japanese quail dosed with ¹⁴C-toxaphene and suggested that this might explain the impaired bone development observed in the birds. Crowder and Dindal (1974) found that 53% of the chlorine of an oral toxaphene dose in rats was excreted as chloride in nine days, 27% in the feces, 15% in the urine. All toxaphene fractions studied by Ohsawa et al. (1975) were approximately 50% dechlorinated in rats. These investigators also concluded that only 2% of the dose was eliminated as carbon dioxide and 3% eliminated unchanged.

The binding of toxaphene with mammalian cytochrome P-450 (Kulkarni, 1975) and the potentiation of toxaphene by piperonyl butoxide (Saleh <u>et al.</u>, 1977) suggest metabolism of toxaphene through the mixed function oxidase system. No information was found on toxaphene metabolism in marine mammals. Aquatic Toxicology

Toxaphene is acutely lethal to fish and invertebrates, being rated second only to endrin in toxicity to fish (Chaiyarach <u>et al.</u>, 1975; Johnson, 1968; Henderson <u>et</u> <u>al.</u>, 1959). Toxicity tests with five marine species yielded unadjusted 48- and 96hour LC₅₀ values from 0.5 μ g/l to 5.5 μ g/l (Schimmel <u>et al.</u>, 1977; Korn and Earnest, 1974; Butler, 1963, 1964). Studies on marine shellfish yielded a 96-hour LC₅₀ value of 0.11 μ g/l for mactrid clams (U.S.EPA, 1978).

Upon fractionation, certain components of toxaphene have been shown to have greater toxicity for fish than the parent mixture (Turner <u>et al.</u>, 1975). Of the usual water quality parameters which may affect the toxicity of toxaphene, only increasing temperature has an effect of significant magnitude (Macek <u>et al.</u>, 1969). Based upon the limited information available, salinity does not appear to affect the toxicity of toxaphene significantly (U.S.EPA, 1978).

Chronic exposure of fish to toxaphene has been associated with the development of bone lesions (Hamilton <u>et al.</u>, 1981; Mayer and Mehrle, 1976; Mayer <u>et al.</u>, 1975; Mehrle and Mayer, 1975a,b). Growth rates were generally reduced by exposure to toxaphene (Mehrle and Mayer, 1975a,b; Mayer <u>et al.</u>, 1975). In saltwater fish, concentrations of toxaphene that did not affect individuals in 96-hour testing were not very different from concentrations causing effects after long-term exposure (U.S.EPA, 1978).

Toxaphene has an inhibitory effect on a number of ATPases in a variety of fish tissues <u>in vitro</u> (Desaiah and Koch, 1975; Davis <u>et al.</u>, 1972) and has been shown to depress mitochondrial oxygen uptake (Hiltibran, 1974). A variety of histopathological, reproductive, developmental and other sublethal effects have been documented in freshwater fish following long-term exposure to toxaphene (Mayer <u>et al.</u>, 1975; Mehrle and Mayer, 1975b; Courtenay and Roberts, 1973; Warner <u>et al.</u>, 1966). Nervous system damage has been reported in carp (<u>Cyprinus carpio</u>) by Kayser and coworkers (1962).

The development of resistance to toxaphene in a number of fish species has been reported (Finley <u>et al.</u>, 1970; Ferguson <u>et al.</u>, 1964). Multiple generation studies indicated that genetic resistance was present rather than development of tolerance. Chronic exposure to toxaphene has been reported to increase sensitivity to toxaphene (Lowe, 1964).

Crustacea in various developmental stages show different sensitivities to toxaphene (Courtenay and Roberts, 1973). Exposure of mysid shrimp to 0.14 ng/l toxaphene in a lifetime study decreased the number of young per female by 82% (Nimmo, 1977). Chronic exposure of oysters (Crassostrea virginica) to 1.0 μ g toxaphene/liter along with DDT and parathion (Lowe et al., 1971) resulted in decreased growth. A variety of histological and other effects were observed including fungal infections. The oysters recovered when placed in clean water. Exposure of clam larvae to 0.15 μ g/liter toxaphene for 12 days did not kill but drastically reduced growth. The development of tolerance has been reported in freshwater shrimp (Naqvi and Ferguson, 1970), freshwater cyclopoids (Naqvi and Ferguson, 1968) and crayfish (Albaugh, 1972). The International Joint Commission (1977) has recommended a water standard of 0.008 μ g/liter for fish. No information was found describing effects of toxaphene in marine mammals.

Public Health Aspects of Toxaphene

The use of toxaphene in animal dips for ectoparasite control and the ingestion of toxaphene-containing feeds exposes livestock to the pesticide. Although toxaphene residues are consistently found in beef fats, the incidence and levels of contamination are low (U.S. Department of Agriculture, 1978). Sporadic occurrence in other animal products was also reported. Toxaphene also occurs in milk from dairy cattle ingesting low levels of the pesticide. Processing and short-term storage had little effect on toxaphene levels (Zweig et al., 1963). The United States National Cancer Institute (1979) concluded that toxaphene was carcinogenic in male and female B6C3F1 mice, increasing the incidence of hepatic carcinomas, and suggested that toxaphene also causes thyroid tumours in Osborne-Mendel rats. Studies on a closely related pesticide, Strobane (chlorinated terpenes), by Innes and co-workers (1969) demonstrated tumour formation in two strains of mice. Studies by Chernoff and Carver (1976) and Kennedy <u>et al.</u> (1973) could not find teratogenic effects of dietary toxaphene (25 mg/kg feed) in rats. There were also no reproductive effects in spite of signs of maternal and fetal toxicity. Epstein <u>et al</u>. (1972), using a modified dominant lethal mutagenic assay in mice, could find no lethal mutagenic effects in mice. Toxaphene was mutagenic in the Ames strain TA-100 Salmonella assay system (U.S.EPA, 1978).

Market basket surveys in the U.S.A. (Duggan and Corneliussen, 1972) estimated that dietary exposure of people in cities not located in areas of high toxaphene usage averaged 0.021 μ g/kg body weight/day and that this average has decreased since then. In the years 1974-1976, fish was the most contaminated foodstuff included in the studies.

The U.S. National Academy of Sciences (1977) has estimated an acceptable daily intake of toxaphene by man of 1.25 μ g/kg body weight, while the U.S. Environmental Protection Agency (1978) has recommended that an intake not exceed 0.042 μ g/kg body weight/day. Tolerance levels for toxaphene in American foodstuffs (U.S.EPA, 1978) range from 0.1 mg/kg in sunflower seeds up to 7 mg/kg for certain vegetables and animal fats. The Canadian tolerance for toxaphene in citrus fruit is 7.0 mg/kg, while in the Netherlands and Federal Republic of Germany the corresponding tolerance is 0.4 mg/kg (Gunther, 1969). The World Health Organization (1974) has recommended toxaphene guidelines from 0.3 mg/kg in milk and milk products to 5 mg/kg for animal fats.

The ubiquitous occurrence of toxaphene in marine biota (Ballschmiter and Zell, 1980; Jansson <u>et al.</u>, 1979) and the recent report (Musial and Uthe, 1983) of relatively high levels of toxaphene in edible portions of certain marine fish as well as the slow degradation of the pesticide suggests that toxaphene levels in marine species should be examined more closely. It is recognized, however, that analysis for toxaphene is still very difficult. The U.S. Environmental Protection Agency has posted notice (Fed. Reg., 1982) that many registrations of toxaphene use will be cancelled.

REFERENCES

- Albaugh, D.W., 1972. Insecticide tolerances of two crayfish populations (Procambarus actus) in South-Central Texas. Bull. Environm. Contam. Toxicol. 8:334-338.
- Arthur, R.D., Cain, J.D. and Barrentine, B.F., 1976. Atmospheric levels of pesticides in the Mississippi delta. Bull. Environm. Contam. Toxicol. 15:129-134.
- Ballschmiter, K. and Zell, M., 1980. Baseline studies of the global pollution 1. Occurrence of organohalogens in pristine European and Antarctic environments. Intern. J. Environ. Anal. Chem. 8:15-35.
- Barthel, W.F., Hawthorne, J.C., Ford, J.H., Bolton, G.C., McDowell, L.L., Grissinger, E.H. and Parsons, D.A., 1969. Pesticides in water. Pestic. Monit. J. 3:8-66.
- Bevenue, A., 1976. The "bioconcentration" aspects of DDT in the environment. Residue Reviews. 61:37-112.
- Bidleman, T.F. and Christensen, E.J., 1979. Atmospheric removal processes for high molecular weight organochlorines. J. Geophys. Res. 84:7857-7862.

- Bidleman, T.F., Rice, C.P., Olney, C.E., 1976. High molecular weight chlorinated hydrocarbons in the air and sea: Rates and mechanisms of air/sea transfer. In Marine Pollution Transfer. H.L. Windom and R.A. Duce (Eds.). D.C. Heath & Co. Ltd. p. 323-351.
- Bidleman, T.F. and Olney, C.E., 1975. Long range transport of toxaphene insecticides in the atmosphere of the western North Atlantic. Nature. 257: 475-477.
- Biessman, A., Muhammed, A. and Slanina, P., 1983. Distribution, metabolism and excretion of ¹⁴C-toxaphene in Japanese quail. Toxicology. In press.
- Butler, P.A., 1964. Pesticide-wildlife studies 1963. A review of Fish and Wildlife Service investigations during the calendar year. U.S. Dept. Interior. Wildl. Circ. 199:5-130.
- Butler, P.A., 1963. Commercial fisheries investigations: pesticide-wildlife studies, a review of Fish and Wildlife Service investigations during 1961 and 1962. U.S. Dept. Interior. Fish. Wildl.Circ. 167:11-45.
- Casida, J.E. and Saleh, M.A., 1978. Toxaphene: Composition and toxicology. U.S.EPA document EPA - 600/1-78-060. NTIS PB 288-412. 68 pp.
- Casida, J.E., Holmstead, R.L., Khalifa, S., Knox, J.R., Ohsawa, T., Palmer, K.J. and Wong, R.Y., 1974. Toxaphene insecticide: A complex biodegradable mixture. Science 183: 520-522.
- Chaiyarach, S., Ratananun, V. and Harrel, R.C., 1975. Acute toxicity of the insecticides toxaphene and carbaryl and the herbicides propanil and molinate to four species of aquatic organisms. Bull. Environm. Contam. Toxicol. 14:281-284.
- Chernoff, N. and Carver, B.D., 1976. Fetal toxicity of toxaphene in rats and mice. Bull. Environm. Contam. Toxicol. 15:660-664.
- Courtenay, W.R. Jr. and Roberts, M.H. Jr., 1973. Environmental effects on toxaphene toxicity to selected fishes and crustaceans. U.S.EPA, Office of Research and Development. Doc. EPA-R3-73-035. 73 pp.
- Crowder, L.A. and Dindal, E.F., 1974. Fate of ³⁶Cl toxaphene in rats. Bull. Environm. Contam. Toxicol. 12:320-327.
- Davis, P.W., Friedhoff, J.M. and Wedemeyer, G.A., 1972. Organochlorine insectticide, herbicide and polychlorinated biphenyl (PCB) inhibition of Na⁺, K⁺ ATPase in rainbow trout. Bull. Environm. Contam. Toxicol. 8:69-72.
- Desaiah, D. and Koch, R.B., 1975. Toxaphene inhibition of ATPase activity in catfish (<u>Ictalurus punctatus</u>) tissue. Bull. Environm. Contam. Toxicol. 13:238-244.
- Duggan, R.E. and Corneliussen, P.E., 1972. Dietary intake of pesticide chemicals in the United States (III). June 1968-April 1970 (with summary of 1965-1970). Pestic. Monit. J. 5:331-339.
- Durkin, P.R., Howard, P.H., Saxena, J., Lande, S. and Santodonato, J., 1980. Reviews of the environmental effects of pollutants. X.Toxaphene. U.S. Environmental Protection Agency. Office of Research and Development Report EPA 600/1-79-044. 500 pp.

- Epstein, S.S., Arnold, E., Andrea, J., Bass, W. and Bishop, Y., 1972. Detection of chemical mutagens by the dominant lethal assay in the mouse. Toxicol. Appl. Pharmacol. 23:288-325.
- Federal Register (U.S.A.). Nov. 29, 1982, page 53784.
- Ferguson, D.E., Culley, D.D., Cotton, W.D. and Dodds, R.P., 1964. Resistance to chlorinated hydrocarbon insecticides in three species of freshwater fish. Bioscience 14:43-44.
- Finley, M.I., Ferguson, D.E. and Ludke, J.L., 1970. Possible selective mechanisms in the development of insecticide resistant fish. Pestic. Monit. J. 3:212-218.
- Gunther, F.A., 1969. Insecticide residues in California citrus fruits and products. Residue Reviews. 28:1-120.
- Hamilton, S.J., Mehrle, P.M. and Mayer F.L., 1981. Mechanical properties of bone in channel catfish as affected by vitamin C and toxaphene. Trans. Amer. Fish Soc. 110:718-724.
- Henderson, C., Pickering, Q.H. and Tarzwell, C.M., 1959. Relative toxicity of ten chlorinated hydrocarbon insecticides to four species of fish. Trans. Amer. Fish. Soc. 88:23-32.
- Hiltibran, R.C., 1974. Oxygen and phosphate metabolism of bluegill liver mitochondria in the presence of some insecticides. Trans. Ill. State Acad. 67:228-237.
- Hughes, R., 1970. Studies on the persistence of toxaphene in treated lakes. Ph. D. Thesis. Xerox Univ. Microfilms, Ann Arbor, Mich. U.S.A. No. 751. pp. 7-24. Dissertation Abstracts 31:6989.
- Innes, J.R.M., Ulland, B.M., Valerio, M.G., Petrucelli, L., Fishbein, I., Hart, E.R., Pollata, A.J., Bates, R.B., Falk, H.L., Gart, J.J., Klein, M., Michell, I. and Peters, J., 1969. Bioassay of pesticides and industrial chemicals for tumorigenicity in mice. A preliminary note. J. Natl. Cancer. Inst. 42:1101-1117.
- International Joint Commission, United States and Canada., 1977. New and revised Great Lakes water quality objectives Vol. II Toxaphene. 189 pp.
- Jansson, B., 1982. Separation of toxaphene components. National Swedish Environment Protection Board. SNV PM 1552.
- Jansson, B. and Widequist, U., 1983. Analysis of toxaphene and chlordane in biological samples by NCI Mass Spectrometry. Intern. J. Environ. Anal. Chem. 13:309-322.
- Jansson, B., Vaz, R., Blomkvist, G., Jensen, S. and Olsson, M., 1979. Chlorinated terpenes and chlordane components found in fish, guillemot and seal from Swedish waters. Chemosphere 4:181-190.
- Johnson, D.W., 1968. Pesticides and fish. A review of selected literature. Trans. Amer. Fish. Soc. 97:398-424.
- Johnson, W.C., 1966. Toxaphene treatment of Big Bear Lake, California. Calif. Fish and Game. 52:173-179.

- Kayser, H., Luedemann, D. and Neuman, H., 1962. Nerve cell injuries caused by insecticide poisoning in fishes and land crabs. Z. Angew. Zool. 49: 135-148.
- Kennedy, G.L. Jr., Frawley, J.P. and Calandra, J.C., 1973. Multigeneration reproductive effects of three pesticides in rats. Toxicol. Appl. Pharmacol. 25:589-596.
- Korn, S. and Earnest, R., 1974. Acute toxicity of twenty insecticides to striped bass (Morone saxatilis). Calif. Fish Game. 60:128-131.
- Kulkarni, A.P., 1975. Cytochrome P-450. Optical difference spectra of insecticide. Comparative study. J. Agric. Food Chem. 23:177-183.
- Lowe, J.I., Wilson, P.D., Rick, A.J. and Wilson, A.J., 1971. Chronic exposure of oysters to DDT, toxaphene and parathion. Proc. Natl. Shellfish Assoc. 61:71-79.
- Lowe, J.I., 1964. Chronic exposure of spot (<u>Leiostomus xanthurus</u>) to sublethal concentrations of toxaphene in seawater. Trans. Am. Fish. Soc. 93:396-402.
- Macek, K.J., Hutchinson, C. and Cope, O.B., 1969. Effects of temperature on the susceptibility of bluegills and rainbow trout to selected pesticides. Bull. Environm. Contam. Toxicol. 4:174-183.
- Mattraw, H.C., 1975. Occurrence of chlorinated hydrocarbon insecticides. Southern Florida - 1968-72. Pestic. Monit. J. 9:106-115.
- Mayer, F.L. and Mehrle, P.M., 1976. Vitamin C distribution in channel catfish as affected by toxaphene. Soc. Toxicol. Abst. 15th Ann. Meeting. pp. 151-152.
- Mayer, F.L., Mehrle, P.M. and Dwyer, W.P., 1975. Toxaphene effects on reproduction, growth and mortality of brook trout. U.S.EPA, Office of Research and Development. EPA-600/3-75-013. 43 pp.
- Mehrle, P.M. and Mayer, F.L., 1975a. Toxaphene effects on growth and bone composition of fathead minnows (<u>Pimephales promelas</u>). J. Fish. Res. Bd. Canada. 32:593-598.
- Mehrle, P.M. and Mayer, F.L., 1975b. Toxaphene effects on growth and development of brook trout. J. Fish. Res. Bd. Canada. 32:609-613.
- Munson, T.O., 1976. A note on toxaphene in environmental samples from Chesapeake Bay region. Bull. Environm. Contam. Toxicol. 16:491-498.
- Musial, C.J. and Uthe, J.F., 1982. Widespread occurrence of the pesticide toxaphene in Canadian east coast marine fish. Int. J. Environ. Anal. Chem. 14:117-126.
- Naqvi, S.M.Z. and Ferguson, D.E., 1970. Levels of insecticide resistance in freshwater shrimp (<u>Palaemontes kadiakensis</u>). Trans. Amer. Fish. Soc. 99:696-699.
- Naqvi, S.M.Z. and Ferguson, D.E., 1968. Pesticide tolerance of selected freshwater invertebrates. J. Mississippi Acad. Sci. 14:121-127.
- National Cancer Institute (U.S.A.), 1979. Bioassay of toxaphene for possible carcinogenicity. Tech. Rept. PCA06/MF A01. 105 pp.

- Nicholson, H.P., Grzenda, A.R. and Teasley, J.I., 1966. Water pollution by insecticides: A six and one-half year study of a watershed. Proc. Symp. Agric. Waste Waters. Rept. No. 10 of the Water Resources Center, University of California. In Guyer <u>et al.</u> (1971). Toxaphene status report. U.S. Environmental Protection Agency, Washington, D.C. pp. 132-141.
- Nimmo, D.W., 1977. Toxaphene: Its effects on mysids. Taken from U.S.EPA document. Toxaphene: Ambient water quality criteria. NTIS PB 296-806. 73 pp.
- Ohsawa, T., Knox, J.R., Khalifa, S. and Casida, J.E., 1975. Metabolic dechlorination of toxaphene in rats. J. Agric. Food. Chem. 23:98-109.
- Paris, D.F., Lewis, D.L., Barnett, J.T. and Baughman, G.L., 1975. Microbial degradation and accumulation of pesticides in aquatic systems. U.S. Environmental Protection Agency, Corvallis, Oregon, Report No. EPA-660/3-75-007. 45 pp.
- Pollock, G.A. and Kilgore, W.W., 1978. Toxaphene. Residue Reviews 69:87-140.
- Pollock, G.A. and Kilgore, W.W., 1980. Excretion and storage of ¹⁴C-toxaphene and two isolated ¹⁴C-toxaphene fractions. J. Toxicol. Environ. Health. 6:127-140.
- Reimold, R.J. and Durant, C.J., 1973. Survey of toxaphene levels in Georgia estuaries. Tech. Report Series No. 72-2. Georgia Marine Science Center, University System of Georgia, Skidaway Island, Ga. 106 pp.
- Ribick, M.A., Dubay, G.R., Petty, J.D., Stalling, D.L. and Schmitt, C.J., 1982. Toxaphene residues in fish: Identification, quantification and confirmation at part per billion levels. Environ. Sci. Technol. 16:310-318.
- Saleh, M.A. and Casida, J.E., 1979. Toxaphene composition, structure-toxicity relations and metabolism. In Advances in Pesticide Science. Geissbuehler, H. (ed.) Pergamon. 3:562-566.
- Saleh, M.A., Turner, W.V. and Casida, J.E., 1977. Polychlorobornane components of toxaphene: Structure-toxicity relations and metabolic reductive dechlorination. Science. 198:1256-1258.
- Saleh, M.A., Skinner, R.F. and Casida, J.E., 1979. Comparative metabolism of 2,2,5-endo, 6-exo, 8,9,10-heptachlorobornane and toxaphene in six mammalian species and chickens. J. Agri. Food Chem. 27:731-737.
- Schafer, M.L., Peeler, J.T., Gardner, W.S. and Campbell, J.F., 1969. Pesticides in drinking water: Waters from the Mississippi and Missouri Rivers. Environ. Sci. Technol. 3:1261-1269.
- Schimmel, S.C., Patrick, J.M. and Forester, J., 1977. Uptake and toxicity of toxaphene in several estuarine organisms. Arch. Environm. Contam. Toxicol. 5:353-367.
- Sundström, G., 1981. Toxaphene in the Swedish environment input via aerial fallout. Nordic Council Environmental series 1981. (in Swedish.)
- Terriere, L.C., Kugemagi, U., Gerlach, A.R. and Borovicka, R.L., 1966. The persistence of toxaphene in lake waters and its uptake by aquatic plants and animals. J. Agric. Food Chem. 14:66-69.

- Turner, W.V., Khalifa, S. and Casida, J.E., 1975. Toxaphene toxicant A. Mixture of 2,2,5-endo, 6-exo, 8,8,9,10-octachlorobornane and 2,2,5-endo, 6-exo, 8,9,9,10-octachlorobornane. J. Agric. Food Chem. 23:991-994.
- U.S. Department of Agriculture, 1978. Modification of objective phase biological residues report for the period 1974 through September 1977. John E. Spalding, Laboratory Services Division, Meat and Poultry Inspection Program, Consumer Marketing Services, USDA, Washington, D.C. reported in EPA 660/1-70-044.
- U.S.EPA, 1978. Environmental Protection Agency. Ambient water quality criteria. NTIS PB 296 806. 73 pp.
- U.S. National Academy of Sciences, 1977. Drinking water and health. A report of the Safe Drinking Water Committee Advisory Center on Toxicology. Assembly of Life Sciences, National Research Council, Washington, D.C.
- Uthe, J.F. and Musial, C.J., 1982. Report on the fourth ICES intercalibration study of PCBs in biological tissues. International Council for the Exploration of the Sea. Cooperative Research Report No. 115. Copenhagen. 53 pp.
- Warner, R.E., Peterson, K.K. and Borgman, L., 1966. Behavioral pathology in fish: A quantitative study of sublethal pesticide toxication. J. Appl. Ecol. 3:223-247.
- Weber, F.H. and Rosenberg, F.A., 1980. Biological stability of toxaphene in estuarine sediments. Bull. Environm. Contam. Toxicol. 25:85-89.
- Widequist, U., Jansson, B., Reutergårdh, L., Sundström, G. and Uvemo, U-B., 1982. The evaluation of a gas chromatographic method for the analysis of toxaphene. National Swedish Environment Protection Board. Internal Report NSL 82-01.
- Williams, W.E. and Bidleman, T.F., 1978. Toxaphene degradation in estuarine sediments. J. Agri. Food Chem. 26:280-282.
- Wolfe, N.L., Zepp, R.G., Baughman, G.L., Finchar, R.C. and Gordon, J.A., 1976. Chemical and photochemical transformation of selected pesticides in aquatic systems. U.S.EPA, Office of Research and Development, Athens, Ga. 153 pp.
- World Health Organization, 1974. Evaluation of some pesticide residues in food. Pesticide Residues Series. No. 3. v + 491 pp.
- Zell, M. and Ballschmiter, K., 1980. Baseline studies of the global pollution. II. Global occurrence of hexachlorobenzene (HCB) and polychlorocamphenes (Toxaphene) (PCC) in biological samples. Fresenius. Z. Anal. Chem. 300:387-402.
- Zitko, V., 1980. PCBs and other organochlorine compounds in sharks and tunas. International Council for the Exploration of the Sea. Statutory Meeting Doc. C.M. 1980/E:21. 10 pp. (mimeo.).
- Zweig, G., Pye, E.L., Sitlani, R. and Peoples, S.A., 1963. Residues in milk from dairy cows fed low levels of toxaphene in their daily rations. J. Agric. Food Chem. 11:70-72.

ANNEX 5

HEXACHLORO-1, 3-BUTADIENE

Mia Kerkhoff Netherlands Institute for Fishery Investigations P.O. Box 68, 1970 AB IJmuiden The Netherlands

Physical Properties

Cl Cl

Hexachloro-1,3-butadiene (HCBD; $Cl_2C = C - C = CCl_2$) is a colourless liquid, which is soluble in organic solvents and relatively insoluble in water. Its molecular weight is 260.76.

Other physical properties are:

melting point	-21 [°] C		
boiling point	215 [°] C (101.3 kPa, 760 mmHg)		
density	1.6820 ²⁰		
vapour pressure 37 ⁰ C 100 ⁰ C	0.1 kPa (0.8 mmHg) 3.1-3.2 kPa (23-24 mmHg)	(Ourisson and Koch, 1980) (Ourisson and Koch, 1980)	
water solubility (23 [°] C)	12 m Mol/m ³ ~ 3 mg/l	(Banerjee <u>et</u> <u>al</u> ., 1980)	
n-octanol/water part.coeff.	60900	(Banerjee <u>et</u> <u>al</u> ., 1980)	
water/air part.coeff.(20°C)	0.97	(Pearson and McConnell, 1975)	

Production / Uses / Discharges

The major point sources of HCBD are emissions from manufacturing plants which produce chlorinated hydrocarbons, and waste disposal practices of these plants. The production of tetrachloroethene, trichloroethene and carbon tetrachloride accounts for 99% of the HCBD release in the United States. Most of the tarry residue produced, called HEX waste, is either incinerated or disposed of in deep wells, land-locked lagoons or land fills. In the U.S.A. in 1974 an annual HEX waste production of 10 million pounds (4 500 tonnes) of HCBD and 5 million pounds (2 250 tonnes) of hexachlorobenzene (HCB) has been estimated (Fishbein, 1979).

The largest industrial use for HCBD in the U.S.A. is for the recovery of chlorinecontaining gas in chlorine plants. It is also used as a solvent for natural and synthetic rubbers, in lubricants, in heat transfer and hydraulic fluids, in antifouling paints, in electric insulating liquids and as a fire retardant. HCBD has been applied as a herbicide in several water systems. In the USSR it is used as a fumigant to control Phylloxera in vineyards (Kotzias <u>et al.</u>, 1975; Vorob'eva, 1980). HCBD reaches the environment via direct emissions into air and water or via leachate from sites of waste disposal (Gorkavenko, 1981).

Persistence / Degradation

HCBD is a stable compound resistant to heat, acids and alkalis. Little is known about the processes by which it is degraded in the environment. In the hydrosphere the breakdown appears to be slower than in the atmosphere, where this unsaturated compound may undergo photo-degradation (Pearson and McConnell, 1975). As biomagnification cannot be observed in mammals, metabolism has been suggested (Ourisson and Koch, 1980) although direct HCBD excretion cannot be ruled out and loss via exhalation cannot be ignored. HCBD does not seem to have the extreme persistence exhibited by the commonly known organochlorine pesticides.

Toxicology / Public Health Aspects

The LC₅₀ values for fishes and aquatic invertebrates vary from 0.009 to 4 mg/1 (U.S.EPA, 1980; Ourisson and Koch, 1980). Exposure to sublethal doses resulted in reversible effects such as abnormal behaviour, equilibrium loss and increased pigmentation (Ourisson and Koch, 1980). HCBD does not seem very toxic to birds. A daily consumption of 5 mg/kg body weight causes no deleterious effects on lifespan, reproduction or behaviour of quails during a 90-day experiment (Ourisson and Koch, 1980). The lethal doses (LD_{50}) for rats vary from 50 to 600 mg/kg depending on the age and sex of the animals. Kidney and liver injuries already occur from an (oral) dose of 110 mg/kg body weight. In a chronic toxicological study a 2-year ingestion of a dosage of 2.0 mg/kg/day caused some degree of toxicity, affecting primarily the kidney. At a lower dosage (0.2 mg/kg/day) no effects have been observed, while a higher dose level (20 mg/kg/day) resulted in irreversible toxicological effects such as the development of renal neoplasms (Kociba et al., 1977). There are not many data on mutagenicity and carcinogenicity in the literature. HCBD has been found mutagenic in Salmonella typhimurium TA 1535 and TA 100 (Fishbein, 1979). No teratogenic effects have been described in studies of birds or mammals. The only carcinogenic effects reported are the above-mentioned renal neoplasms in rats.

According to the U.S. Environmental Protection Agency, HCBD is suspected of causing cancer in man and it is one of the hazardous substances listed in the "Clean Water Act". The levels which may result in an incremental increase in cancer risk over a lifetime are estimated at 10^{-5} , 10^{-6} and 10^{-7} . The corresponding water quality criteria are $4.47 \ \mu g/1$, $0.45 \ \mu g/1$ and $0.045 \ \mu g/1$, respectively. If the estimates are made for the consumption of aquatic organisms only, excluding the consumption of water, the levels are $500 \ \mu g/1$, $50 \ \mu g/1$, and $5 \ \mu g/1$, respectively (U.S.EPA, 1980).

Bioaccumulation

Like many other chlorinated hydrocarbons, HCBD is stored in the lipids of organisms and concentrations in the tissues reflect those in the surrounding water. Goldbach found a significant positive correlation between HCBD contents and lipid contents in common bream and roach (Goldbach et al., 1980). Laboratory experiments with dab, plaice and mussels have resulted in bioaccumulation factors in the order of 10³. From data in the Liverpool area, the same factor can be estimated for mussels and several fishes (Pearson and McConnell, 1975). Concentrations in the River Rhine suggest a bioaccumulation of 10⁴ for eel (author's data). If these factors on a wet weight basis are recalculated on a lipid basis, a bioaccumulation factor between 104 and 105 can be obtained, which is in agreement with the n-octanol/water partition coefficient (Banerjee et al., 1980). In clean water a decrease in HCBD content has been observed in the laboratory as well as in the field. The half-life time in fish is of the order of weeks. In an ecosystem, no significant biomagnification through the food chains to higher trophic levels has been observed. Birds and mammals do not seem to accumulate HCBD and a rapid elimination of HCBD in rats has been reported (Ourisson and Koch, 1980).

Occurrence in the Environment

HCBD has been found in water, soil and several aquatic organisms. HCBD residues are always accompanied by HCB residues, as the industrial discharges contain both compounds in concentrations of the same order of magnitude. HCBD contamination has been reported more often in fresh water than in the marine environment. HCBD residues have been reported in fish from both North American and European waters. Freshwater fishes from the lower Mississippi River (Louisiana, 1975), including the delta region opening into the Gulf of Mexico, contained HCBD at concentrations ranging from 10 to 1200 μ g/kg. HCBD was identified in fish from the Ashtabula River (Ohio, 1976), the Wabash River (Indiana, 1976), the Niagara River (New York, 1976) and Lake Ontario (1972) (Ourisson and Koch, 1980). In eel from the River Rhine, concentrations between 800 and 1700 μ g/kg have been detected in the period 1978-1982. Eels from the Meuse contained about 100 μ g/kg, while in other Dutch inland waters lower values have been observed (author's data). Two of 20 saltwater fishes from an area near the outflow of the Mississippi River had detectable HCBD concentrations (10-20 μ g/kg). In Liverpool Bay which is influenced by effluents containing HCBD, the concentrations in fish tissues were below 1 μ g/kg (1973, 1980), while mussels from the same area contained 3.2-3.8 μ g/kg HCBD (1973) (Pearson and McConnell, 1975; Allchin and Portmann, 1981). Cod livers from the Southern Bight of the North Sea (Dutch coastal waters) had HCBD levels between 20 and 40 μ g/kg (1978-1981), but in livers of fish from the central and northern part of the North Sea and the Atlantic Ocean, HCBD could not be detected (author's data).

Several HCBD concentrations in river water have been reported, e.g., Mississippi River: 0.7-1.9 μ g/l (1975) (Laska <u>et al.</u>, 1976), River Rhine: 0.03-1.7 μ g/l (1975-1981) (Dijkzeul, 1982). Only one value is known for seawater: Liverpool Bay 0.004 μ g/l (1973) (Pearson and McConnell, 1975). The reported concentrations in tap water vary from 0.05 to 0.45 μ g/l (Ourisson and Koch, 1980). Pearson has given data for birds (max. 9.9 μ g/kg in eggs) and grey seals (0.4-3.6 μ g/kg) (Pearson and McConnell, 1975), but in the liver and kidney of a great cormorant from the Rhine - Meuse delta (1981) HCBD was undetectable, although HCB levels from 10 to 15 mg/kg indicated the presence of HCBD in the food as well (author's data).

Distribution in the Environment

Wherever HCBD has been found, a direct source of contamination can be identified. The highest concentrations have been reported in rivers with emissions of plants producing chlorinated hydrocarbons. In the marine environment, HCBD has been detected only in coastal waters influenced by those rivers. Yet, the rivers transport just a small part of the total freshwater contamination to the sea. The HCBD contents in fish decrease downstream in the River Rhine to 5-50% of the initial values at the Dutch/German border depending on the water residence time (author's data). As adsorption onto particulate material is suspected to be one or two orders of magnitude, sediments can be a sink for HCBD. But this adsorption does not sufficiently explain the distribution observed in the River Rhine and the relatively high volatility of HCBD seems a more likely explanation for the decrease. A disequilibrium between air and (river)water is assumed with a nett transport to the air. HCBD enters the air by evaporation and by direct emissions, and atmospheric transport may cause a world-wide distribution. Theoretically, above the oceans the air-water equilibrium will be turned in the opposite direction with a nett HCBD transport from the air into the seawater. However, Pearson's experiments suggest a fairly rapid photodegradation of HCBD in the atmosphere, partly as a result of its unsaturated character (Pearson and McConnell, 1975). In addition, a metabolic degradation has been mentioned (Ourisson and Koch, 1980).

Conclusions

Assuming that a rapid degradation in the atmosphere and in organisms really occurs, HCBD has to be considered as less persistent than other commonly known chlorinated pesticides. Although HCBD is present in some coastal waters, marine environmental problems are not to be expected. Contamination problems will be restricted to areas influenced by discharges, where a good control system should be maintained. In almost all cases of industrial release of HCBD, HCB is released in the same effluents. HCB is more persistent than HCBD, and HCBD is of relatively low toxicity compared to concentrations found in the marine environment. It is therefore not necessary to analyse HCBD on a routine basis in the marine environment unless HCB is found in high concentrations.

REFERENCES

- Allchin, C.R. and Portmann, J.E., 1981. Results of a Brief Survey for HCB and HCBD in fish and shellfish from an area off the coast of England and Wales adjacent to a major site of manufacture. ICES Doc. C.M.1981/E:14 (mimeo.).
- Banerjee, S., Yalkowsky, S.H. and Valvani, S., 1980. Water Solubility and Octanol/ Water Partition Coefficients of Organics. Limitations of the Solubility -Partition Coefficient Correlation. Environm. Sci. Technol. 14:1227-1229.
- Dijkzeul, A., 1982. De waterkwaliteit van de Rijn in Nederland in de periode 1970-1981. Rijkswaterstaat Nota nr. 82 - 061. (In Dutch).
- Fishbein, L., 1979. Potential Halogenated Industrial Carcinogenic and Mutagenic Chemicals I. Halogenated unsaturated hydrocarbons. Sci. Total Environm. 11:111-161.
- Goldbach, R.W., Genderen, H.v. and Leewangh, P., 1976. Hexachlorobutadiene residues in aquatic fauna from surface water fed by the River Rhine. Sci. Total Environm. 6:31-40.
- Gorkavenko, A.S., 1981. Important questions on defending vineyard roots from Phylloxera. Vinodel. Vinograd, USSR. 4:32-34. (In Russian).
- Kociba, R.J., Keyes, D.G., Jersey, G.C. <u>et al</u>., 1977. Results of a two-year chronic toxicity study with hexachlorobutadiene in rats. J. Am. Ind. Hyg. Assoc. 38:589-602.
- Kotzias, D., Klein, W. and Korte, F., 1975. Beiträge zur ôkologischer Chemie CVI. Vorkommen von Xenobiotika im Sickerwasser von Mulldeponien. Chemosphere 5:301-306.
- Laska, A.L., Bartell, C.K. and Laseter, J.L., 1976. Distribution of hexachlorobenzene and hexachlorobutadiene in Water, Soil and Selected Aquatic Organisms along the lower Mississippi River, Louisiana. Bull. Environm. Contam. Toxicol. 15:535-542.
- Ourisson, G. and Koch, P., 1980. Evaluation de l'impact de l'hexachlorobutadiène, de l'endosulfan du pentachlorophénol, des trichlorophénols sur l'environment aquatique. Université Louis Pasteur, Strasbourg. Rapport No. ENV/223/74 - FR/ULP 80.05.12 (5 Nov. 1980). (In French).
- Pearson, C.R. and McConnell, G., 1975. Chlorinated C₁ and C₂ hydrocarbons in the marine environment. Proc. R. Soc. London B. 189:305-332.
- U.S.EPA, 1980. Notice of Water Quality Criteria Documents. Federal Register <u>45</u> (31), Nov. 28 (1980) 79318 - 79346 p. 79335.
- Vorob'eva, T.K., 1980. Residual amounts of hexachlorobutadiene in the soil. Khim Selsk Khoz <u>18</u> (11):39-40 (in Russian).

ANNEX 6

OIL-SPILL COMBATTING - RECENT DEVELOPMENTS

Dr J.E. Portmann Fisheries Laboratory Remembrance Avenue, Burnham-on-Crouch Essex CMO 8HA, England

Oil spilt on the sea has two characteristics which bring it to the forefront of public attention: it is black and sticky and, at least initially, it floats both characteristics mean it is highly visible and the public are likely to come in physical contact with it. National and/or local authorities therefore often experience, or expect to experience, real pressure from the public "to do something" in the event of an oil spill.

At the time of the Torrey Canyon incident, oil-combatting technology was in its infancy. Oil dispersants were available but in most cases comprised rather crude mixtures of solvent and detergent which were highly toxic to marine species, especially intertidal flora and fauna. Oil recovery and removal devices and methods were equally crude and only available on a small scale. The end result was that considerable quantities of oil dispersants were applied and considerable additional damage to marine life occurred with often not very effective results in terms of oil removal.

Since that incident, very considerable advances in knowledge have been achieved. It is now possible to predict reasonably accurately the path an oil slick will take under the influence of wind and surface currents. A wide range of oil-combatting devices and pollution prevention measures have been developed and there is now a much better understanding of how oil degrades and the real extent of the damage it causes. As a consequence, there is a much clearer understanding of when "something needs to be done" about an oil spill, what form that action should take and how best to conduct the response action.

Fate of Oil

It is obvious that oil spreads, disperses and weathers naturally. Thus, if a spill is left untouched, either at sea or onshore, it will disappear as the various natural processes of physical, chemical and biological activity act upon it. The rate of disappearance will depend upon the local conditions, e.g., temperature, wind speed, wave height and light intensity, and in particular upon the nature of the oil. Large proportions of many light crudes (>50%) can be expected to evaporate within a few hours of release, whereas a heavy crude will weather and degrade only slowly.

It is also apparent that little can be done to prevent these processes; thus, once released, the soluble fractions of floating oil will dissolve rapidly and if they are going to have a damaging effect on fish or plankton that effect will occur. Photo-oxidation, dispersion and/or emulsion formation will also proceed and marine organisms will be exposed to fractions or compounds from the oil, all of which will be toxic to some extent. However, unless the spill affects an extremely large area, it is unlikely that the nett effect will be of any biological significance in terms of total stock or recruitment of that species - commercially exploitable or otherwise. Until a few years ago such a general statement might have been accepted with the exception of certain sea-bird species, but it is now generally agreed that although dead oiled sea birds are often found on shores, sometimes in distressingly large numbers, the effect in terms of total population in relation to other purely natural events is probably minor.

Once oil is stranded on a shore, it will certainly be unsightly and may smell badly but these are aesthetic effects. The damage to intertidal marine species will, except where the oil is present in very large quantities, be transitory and, unless it soaks into or is buried by beach material, for the most part it will be removed by natural processes without leaving a lasting effect.

For these reasons, in many situations where oil is spilt well offshore or is stranded on a rocky shoreline, it is best left alone to disperse and weather naturally.

Nevertheless, there will be occasions when an oil spill does require that some action be taken, for example, when an amenity area is threatened or affected, or when a nursery or breeding area for some marine species is at risk, or when nature reserves or shellfish or fish cultivation areas are liable to be affected. There are however various treatment options available and most of the recent research activity has been aimed at defining which option is most suitable for particular circumstances. Perhaps the most important point, however, is the recognition that in many situations it is best to let nature take its course.

Pollution Prevention of Shore-Line or Sensitive Areas

Recovery

There are a wide variety of devices available which are designed to enclose oil slicks. Most of these are based on the floating boom principle and they can also be deployed to direct oil away from intake structures or to prevent entry to particularly sensitive areas, e.g., shellfish hatcheries. They can also be towed along oil slicks to collect spreading oil. Unfortunately, the effectiveness of such booms is limited to fairly calm sea conditions as otherwise the enclosed oil is liable to be washed over or under the boom by wave action. They can also only be used in current conditions below about 0.25 m/sec (0.4 knots). Current speeds above this are liable to cause the oil to slip under the boom, even if it has a skirt attached. However, with care, a boom can be used to collect spilt oil and there are then various means available for removing the collected oil.

These include:

skimmers - devices which float on the water and pump the surface oil away to an adjacent holding tank;

absorbent pads - these can be removed, centrifuged or squeezed clean of oil and reused;

absorbent rope mops which can be spread out on the oil and then rolled in, squeezed and redeployed. These devices are usually available in forms which operate on an endless belt principle;

absorbent chips, straw, etc., which can be gathered in and burnt.

Pumps or vacuum trucks based on shore. The actual device used must be chosen according to the viscosity of the oil or emulsion being recovered. Emulsions may have to be scooped out and treated with a demulsifier first.

A relatively recent development, which may be applicable under quiescent conditions and for small quantities of oil, is the use of chemical agents known as "herders" which when sprayed around an oil slick "drive" the oil together to form a patch more amenable to recovery by one of the devices mentioned above.

Certain types of oil and weathered oil or emulsions are only just buoyant and may even become neutrally buoyant or sink. It has been known for many years that sunken oil can be caught by fishing nets and use has recently been made of this principle, on a trial basis, using specially modified seine nets and gear. The net used is much shorter in depth than a normal seine net and is fitted with floats; it can therefore be made several kilometers long. By making the net of double thickness fine mesh, it can be deployed around a large area of slick and hauled in around the ship, thereby collecting the oil for recovery by a skimmer, pump, suction or absorbent device.

Dispersal

In certain situations, e.g., to prevent pollution of a sandy bathing beach, it may be necessary to use oil dispersants. Modern oil-spill dispersants are much more effective than those available at the time of Torrey Canyon. They are also much less toxic and typically when mixed with equal proportions of oil (concentrates being first diluted 1:10 with water), the resultant mixture is no more toxic to shrimp than dispersed oil alone. Nationally approved dispersants have usually undergone simple tests which have shown them to be of acceptably low toxicity to selected marine organisms. This does not mean that modern oil dispersants are not toxic, nor does it mean that their use has no side effects. For example, they will be more or less degradable in their own right; the dispersed oil may be photo-oxidised more rapidly with attendant increase in photo-induced toxicity. High concentrations of dispersions are therefore likely to cause some mortality to marine organisms with which they come in contact and dispersal in shallow coastal waters should not be undertaken where fish and shellfish resources may be at risk. The simple toxicity tests used do no more than screen out unacceptably toxic dispersants, although in some countries the test data are used to rank dispersants in order of toxicity.

It has become apparent that the heavier the oil product or the more weathered the crude oil, the less amenable it is to dispersant action. This finding has led to the view that if an oil spill is going to have to be dispersed, then the sooner the dispersant can be applied the better. More recently, self-mix concentrates have been developed which need less wave energy to achieve dispersion than the previous formulation, given that the oil is one which is amenable to treatment. Trials of spraying neat dispersant from aircraft (which have a limited load capacity) showed these dispersants to be effective and this method is now an accepted operational procedure. Large areas can be treated very quickly and the response time is usually shorter than that required to deploy spraying vessels. It must be emphasised, however, that the concentrates used are no different from those which can be applied from boats, which are more likely to be used when dispersant spraying is needed in inshore areas, such as oil terminals or oil-transfer stations. Therefore, although chemical dispersion of oil into the water column is not without attendant risks, there will be situations where these risks are small and acceptable. The fact that dispersed oil can under some circumstances harm aquatic resources is a limitation to the operational use of oil dispersants, but it does not imply that their use should be banned under all circumstances.

Removal or treatment of oil once stranded

As already stated, experience has shown that chemical removal or treatment of oil once ashore is likely to be more damaging to intertidal species than if it is left alone. Rocky shores are high energy zones and natural weathering and dispersal is likely to be less damaging than dispersants, or indeed other clean-up methods. Application of dispersants to rocky shores or to salt marshes is likely to thin the stranded oil and bring it into contact with more intertidal species (especially those in permeable substrate) causing more damage than if it is left undisturbed.

In sandy or shingly beaches, physical removal by mechanical means or by pumping or scooping the oil from collecting pits or channels is generally accepted as an effective means of clean-up. If the beach is an amenity one, then a final "polish" using a dispersant may be considered necessary - large-scale damage to marine life from such usage is unlikely. Reference has been made on a number of occasions in this brief review to emulsions. Crude oil, when subjected to wave action, tends to form water-in-oil emulsions. These can be very viscous and may contain 50-80% water. They are rather stable and do not respond readily to oil dispersants. They are amenable to recovery or physical removal, but in order to reduce volume for subsequent disposal or to allow use of the recovered oil, special measures have to be employed to break the water-in-oil emulsion. Special demulsifiers have now been developed for this purpose. The separated oil is removed for recovery or other form of disposal and the aqueous effluent is discharged to the sea. The aqueous effluent produced by use of presently available demulsifiers should not be excessively harmful to marine organisms when discharged under operational conditions.

Response plans or guidelines can be established in readiness for oil spills. Indeed, most ICES countries have well-developed plans for such eventualities, and there are international agreements on cooperative action in readiness for major spills. Such preparations are valuable, but as has been indicated on several occasions in this review, the response to an oil spill should depend upon the particular circumstances. This is a fact which cannot be over-emphasised; experience has shown that oil spills all tend to have unique features, consequently no universally applicable rules of procedure can be laid down. The action which can be taken will to some extent be dictated by the weather and by the nature of the oil. The need for action will be governed by the resource likely to be affected. Finally, the actual action which it may be decided to take should be governed by the particular type of resource it is desired to protect or recoup and the nature of the substrate to be protected or cleansed.

The use of concentrate oil dispersants, whether applied at sea from the air or from ships, or from vehicles or other means on beaches, should be seen against this background. There will undoubtedly be situations in which their use will be seen as the best solution to a problem but other responses, including no action at all, will be equally correct in other circumstances.

ANNEX 7

INFORMATION ON CAPPING OF CONTAMINATED DREDGED MATERIAL

John B. Pearce U.S. Department of Commerce National Oceanic and Atmospheric Administration National Marine Fisheries Service Northeast Fisheries Center Sandy Hook Laboratory Highlands, New Jersey 07732 (USA)

1. HISTORICAL BACKGROUND

1.1 Well over a decade ago, the U.S. Environmental Protection Agency (U.S.EPA) began to consider how certain toxic substances, including mercury, could be isolated in sediments that were contaminated by dredged materials which were disposed of in spoiling areas (U.S.EPA, 1972). Subsequently, Pratt and O'Connor (1973) developed information on techniques to be used to cover dredged materials dumped in Long Island Sound. The results of these earlier studies suggested that it might be possible to dump contaminated dredged materials and other wastes and to isolate the contaminants from the marine ecosystem by using clean sediments to cover contaminated wastes, thus preventing the uptake of toxic substances by living marine resources.

1.2 Research and engineering problems that were identified had to do with:

- (1) how thick the capping layer should be to isolate contaminants,
- (2) what the capping materials should consist of in terms of sediment types,
- (3) what water depths should be considered when disposing of contaminated dredged materials and subsequent capping of them,
- (4) what kinds of navigation systems are required for the precise dumping and capping activities that are required,
- (5) what are the effects of storms and wave action on capping projects, and
- (6) what are the effects on marine biota that might result from dumping highly contaminated materials and subsequently capping them?

2. RECENT INVESTIGATIONS AND RESULTS

2.1 In a report from the International Association of Ports and Harbors (IAPH) to the Intergovernmental Maritime Consultative Organization (1981) there was extensive discussion of clean material capping under the heading of "Application of Special Care Measures". This report indicated that clean material capping (CMC) could be used to prevent the escape and transport of polluted materials and that sufficiently thick caps could be developed to accommodate the needs of burrowing benthic organisms. The report was based largely on studies that are being conducted by the U.S. Army Corps of Engineers in the Long Island Sound and New York Bight areas.

It was the judgment of the IAPH report that CMC is an environmentally sound method to be used to dispose of polluted dredged material in moderate depths. The report suggested that where "deep water" disposal sites were to be used, dredging should be done only with a commercial dredge and the dumping accomplished using precision methods. It was further indicated that the final surface of the mound resulting from capping should be as smooth as possible to reduce erosion from waves or currents. Smoothness is most easily achieved if the capping material is coarse sand rather than silt.

The IAPH report concluded that after final deposition of two-thirds of the capping material, the rest should be dumped in a circle with a radius approximating that of the original mound to ensure that the flanks of the cap are sufficiently covered.

The IAPH report also indicated that borrow pit disposal could be another approach to be used in clean material capping. Sand mining operations in the New York Harbor (Raritan Bay) area have left several large pits. The State University of New York at Stony Brook has proposed using such pits for disposal of dredged material. Once the pits are partially filled with contaminated dredged material, it has been proposed that the pits would be covered with clean dredged material.

- 2.2 Very recently, capping has been identified by groups responsible for dredged material management in New England as a way to seal off effectively highly contaminated (so-called class III) materials dumped at nearshore disposal sites (The Oceanic Society, 1982). Moreover, dumping in subaqueous borrow pits, along with capping, was suggested as offering an extra measure of protection, although it was stated that such a practice should be examined further and the benefits quantified.
- 2.3 Three recent studies have produced or reviewed data which, in part, answer the questions posed in section 1.2. Freeland et al. (1983) investigated the results of capping 510,565 yd³ of dredged material (spoils) which was evaluated as not being suitable for ocean disposal given present U.S. local criteria. The spoils were dumped in 1980 and subsequently covered with 119,536 yd^3 of fine-grained and 1,226,737 yd^3 of sand-sized materials. The area set aside for the experiment was in the Southeast quadrant of the designated site in the New York Bight (see Figure 1). The area is in the open ocean and is subjected to tidal and wind-generated currents and to the effects of major low-pressure storm cells. At the beginning of their studies, the dimensions of the cap were assessed and the sediment types were quantified. Using a range of weather data, hydrographic measurements and the geological information, as well as field measurements, "models" were used and hindcasting was done. Their conclusions were that, based on evidence from in situ, experimental and mathematical data, there were "... relatively small amounts of erosion at the capping site on an annual basis assuming 'normal' yearly conditions. The 2 to 5 cm erosion over three years from mathematical modelling translates into 0.02 and 0.05 ft/yr, or 45.7 and 18.3 yrs/ft of erosion. Thus the cap, which is four to eight feet thick, appears to be safe for the time being. However, the severe effects of a 'hundred year' storm could very likely be an order of magnitude or more larger so that portions of the cap might be breached from that storm alone. Bear in mind that the cap material is fine sand, the most easily eroded material."

"For a margin of safety, it is recommended that additional cap material be placed over the present cap. This should be sediment consisting of clean sand as coarse as is reasonably possible with grain size larger than 0.25 mm."

2.4 The early unpublished results of the 1980 study subsequently were reviewed and evaluated on the basis of additional investigations (O'Connor, 1982) by O'Connor (1982a) in a report to the U.S. Army Corps of Engineers. Special attention was given to (1) sediment losses at the capped area of the dump-

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site, (2) chemical losses at the site, and (3) bioaccumulation of contaminants in the dredged materials. He concluded that:

- (1) The New York Bight capping project had demonstrated that, using precision dumping, contaminated dredged materials were covered with a cap of clean material. The cap, consisting primarily of fine sand, resisted erosion for 16 months, at which time it <u>averaged</u> more than 1 meter in thickness. Natural sedimentation and mechanical reworking of the cap resulted in a mound having a smooth contour, with surficial sediments composed of fine sands and muds; previous studies have shown that these characteristics make deposits of spoils resistant to erosion. The sand cap at the New York Bight dredged material site should remain in place for as long as 20 years, under normal conditions of weather, tide and current. Estimates of erosional rate showed that, at the slow rate observed, it will take 18 to 46 years for erosion of the top 0.3 m of the cap. Unique events or major storms might, however, cause erosion and possible breaching of the cap.
- (2) Moreover, the presence of the cap was expected to reduce the movement of metals and organic toxicants from contaminated sediments to the water column. Other studies have shown that capping decreases the release of chemicals from contaminated sediments. In Japan, sand caps of 0.3 m depth reduced losses of nutrients and metals from sediments; in Long Island Sound, caps on contaminated sediments reduced migration of metals, PCBs and other toxicants to the water column.

Finally,

- (3) bioaccumulation studies were inconclusive as to the ability of capping to prevent or reduce contaminant uptake by blue mussels. However, the low bioaccumulation rates observed in a mussel study (Koepp <u>et al.</u>, 1982), in conjunction with the positive results from other capping studies, indicated that contaminant uptake due to loss of metals or organics from the capped material is unlikely to occur.
- 2.4.1 <u>Given the conditions prevailing in the New York Bight</u>, O'Connor (1982a) stated that capping can be an effective and efficient procedure for dealing with contaminated dredged material.
- During the same general period that the aforementioned studies and evalu-2.5 ations were being conducted, the State University of New York (SUNY) at Stony Brook conducted research on the use of borrow pits as containment sites for dredged materials. In his paper entitled "Burial of dredged sediment beneath the floor of New York Harbor", Bokuniewicz (1982) discussed progress to date in regard to using pits which result from aggregate extraction for the disposal of contaminated dredged materials. The studies by SUNY reported on progress in which pits have been partially filled using precision engineering techniques to ensure the stabilization of the pits following the period when they are filled to capacity and capped. The engineering techniques included initial measurements of the pre-disposal bathymetry and changes in bathymetry that occurred as the pits were being filled. Results of their studies to date indicate that it is feasible, from an engineering point of view, to use these techniques in inshore estuarine areas. It was pointed out, however, that successful implementation of such waste disposal procedures will demand more careful control of the discharge location and procedures than is usually exerted. In a more recent report, Bokuniewicz (1983) considered additional aspects of dredged material disposal including: (1) how much dredged sediment will escape from the pits during disposal operations? (2) what will be the form of the deposit of dredged sediment? (3) will the dredged sediment remain in the

contaminant pit until it can be capped? (4) how thick must the sand cap be to isolate contaminated materials? and (5) once the sand cap is in place, will it be mechanically stable?

Bokuniewicz concluded that only a few percent (between 1 to 5%) of the dredged material should be expected to escape during dumping operations and that the experimental pit would have to be half-full before surges would result in losses from the uncapped muds in the pit. He stated that the most efficient form of the contained dredged material in the pit should be a truncated cone or pyramid. As to whether the dredged materials will remain in the experimental pit until capping takes place, he said that this will depend on (1) the susceptibility of the dumped material to erosion, (2) the time during which the surface of the dredged material remains uncapped, and (3) the current and wave regime, especially during storms. Since muds, natural depositions, have accumulated in the experimental pit during the decade it has been open, he felt that dredged materials as these are understood will not undergo net erosion over prolonged periods when additional spoils are being added. He did note that some loss of surface material would be possible because of resuspension during storms; it was therefore suggested that capping should be done as soon as possible and that the dredged material in the pit should not be exposed during periods of winter storms.

In regard to the thickness of the cap, he stated that it should be at least 0.5 m, based on the water depths and hydrography known for the area. In some cases, it will be desirable to return the seafloor to its original condition and in such instances the cap would have to be several meters thick. In all cases, it would be desirable to have the cap sufficiently thick to avoid having burrowing organisms coming into contact with the contaminated dredged materials under the cap.

Finally, in regard to the stability of the sand cap, calculations have been made which indicate that it is technically possible to develop a stable sand cap over the unconsolidated dredged materials. For details, one should consult Bokuniewicz (1983) and the references provided in his report.

2.6 In addition to the various studies reported in sections 2.1 - 2.5, other investigations have resulted in important findings in relation to the capping of dredged materials and other solid wastes that might be disposed of at sea. The accuracy of dredged material disposal has been reported upon by Science Applications (1980). Through the use of computer-enhanced Loran C navigation, scientists have been able to demonstrate in central Long Island Sound that dredged material and capping operations can be conducted in areas where the use of navigational buoys is impractical. The use of this navigational system can greatly increase the rapidity of operations, thus saving time and energy (diesel fuel) during periods of low visibility as well as under normal conditions.

Morton (1980) also has shown that capping procedures in Long Island Sound can be carried out efficiently and that under many conditions the use of uncontaminated dredged material to cap contaminated sediments is an operationally feasible, cost-effective, and environmentally sound method for disposal in the marine environment. Bokuniewicz <u>et al</u>. (in press) have established criteria for capping subaqueous disposal sites and Bokuniewicz and Liu (1982) have reported on the stability of layered sediment deposits.

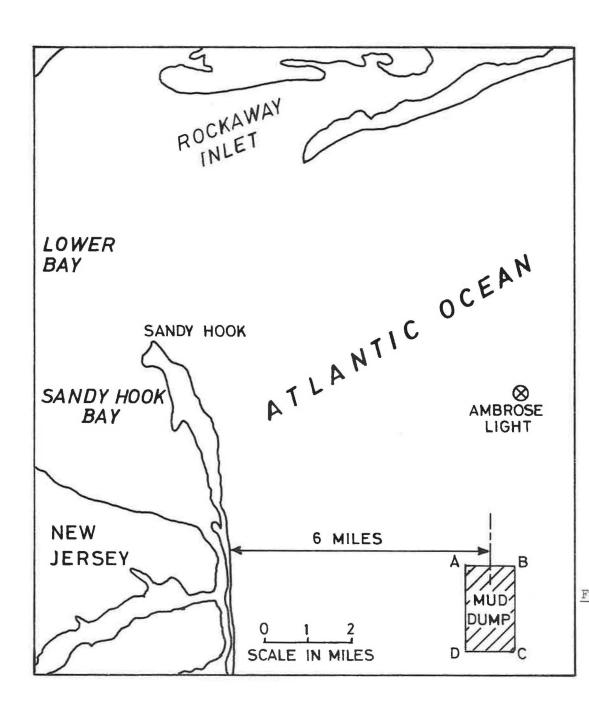
Finally, studies in Japan (Kuroda, 1982) also suggest that capping, or clean sand layovers, can effectively isolate contaminants in dredged materials. Capping was shown to reduce oxygen consumption at the sediment-water interface, reduce the rate of COD, improve interstitial water quality, and increase the diversity of benthic populations. 2.7 In conclusion, research ongoing within several laboratories has produced results indicating that capping is technologically feasible and, moreover, offers the possibility to isolate contaminants in dumped solid wastes from the overlying water masses and benthic, demersal and pelagic organisms. Aspects of capping have been investigated in inshore estuarine habitats (Long Island Sound and Raritan Bay) and at exposed sites in the open ocean.

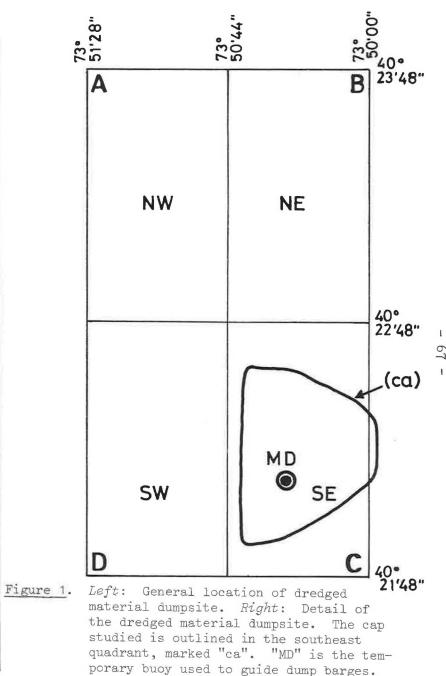
Most investigators have cautioned that additional studies are needed in regard to the long-term stability of caps, but encourage further trials using the technique to improve the management of ocean disposal of dredged materials and to protect living marine resources.

REFERENCES

- Bokuniewicz, H., 1982. Burial of dredged sediment beneath the floor of New York Harbor. Marine Pollution Papers, Oceans '82. Proceedings of Conference and exposition, September 20-22, 1982, Washington, D.C. National Oceanic and Atmospheric Administration, Office of Marine Pollution Assessment, Rockville, MD 20852, pp.1016-1020.
- Bokuniewicz, H., 1983. Submarine borrow pits as contaminated sites for dredged sediment. <u>In</u> Kester, D.R., Ketchum, B.H., Duedall, I.W. and Park, P.K. (eds.). Wastes in the Ocean, Vol. II, p. 215-227. John Wiley and Sons, Inc.
- Bokuniewicz, H., Cerrato, R. and Mitchell, A. In press. Criteria for caps on subaqueous disposal sites. Ecological Analysts Inc., Sparks, MD, 7 pp.
- Bokuniewicz, H. and Liu, J.T., 1982. Stability of layered dredged sediment deposits at subaqueous sites. Marine Pollution Papers, Oceans '82. Proceedings of Conference and exposition, September 20-22, 1982, Washington, DC. National Oceanic and Atmospheric Administration, Office of Marine Pollution Assessment, Rockville, MD 20852, pp. 752-754.
- Freeland, G.L., Young, R.A., Drapeau, G., Clarke, T.L. and Benggio, B.L., 1983. Sediment cap stability study, New York dredged material dumpsite. Report prepared for U.S. Army Corps of Engineers and the National Oceanic and Atmospheric Administration, 5 pages + appendices.
- International Association of Ports and Harbors, 1981. Special care measures for safe disposal of polluted dredged material in the marine environment. Submission to the <u>Ad Hoc</u> Scientific Group. Inter-governmental Maritime Consultative Organization, May 1981 Meeting, Halifax, Canada, 64 pp.
- Koepp, S.J., Santoro, E.D., Zimmer, R., Nadeau, J.E. and Ciaccio, L., 1982. Bioaccumulation monitoring in the New York Bight using the blue mussel (<u>Mytilus edulis</u>). Final Report to U.S. Army Corps of Engineers. New Jersey Marine Sciences Consortium, 42 pages + appendices.
- Kuroda, H., 1982. Bottom sediment improvement effect on water quality effect of dredging and clean sand layover. Management of Bottom Sediments Containing Toxic Substances, Proceedings of the 6th U.S./Japan Experts Meeting, 16-18 February, 1981, Tokyo, Japan. U.S. Army Corps of Engineers. Water Resources Support Center, Fort Belvoir, VA 22060, pp. 328-360.

- Morton, R.W., 1980. "Capping" procedures as an alternative technique to isolate contaminated dredge material in the marine environment. DAMOS Contribution No.11. Written statement submitted to: U.S. House of Representatives, Committee on Merchant Marine and Fisheries, May 21, 1980. Science Applications, Inc., Newport, RI 02840, 26 pp.
- Oceanic Society, 1982. Dredging and dredged materials management in the Long Island Sound region. Final Report submitted to the New England Governors' Conference. The Oceanic Society, Stamford, CT 06902, 197 pp.
- O'Connor, J.M., 1982. Identifying chemical signatures for disposed dredged materials. Final Report to U.S. Army Corps of Engineers. New York University Medical Center, Tuxedo, NY 10987, 85 pp.
- O'Connor, J.M., 1982a. Evaluation of capping operations at the experimental mud dump site, N.Y. Bight apex, 1980. Final Report to U.S. Army Corps of Engineer. New York University Medical Center, Tuxedo, NY 10987, 70 pp.
- Pratt, S.D. and O'Connor, T.P., 1973. Burial of dredge spoil in Long Island Sound. Report submitted to United Illuminating Co., New Haven, CT. Normandeau Associates, Inc., Manchester, NH, 37 pp.
- Science Applications, Inc., 1980. Precision disposal operations using a computerized Loran-C system. DAMOS contribution No. 12, 30 May 1980, submitted to New England Division, Corps of Engineers. Science Applications, Inc., Newport, RI 02840, 16 pp.
- U.S. Environmental Protection Agency, 1972. Sand and gravel overlay for control of mercury in sediments. Water Pollution Control Research Series, 16080 HVA 01/72, Office of Research and Monitoring, U.S.EPA, Washington, D.C., 45 pp.





Indication of spine colours

Reports of the Advisory Committee on Fishery Management	Red
Reports of the Advisory Committee on Marine Pollution	Yellow
Fish Assessment Reports	Grey
Pollution Studies	Green
Others	Black

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