International Council for the
Exploration of the Sea

July 1981

REPORT OF THE ADVISORY COMMITTEE ON MARINE POLLUTION, 1981

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List of Members

Prof. G. Kullenberg	Chairman
Dr. J. B. Pearce	Chairman, Marine Environmental Quality Committee
Dr. L. Otto	Chairman, Hydrography Committee
Dr. K. Vagn Hansen	Chairman, Biological Oceanography Committee

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Dr. R. H. Cook
Dr. V. Dethlefsen
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Dr. A. D. McIntyre
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Dr. J. E. Portmann
Ms. F. Soudan
Mr. L. Thorell

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

*) Prevented from attending the meeting 30 March - 3 April 1981.

REPORT OF THE ICES ADVISORY COMMITTEE ON MARINE POLLUTION, 1981

INTRODUCTION

1. The Advisory Committee on Marine Pollution (ACMP) has been established by the International Council for the Exploration of the Sea with the task to formulate 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 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 the present report, the Advisory Committee on Marine Pollution has prepared one overall report in anticipation that most of the material, even when prepared specifically for one Commission, will be of interest to all three regional Commissions. Thus, information both of a general nature as well as in response to specific requests is contained herein.

STATUS OF INTERCALIBRATION/INTERCOMPARISON EXERCISES

Trace Metals in Biological Materials

4. The report of the sixth intercalibration exercise on trace metals in biological materials was discussed by ACMP. Previous intercalibrations had shown that relatively poor interlaboratory agreement had been obtained for cadmium and lead at the low concentrations of these metals in fish tissue. Thus, this exercise had been devised with the aim of determining whether a better level of agreement could be reached at the higher concentrations of these two metals in shellfish. Two samples, one consisting of the white meat of edible crab and the other of a flour made from commercial fish meal, had been distributed to all participants, while a more limited distribution had been made of the third sample, lobster liver. Fifty-two participants had taken part in the exercise.

5. The results of the analyses for cadmium showed a coefficient of variation of 17% at the level found in shellfish (ca. 1 µg/g dry weight), which was considered by the Marine Chemistry Working Group to be probably the best result possible with so many participants. For lead, however, the results were still poor, even for the sample with a high concentration (ca. 2.5 µg/g dry weight) for which a coefficient of variation of 47% had been found. In reviewing these results, the Marine Chemistry Working Group had agreed that the best way to advance the state of the art of lead analyses was to conduct an examination of the various steps of the analytical procedure. An experimental programme was devised which will be carried out intersessionally.

6. The ACMP endorsed the conclusions of the report of the intercalibration results and approved it for publication. It agreed that the approach taken by the Marine Chemistry Working Group for intersessional work to study

the problems of lead analyses was very good and the ACMP strongly supported this work. The ACMP expressed its gratitude to the Coordinator of this exercise, Dr G. Topping, for his excellent work.

Organochlorines in Biological Materials

7. The ACMP then considered the report of the fourth intercalibration exercise on the analysis of organochlorine residues in biological materials, which had concentrated on PCB determinations. The results had shown that coefficients of variation of 28% at 2 µg PCB/g and 31% at 1 µg PCB/g had been obtained among the 23 laboratories reporting data. The exercise had examined the influence of several factors on the comparability of results obtained. No differences in values had been found regardless of whether the participants had used their own PCB standard or the common standard and regardless of whether they had quantified using their own method of calculation or the common method. Differences had, however, been revealed depending on the type of gas chromatography employed and the material used in the clean-up step.

8. The ACMP further noted that the Marine Chemistry Working Group had, after approving this report, considered the continuation of this work to improve interlaboratory comparability of PCB determinations. Intersessional work had been agreed to investigate the possibility that analyses of individual PCB compounds would yield interlaboratory results with a much lower variance than previously achieved. The Marine Chemistry Working Group had, however, noted that information on the toxicity of the individual isomers was an important factor in the ultimate decision of which compounds to quantify.

9. Having considered this information, the ACMP highlighted the fact that PCB analysis is complex and that proposals for further development of the techniques are required. The ACMP stressed that, in relation to the development of better analytical techniques, it is necessary to pay particular attention to the relative toxicity of individual PCB compounds, including their persistence and bioaccumulation.

10. In concluding this discussion, the ACMP expressed appreciation to the Coordinator of the PCB exercise and the further intersessional programme, Dr J.F. Uthe, for his excellent work.

Summary of the Results of the ICES Intercalibration Programme on Biological Materials - Experiences and Recommendations

11. Having considered the results of the two above-mentioned intercalibration exercises, the ACMP discussed the overall results obtained and experience gained in the series of six intercalibrations on analyses of trace metals in biological materials and four intercalibrations on analyses of organochlorine residues in biological materials. This information was considered together with the conclusions of the Marine Chemistry Working Group on their experience to date and the comments of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic. It was agreed that, for several determinands, substantial progress has been made over the past six years and that the ICES exercises have produced better results than most similar exercises carried out by other organisations.

12. There was general agreement that, although these results were encouraging, considerable caution should still be exercised when comparing monitoring data from different areas produced by different laboratories. However, it was noted that the ICES Coordinated Monitoring Reports do not in fact do this and, indeed, they caution against reading too much into even two- and three-fold differences between areas. Furthermore, on the basis of the results of the intercalibration exercises, some data (e.g., on lead and cadmium) are rejected when the reports are compiled. However, the exercises have made it possible for the Marine Chemistry Working Group to compile tables of the coefficients of variation obtained for particular contaminants at particular concentrations in the tissues, which are of real value in interpreting the results of coordinated monitoring. These tables are attached as Annex 1.

13. For heavy metals (see Table 1), it would seem that :

a) The majority of participants in these exercises are capable of producing data for copper, zinc, mercury and cadmium at tissue concentrations (on a dry weight basis) of about 1 µg/g, 20 µg/g, 0.2 µg/g and 1 µg/g, respectively, with coefficients of variation as indicated in the table.

b) At lower concentrations of cadmium (i.e., those found in fish flesh, < 0.02 µg/g), most participants experienced difficulty in their analysis and, consequently, the coefficients of variation were higher.

c) Although there are a small number of participants capable of analysing lead at concentrations of 0.02 to 0.3 µg/g, the coefficient of variation exceeded 50% for most participants at levels greater than 2 µg/g (dry weight).

14. As noted above, the fourth organochlorine exercise (see Annex 1, Table 2) has demonstrated that interlaboratory coefficients of variation of 31% at 1 µg PCB/g and 28% at 2 µg PCB/g have been found among the 23 participating laboratories. Much higher variance was obtained on the results of analysis for other organochlorine compounds, probably owing to their low concentrations in the sample.

15. Many of these exercises included other participants in addition to those normally contributing data to the Coordinated Monitoring Programme. The results of this latter group, however, were not significantly better than those of the group as a whole.

16. The ACMP noted that the analysts were not entirely satisfied with these levels of accuracy. They expect further improvements, notably in cadmium, lead and organochlorine (particularly PCB) analysis, to result from advances in methodology. However, the practical requirements for accuracy depend very much on the objectives of the monitoring programme. For public health monitoring, it would normally be adequate to ascertain that pre-determined levels of contaminants (derived from public health considerations) have not been exceeded. By contrast, where it is necessary to measure accurately actual concentrations, as in trend monitoring, organisms or tissues should be chosen in which higher concentrations occur.

17. It was felt that, at this stage, in terms of human health and probably also environmental protection, the analytical results for copper, zinc and mercury are reasonably good because the levels at which they can be accurately measured are well below the levels of concern. For cadmium, the concentrations in shellfish tissue and fish liver can be measured with sufficient accuracy for public health monitoring. However, while methods do exist for the determination of cadmium at lower levels such as occur in fish muscle (0.001 mg/kg wet weight), these are too demanding and expensive to be applied routinely.

18. Improvements in the accuracy of lead measurements are definitely required, however, and this is also the case for organochlorines (particularly PCBs, which are known to occur in some areas in some species in concentrations which might be significant in human health and biological effects terms). Since progress in PCB determination may well depend on the analysis of individual isomers (using glass capillary chromatography), research into the relative environmental importance of isomers (toxicity, bioaccumulation, etc.) is needed. The ACMP noted that investigations aimed at solving these issues, which are being undertaken under the auspices of the Marine Chemistry Working Group, involve only a limited number of laboratories. They are expected to analyse samples using particular techniques and it was hoped that the outcome will be a series of recommendations on techniques to be followed in future by all laboratories concerned with obtaining accurate and precise results for lead and PCBs. The ACMP agreed that this was the correct approach at this stage.

19. While the ACMP considered the results to date to be very encouraging, the question was raised as to whether it might not have been possible to have proceeded directly to this position, thus saving considerable time and expense. It was concluded that this probably would not have been possible considering the initial substantial differences between laboratories in the availability of equipment and the level of experience. Furthermore, for both the participants and the co-ordinators of the exercises, there had been a necessary learning stage (e.g., the identification of the need to ensure the accuracy of laboratory standards, the solution of homogeneity problems for the intercalibration sample material).

Petroleum Hydrocarbon Studies

20. The ACMP considered the report on the results of the first ICES intercomparison exercise on the analyses of petroleum hydrocarbons in marine samples. Three samples had been distributed to most participants: a crude oil (slightly weathered), a naturally contaminated marine sediment, and a mussel homogenate. A fourth sample, an aliphatic fraction of the crude oil, had been sent to only those analysts specifically requesting it. Of the 36 sets of samples distributed, results had been received for 26, from laboratories in eleven countries. As no analytical techniques had been specified for the exercise, a broad range of techniques had been used. The results showed that reasonable agreement had been obtained for broad fraction analysis, but greater

variation had been found in the determinations of the concentrations of specific hydrocarbons. Better interlaboratory agreement had been obtained for the analyses of petroleum hydrocarbons in the sediment sample than in the biological sample, but the source of this difference could not be ascertained. On the whole, a good level of agreement had been achieved among laboratories using the UV fluorescence method of analysis and employing the same standard and similar wavelengths. Based on these results, recommendations were made in the report for further work on this subject.

21. The ACMP supported the publication of this report, together with the results of an associated questionnaire survey on analytical methods, in the Cooperative Research Report series. It expressed its great appreciation to the Coordinators of the exercise, Dr. J. E. Portmann and Mr. R. Law, for their excellent work.

22. It was noted that the Marine Chemistry Working Group had recommended that a second intercalibration exercise be held for petroleum hydrocarbons using samples of marine sediments and biological tissues. This exercise would have the aim of determining interlaboratory comparability of analyses for total oil (or oil equivalents) and specified compounds.

23. Concerning analyses of petroleum hydrocarbons in sea water, the ACMP supported the Marine Chemistry Working Group decision that, before an intercomparison exercise could be carried out, certain studies needed to be conducted on the analytical problems involved in the determination of oil in sea water. A programme of study has been developed to test certain aspects of UV fluorescence methodology and it was expected that this could be accomplished intersessionally.

ISSUES RELATED TO MONITORING

Principles in Deriving Criteria and Setting Standards

24. It was recalled that a paper presenting an idealized framework for the derivation of criteria and the setting and application of standards for the regulation of environmental quality had been prepared and reviewed at the 1979 ACMP meeting (see Coop.Res.Rep. No. 92 (1980), para. 5). A revised draft of this paper had been reviewed at the 1980 ACMP meeting, which had approved the report for publication subject to minor amendments and the addition of practical examples (see Coop.Res. Rep. No. 103 (1981), para 22). The paper had been amended intersessionally and the ACMP agreed to attach it as Annex 2, without further discussion.

Coordinated Monitoring Report, 1979

25. The ACMP reviewed the draft report of the 1979 results of the Coordinated Monitoring Programme. Data were presented from Belgium, Canada, England/Wales, the Federal Republic of Germany, Ireland and the Netherlands concerning the concentrations of heavy metals in several species of fish and shellfish and the concentrations of organochlorines in several species of fish. The report had been reviewed and approved by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, which also agreed that data submitted later from France

and Denmark should be included. The ACMP approved the report, subject to minor amendments and inclusion of additional data, for publication in the Cooperative Research Report series.

26. It was noted that, in comparison with previous years, the amount of data submitted in 1979 was very small. While this may have been partly due to changes in and priorities of national programmes, it was noted that some countries had submitted data to the Joint Monitoring Programme of the Oslo and Paris Commissions, which had commenced that year, but had not sent it to ICES. It appeared that the overlap between the Joint Monitoring Programme and the ICES Coordinated Monitoring Programme, at least concerning the monitoring of contaminant concentrations in biota, is quite large. The ACMP was informed that the Commissions had asked for a meeting to discuss this and related matters.

27. The ACMP strongly re-emphasized that ICES has a legitimate and continuing interest in collecting this type of data, independent of its commitment to assist the Commissions, and urged that ICES member countries continue to submit data to the Coordinated Monitoring Programme. In relation to both the North Atlantic and the Baltic Sea, it was noted that ICES has a particularly wide geographical coverage and is concerned with a wide range of topics of relevance in pollution studies. This gives it a particularly good basis for developing statements and advice on the health of the marine environment in those areas.

Review of the Coordinated Monitoring Programme

28. The ACMP recalled that at its 1980 mid-term meeting it had considered a draft review of the results and experience gained in the course of five years of coordinated monitoring of contaminant levels in fish and shellfish (1974-1978). The review had contained tentative proposals for the conduct of future coordinated monitoring. It had been considered at that time that it would be unwise to finalise the proposals for revision of the guidelines on monitoring until after advice was available from the statisticians on procedures to use in trend monitoring. It had also been considered that a number of additions and changes to the text of the report were desirable.

29. At the meeting of the statisticians and the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic in February 1981, the expected advice had been obtained and a revised draft of the review was thereafter considered by the ACMP. This revised draft took account of the six years of coordinated monitoring reports (1974-1979) available. Also, especially in the latter sections, it had been substantially redrafted to take full account of the deliberations on the objectives of monitoring and how these objectives might be met in the most complete and efficient manner.

30. The ACMP concurred with the general comments that were made in the review concerning the findings of the six years of monitoring, but noted that coverage of the ICES area was patchy and irregular from year to year. This was considered to be undesirable and it was felt that this situation should be improved upon in the future.

31. The ACMP noted that three separate objectives of monitoring using fish and shellfish are given in the review and that it is suggested that in future different procedures should be employed to meet these separate needs. It was also noted that the frequency of observations considered necessary in order to meet each objective was different. The objectives and frequency suggested are as follows:-

(1) the provision of a continuing assurance of the quality of marine foodstuffs with respect to human health - observations every two years;

(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 - observations every five years;

(3) the provision of an analysis of trends over time in pollutant concentrations in selected areas, e.g., estuaries, coastal waters, especially in relation to the assessment of the efficacy of control measures - observations every year.

32. The ACMP endorsed the identification of these separate objectives and agreed on the suggested frequency of observations. It also agreed that in future the reports should be retitled to "ICES Cooperative Monitoring Studies". After consideration of the detailed recommendations for sampling, sample preparation and reporting, the ACMP also agreed that the Council should be recommended to urge all countries concerned to follow the guidelines for monitoring as closely as possible. It was noted that under these guidelines all laboratories are expected to ensure the quality of their data by participation in appropriate intercalibration exercises. Data from studies carried out under these guidelines should be submitted by each country to the ICES Secretariat at the recommended intervals, together with brief commentaries on the significance of the results obtained in the reporting year as compared with previous years. For the benefit of those countries who wish to report data which have not been obtained according to the agreed guidelines, there will also be the option to report this type of information to ICES. However, in that case no attempt will be made to compare the data either from year to year or with data which have been obtained according to the guidelines.

33. The ACMP concluded its deliberations on this subject with the agreement that, after the incorporation of a number of small amendments, a few example tables, and figures showing the sampling areas, the report should be published as a separate document in the Cooperative Research Report series, with appropriate credits to the main author of the review but with the clear endorsement of the ACMP.

Trend Monitoring Using Marine Organisms

34. In its 1980 report, the ACMP took note of the need to consider further the kinds of statistical analyses which might be used to eliminate "noise" which results from biological variability where the objective is to assess trends in contaminant levels in fish and shellfish. The report noted that a number of statistical techniques had been used to analyze coordinated monitoring data and that these produced results which were not always consistent. Furthermore, it was noted that a closer dialogue between statisticians, chemists and biologists was to be arranged. Such a dialogue was implemented through an *ad hoc* group which was convened in Nantes in February 1981, immediately before the meeting of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic.

35. The report from the *ad hoc* statistical group stated that the data from the past coordinated monitoring efforts could provide the basis for modifications to the sampling procedures, but suggested that at this time major change should be made in the existing sampling protocols, with the exception of the addition of length stratification of fish.

36. Furthermore, the *ad hoc* group had advised that a centralized data bank be established to store data from the Coordinated Monitoring Programme which could then be circulated in computer-readable form. The Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic would then summarize the results of the statistical analyses of such data and recommend future modifications to the Coordinated Monitoring Programme. Finally, the *ad hoc* group had advised that member nations conduct studies of a selected fish stock taken from a specific sampling area using a length stratified technique.

37. The draft report of the *ad hoc* group had subsequently been considered by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, which advised that two sampling criteria be adopted for trend monitoring purposes not later than in 1982. These were that fish samples should consist of at least 25 individuals, and preferably 60 or more, and that samples should be stratified according to length. The Working Group had also supported the establishment of a central data bank to facilitate, among other things, the analysis of trends in concentrations of contaminants.

38. This information was considered by ACMP. It was noted that a number of statistical treatments had produced similar results using the same data. However, it was not yet possible to agree on one single technique. Moreover, there was expressed the concern that supernumerary biological and physical variables will tend to be a continual problem in refining trend assessment data. Therefore, the ACMP endorsed the recommendation of the Working Group that ICES member nations conduct studies of contaminant levels in a single fish stock, emphasizing sampling in circumscribed areas with the use of length stratified techniques. It was further noted that no single statistical test may be appropriate for trend analysis of all contaminants.

39. The ACMP also concurred that the *ad hoc* group should continue to work by correspondence and to interact with the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic by having representative statisticians participate in future Working Group meetings. Moreover, it was deemed appropriate for other statisticians to become involved with the *ad hoc* group through correspondence.

40. Finally, the ACMP endorsed the concept of a centralized data bank in which data from the Coordinated Monitoring Programme and other monitoring data (including biological effects data) could be stored.

Mussel Watch Reviews

41. The ACMP considered three papers presented on this topic, two concerning the mussel watch programme in the United States and the third giving a Canadian perspective on mussel watch, as well as the discussions of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic. From the subsequent discussions, it was clear that the mussel watch concept had expanded both in geographical coverage and in scientific scope. Programmes had been or were being executed in the USA, Canada, and several

countries of Europe, and plans were underway to extend such work in the Pacific. The approach was being applied to other organisms besides molluscs - the lobster, for example, had been found useful in one Canadian programme. The Canadian work also highlighted the use of mussel watch studies for trend monitoring. Finally, by including a range of biological observations as well as the measurement of contaminant concentrations in specimens sampled, it was possible to comment on the well-being of the populations studied. Mussel watch type programmes can thus provide for the detection of contamination and also for the evaluation of pollution. A more detailed account of the current status of mussel watch programmes is given in Annex 3.

TRANSFER AND CYCLING OF SUBSTANCES IN THE MARINE ENVIRONMENT

Overviews on PCBs and Cadmium in the Marine Environment

42. The ACMP considered two overview papers, one on PCBs and the other on cadmium in the marine environment. These papers had been prepared initially by members of the Marine Chemistry Working Group and had been discussed by that Group and subsequently revised for presentation to the ACMP.

43. It was noted that the Marine Chemistry Working Group had prepared a brief statement of the objectives of the overviews. This statement was intended as a preface to the overviews and cautioned against the use of the conclusions in relation to limited scale areas. This restriction was necessary because both papers were prepared literally as overview statements on the overall behaviour of PCBs and cadmium in the marine environment as a whole. The ACMP concurred with this expression of caution, which in fact followed the same lines as its own statements on the previously endorsed overview on mercury (1980 ACMP Report, Coop.Res.Rep. No. 103 (1981), Annex 2). This led to a discussion of whether it might not be possible to modify the budgetary estimates to, for example, a North Atlantic scale, especially as it was noted that much of the data which had been used related to this part of the marine environment. There was general agreement that with suitable caution it might be possible to make such a modification, but that for the reasons stated in the Marine Chemistry Working Group's preface to the overviews it would probably not be possible to apply the same system to smaller scale areas.

44. The ACMP wished to emphasize that this does not mean the overviews are of limited value, since on the basis of the estimates of global scale movements it was possible to make generally applicable statements. Examples were the conclusion that cadmium concentrations are not in a steady state condition and can be expected to rise and the conclusion that there is likely to be contamination by PCBs for a considerable time despite control measures, although some reductions in peak concentrations might be expected in inshore areas.

45. The ACMP approved the two overviews, which are attached to this report as Annex 4, together with the preface prepared by the Marine Chemistry Working Group. At the same time it endorsed the two overviews, the ACMP wished to draw attention to the following points of elaboration and requirements for further work.

46. In relation to the PCB overview, it was noted that some very recent work in the United States suggests that although it is perhaps generally correct to state that biota may absorb the higher chlorinated compounds preferentially, there is evidence that some forms of marine biota do discriminate against the higher isomers. It was noted also that so far there was

only limited evidence of a reduction in PCB concentrations in coastal areas and it, therefore, seems probable that the evening out process will be rather gradual, the first obvious signs being a decrease in the incidence of individual high concentrations in biota rather than a decrease in the mean concentrations for the population as a whole.

47. In relation to the cadmium overview, it was pointed out that estimates of the residence time of cadmium in the ocean are very difficult to make and can vary greatly depending on the basis used in developing the estimate. Further background information for estimating the residence time of cadmium in the ocean would be useful. The information in the overview concerning the strong relationship often found between dissolved cadmium, dissolved phosphate, and dissolved nitrate in the ocean was found to be very interesting and it was felt that further information on this subject could be useful.

48. It was noted that in spite of the fact that PCBs are wholly man-made substances, considerable problems had been encountered in making budgetary estimates when it came to the collection of reliable and comparable data. This had been particularly difficult for the separate compartments of the marine environment and for areas outside the ICES area. This was considered to be rather disturbing, since it limited the possibility of estimating fluxes for smaller scale areas. The ACMP therefore felt that it would be valuable if detailed studies could be conducted in local areas subject to significant inputs. Also, on a more general scale, accurate data should be obtained for concentrations of PCBs and cadmium in the different compartments of the marine environment.

Results of the Mini-Symposium on Transport Processes in Estuarine and Near-Shore Zones

49. The ACMP took note of the "Extended Report on the Mini-Symposium on Transport Processes in Estuarine and Nearshore Zones", which had been composed by the Convener (G. Kullenberg). Five papers had been presented at the Mini-Symposium, covering both general questions regarding the processes regulating the fluxes of materials between land and the open sea, including factors influencing whether materials are retained in the near-shore zone or are transported to the open sea, and specific questions on the budgets and fluxes in certain areas, e.g., the Scheldt Estuary and the Gulf of St. Lawrence. Highlights from this report on the Mini-Symposium are given in Annex 5.

50. The ACMP further noted the views expressed by both the Marine Chemistry Working Group and the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic that a follow-up symposium on the subject under the auspices of ICES in 1983 or 1984 would be very valuable. Both Working Groups had expressed the view that such a symposium should be truly multi-disciplinary, taking a broad approach to the subject, including physical transfer, biological uptake and transport, and sedimentary and chemical aspects. The ACMP endorsed these views.

51. The Chairman then introduced a note to the ACMP summarising the outcome of his correspondence with several colleagues. Support had been expressed for ICES organising a symposium or workshop on the subject of coastal zone exchange in 1983 or 1984, which should be interdisciplinary and address recent research results in an attempt to interpret the environmental and practical implications of these results. The ACMP expressed the view that

ICES should organise an interdisciplinary symposium/workshop with the overall aim of presenting a review of exchange processes in the coastal zone and implications for the conditions there as well as for man's use of the coastal zone and its resources. It was generally considered that there was a substantial interest in the member countries for this problem area. It was discussed whether to have a symposium or a workshop, the latter being considered the more efficient approach. It was recognised that an open attendance supplemented with invited reviews would be a practical compromise, and that the total number of participants should be limited to about 50. Bearing in mind other related events, a reasonable timing would be towards the end of 1983 or early 1984. It was felt that the Council should make a decision at the next Statutory Meeting, and the Chairman agreed to present a paper to relevant Committees with the themes, objectives and a programme proposal.

Flushing Times of the North Sea

52. The ACMP considered a document giving the table of contents and the general summary of the report on the "Flushing Times of the North Sea", as prepared in draft by the ICES Study Group on the project at its meeting on 27 - 28 February 1981. This report was prepared on the basis of a request by the ACMP to the Hydrography Committee.

53. Time scales are important in pollution problems for various reasons, but sometimes their significance is not clear to everybody. In the report, a neutral term "turn-over time" is used, giving the volume of a sea area divided by the mean flux entering. Under special conditions, this time scale is equal to the "mean transit time", "mean age" or "mean flushing time" of the area.

54. The ACMP briefly discussed the use of this concept in pollution problems. It was considered useful in a general way, when the role of physical oceanographic processes in pollution has to be evaluated using a step-by-step approach, and it may be helpful in discussions on monitoring frequency. However, one should be careful in using such figures, especially in box models that are based upon these principles, as the assumptions that go into these models are only of limited validity.

55. It was noted that the sub-division as proposed for the North Sea does not give the complete refinement that is needed in a number of problems where eddy-like patterns may result in locally longer time scales. However, smaller areas are considered impracticable for this work. The figures that are produced for an area such as the North Sea, which is comparatively well known, are still of limited accuracy, due to a lack of data and the variability of water movements.

56. The ACMP concluded that the turn-over time is a useful parameter in the investigation of pollution problems, but that for the time being general estimates may suffice in most cases and certainly for areas with fewer data than for the North Sea. In closing discussion on this subject, the ACMP looked forward to reviewing the final document at its next meeting.

PROGRESS IN THE WORK REQUESTED BY THE OSLO AND PARIS COMMISSIONS

57. The ACMP considered the programme of work which ICES had been requested to perform in 1981 by the Oslo and Paris Commissions, on the recommendation of the Joint Monitoring Group (JMG), and noted the progress in this work as reported in the following paragraphs.

Intercalibration Exercises

58. The ACMP noted that the final report on the results of the third intercalibration exercise on the analysis of PCBs in organisms, which had been conducted for the JMG, had been submitted by the Coordinator, Mr. A. V. Holden, and will be printed in Cooperative Research Report No. 108.

59. In response to the request to receive reports on the results of the sixth intercalibration exercise on cadmium in biological tissues and the fourth intercalibration on PCBs in biological tissues, the ACMP referred to its discussion of these reports in paragraphs 4 to 10, above, and noted that the full reports on these exercises will be published in due course in the Cooperative Research Report series.

Specimen Banking

60. Two papers on this subject were presented and discussed. Dr. J. Pearce presented a status report on on-going specimen banking activities in the United States. This review, based on a survey of fourteen investigations, indicated that in spite of specific recommendations that specimens for organic analysis be stored at -80°C, and in spite of at least one indication in the literature that some inorganics are lost at storage temperatures above that level, the most prevalent storage is in commercial-type freezers at temperatures ranging between -14 and -18°C. In the ensuant discussion, a distinction was made between short-term storage, i.e., that period which falls between the time the sample is collected and the time when analysis may be initiated, and long-term storage, the intent of which is to conduct retrospective analyses at some quite distant future date, on the order of years. It was recommended by ACMP that Dr. Pearce expand his survey of on-going practices for short-term storage to include current practices of investigators from other ICES nations. A paper giving the results of this expanded survey is expected to be presented at the 1981 Statutory Meeting in the Marine Environmental Quality Committee. It was further recommended by ACMP that an ad hoc group determine the views of scientists within the ICES community on the aspects of long-term specimen banking for the purposes of retrospective analyses.

61. Dr. D. Phelps presented a brief status report on the bilateral agreement between the Federal Republic of Germany and the United States regarding the development of specimen banking. A functioning specimen bank will be dedicated at Saarbrücken, Federal Republic of Germany, on 10-15 May 1982. At that time, there will be a third meeting to discuss the implementation of analytical chemical methodology, specimen selection, and specimen banking involving the international scientific community. A pilot specimen bank is operative in the United States at the National Bureau of Standards of the US Department of Commerce. It is closely coordinated with the US Mussel Watch Program as it investigates methods for collection, preparation and storage of environmental specimens for long-term banking. Its primary function is to develop and recommend standard methods related to specimen banking as well as to maintain a limited specimen banking facility.

Transport of PCBs and Cadmium in the Marine Environment

62. In response to this request, the ACMP referred to the overviews on the transfer and cycling of PCBs and cadmium in the marine environment which are attached as Annex 4 and to its discussion of them in paragraphs 42 to 48, above.

Aspects of Trend Monitoring

63. The ACMP consideration of this subject has been covered in paragraphs 34 to 40, above. Modifications to the sampling guidelines (now contained in Coop.Res.Rep. No. 84 (1979), Annex II) taking account of this new information will be published in a volume of the Cooperative Research Report series (see relevant discussion in paragraphs 28 to 33, above).

Biological Effects Monitoring Strategy

64. The ACMP noted that the work programme for ICES included the request "to plan a strategy for biological effects studies and to report on the experience gained by laboratories within the ICES framework". It was relevant that since the last ACMP report, the proceedings of the ICES workshop on biological effects monitoring had been published (Rapp.P.-v. Réun.Cons.int. Explor.Mer. Vol. 179 (1980)) and also the report of a GESAMP Working Group on the monitoring of biological variables related to marine pollution (GESAMP Reports and Studies No. 12 (1980)). In the Baltic, work on biological effects monitoring was being conducted within various national programmes. In addition, the ICES Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic had engaged in extensive discussions of biological effects monitoring at its meeting in February 1981 and the report on this meeting was available. The ACMP referred to these documents in discussing effects monitoring.

65. It was clear that the activities referred to above had produced a considerable amount of information and advice for the international scientific community, and it was agreed that the role of ICES in the immediate future was to develop a strategy for applying this information. It was noted that the initial step had been taken by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, which had requested countries to undertake observations on tumours, finrot and skeletal abnormalities in relation to pollution and report results by the end of 1981 to the ICES Secretariat. This Working Group had considered it valuable for scientists from different countries to go to sea together on cruises to "intercalibrate" techniques for the identification of pathological effects. The Working Group had also arranged that countries utilising other biological effects techniques should report and evaluate results by the same date. Marine mammals were recognised as being a special case and it was further noted that this subject would be discussed at the next ICES Statutory Meeting.

66. The ACMP considered that these ICES initiatives are likely to advance the experience on biological effects studies and provide input for its deliberations in 1982. Finally, it was noted that a number of the techniques involved in biological effects monitoring, although not particularly difficult, did require some expertise, and that a training workshop on these techniques would be valuable.

Sampling Methodology for Measuring the Input of Contaminants via Rivers

67. The ACMP noted that no report on this subject was available owing to the illness of one of the coordinators of this work. It was hoped that a report would be available for the 1982 ACMP meeting.

Open Ocean Monitoring and Fifth Round Intercalibration for Trace Metals in Sea Water

68. In connection with the discussion of the fifth round intercalibration for trace metals in sea water, the ACMP noted that plans were well underway within IOC for the conduct of a baseline survey of contaminant levels in the open North Atlantic. It was recalled that ICES had earlier been associated with IOC in the preparation of a document on the conduct of baseline studies. There was a general feeling that it was highly desirable that ICES should continue to be associated with the IOC in the conduct of the open ocean baseline study. It was pointed out that several laboratories which were expected to be involved in the IOC exercise were also associated with ICES and that much of the early planning for the baseline study had been conducted within ICES Working Groups. The ACMP felt that this was ample justification for ICES to seek associate status with IOC in the open ocean baseline study.

69. Recognising that by this means a broad-brush picture would emerge of contaminant levels in the open ocean, it was emphasized that the main problems almost certainly lie in the coastal zones of the North Atlantic. For this reason, ICES should use the open ocean baseline study results for comparative purposes and pursue with as much urgency as possible the fifth round ICES intercalibration exercise for trace metals in sea water. Following this, it would then be possible to proceed with the long-awaited cooperative baseline study of metal levels in the coastal zones of the ICES area and thereby complete the picture for metal distribution.

70. It was noted in this context that the JMG had expressed its strong support for the fifth round exercise, on which it hoped to have a report by the time of its meeting in late 1982/early 1983. It was further noted in this connection that the Marine Chemistry Working Group had indicated that offers of ship-time must be received no later than at the time of the 1981 Statutory Meeting if plans were to be completed in time for the exercise to be conducted in 1982. The ACMP expressed the hope that every effort would be made by the Delegates to secure the necessary offer of ship-time before the 1981 Statutory Meeting.

Studies of Pollutants in Sediments

71. The ACMP reviewed the history of its consideration of this topic, which had begun in 1975 when the ACMP had requested that a special meeting be convened on the subject of sediments and their relationships to pollutants in order that advice could be formulated on how to monitor and interpret pollutant levels in sediments. This *ad hoc* meeting of sediment specialists was held in 1976 and the ACMP reviewed its report at its 1977 meeting, noting that the *ad hoc* meeting did not feel that a coordinated monitoring programme for determining pollutants in estuarine or near-shore sediments

should be established at that time. The ACMP supported the recommendation of the ad hoc meeting that a Workshop be held on pollutant and sediment interchange in shallow seas and recommended further that one task of the Workshop should be to give preliminary consideration to outline plans for a pilot study of pollutant concentrations in offshore sediments.

72. The Workshop on Sediment and Pollutant Interchange was held on Texel in September 1979. At this Workshop, discussions had been held on the standardization and intercalibration of techniques for sediment sampling, preservation and analysis for heavy metals. Outline plans had also been developed for a pilot survey of pollutants in several fine-grained sediment deposition areas. At the Statutory Meeting following the Workshop, an interim Coordinating Group for Sediments had been set up to initiate work on this pilot survey. This was followed, at the 1980 Statutory Meeting, by the establishment of the Working Group on Marine Sediments in Relation to Pollution, which should address the issues brought up by the former Coordinating Group on Sediments, particularly the pilot sediment survey, and the recommendations of the ACMP on sediment studies.

73. The ACMP took note of the terms of reference of this new Working Group, set forth in C.Res.1980/2:1 as follows:

> It was decided that a Working Group on Marine Sediments in Relation to Pollution should be established to promote relevant studies of physical, chemical and biological processes. It shall:
>
> (i) review the role of sediments as monitoring devices and in relation to the pathways of materials entering the marine and estuarine environment and biota, based on existing knowledge,
>
> (ii) identify areas where research is required in order to develop sediment studies, including those involved in monitoring the pathways and effects of pollutants discharged into the marine environment,
>
> (iii) work in close collaboration with the Marine Chemistry Working Group, the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, and the ICES/SCOR Working Group on the Study of Pollution of the Baltic. It shall report to the Marine Environmental Quality, the Hydrography, and the Biological Oceanography Committees.

It was further noted that the first meeting of this Working Group would be in June 1981.

74. The ACMP considered the relevant portion of the report of the 1981 meeting of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, which had reviewed the terms of reference of the Working Group on Marine Sediments in Relation to Pollution and had approved the following statement for transmission to this latter Working Group:-

> The Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic recommends to the Working Group on Marine Sediments in Relation to Pollution that, as far as the second term of reference of this latter group is concerned, the first priority should be to identify those sedimentological

research areas which are particularly relevant to monitoring the pathways and effects of pollutants in the marine environment. The Working Group on Marine Sediments is also requested to bear in mind particularly the questions outlined in para 4.3.8 of the 1980 Marine Chemistry Working Group Report, namely, (1) what is being done in relation to studies of pollutants in sediments, (2) why is it being done and how, and (3) what are the limitations on this work and what can be recommended to the pollution regulatory commissions (Doc. C.M.1980/C:1). It is further recommended that the Working Group on Marine Sediments give some consideration at a future stage to problems of intercalibration of sediment analyses for metals, PCBs, etc., when required for the conduct of effective monitoring programmes.

The ACMP endorsed this statement.

PROGRESS IN THE SCIENTIFIC STUDIES OF THE BALTIC SEA

75. In reviewing the progress in the activities of the ICES/SCOR Working Group on the Study of Pollution of the Baltic, the ACMP took note of the following items:-

a. A number of papers on results from the Baltic Open Sea Experiment (BOSEX) 1977 had been published and the Working Group was now undertaking to prepare an overall report on the BOSEX results, which, however, would probably not give an interdisciplinary interpretation, mainly due to the scarcity of biological results from the experiment.

b. Plans for coordinated, interdisciplinary studies of the physical, chemical and biological patchiness of the Baltic Sea are being developed and, as a result of the work so far, the Council passed the following resolution at the 1980 Statutory Meeting (C.Res. 1980/4:5):

"It was decided, that pilot studies on patchiness of physical, chemical and biological parameters should be carried out in different regions of the Baltic in the next two years with the aim to get a better overview on critical spatial and time scales for preparation of cooperative investigations in 1984. The Council should be informed in 1983 on the results and with proposed actions to be taken."

During the year a number of studies will be carried out and in 1982 the Working Group will devote time to a penetrating discussion of the results. For 1983, a workshop is proposed on the patchiness problem with the possible aim of planning a joint effort for 1984.

It was noted that one of the goals of these patchiness studies is related to the question of how representative low-frequency observations at a very limited number of stations over the Baltic are for the conditions and how series of such observations can be interpreted.

c. Although biological effects studies of various types are being carried out in different parts of the Baltic Sea, the attempt to establish contact between these research groups had so far not made much progress. The Working Group would, however, continue its efforts in this direction, and had also decided to collaborate with the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic on collecting information regarding results of on-going activities in the Baltic on pathological effects, recognising that a number of relevant programmes are being carried out.

d. The Working Group would attempt to formulate biogeochemical cycles for some selected substances in the Baltic Sea, working by correspondence among interested scientists. In this connection, the Working Group wished to suggest that the new Working Group on Marine Sediments in Relation to Pollution include in its considerations the influence of aperiodic fluctuations between oxic and anoxic conditions on the deposition and resolution of substances.

e. The Working Group would give specific consideration to the CO_2 cycle and budget in the Baltic Sea, bearing in mind the special nature of the brackish water system and its potentially limited buffer capacity.

f. Nutrient supplies, eutrophication and increased primary production were unresolved issues in the Baltic Assessment Document (see paras 77 and 78 below) and the Working Group had agreed to consider the use of flow diagrammes linking physical, chemical, biological and ecological processes, inputs and productivities in an attempt to elucidate the inter-relationships, again working intersessionally by correspondence.

g. The Working Group had emphasized that an overview paper on PCBs and DDT in Baltic marine mammals ought to be presented at the 1981 Statutory Meeting and initiatives were being taken to implement this.

76. The ACMP endorsed these ideas and activities and, additionally, pointed out the need for further investigations on lignin sulfonate compounds, phthalate esters, benz(a)pyrenes and possible other new substances and their effects on the Baltic ecosystem.

HELSINKI COMMISSION STWG/ICES PROJECT "ASSESSMENT OF THE EFFECTS OF POLLUTION ON THE NATURAL RESOURCES OF THE BALTIC SEA"

77. The ACMP recalled briefly the background to this project (see paras. 32-36, 1979 ACMP Report, Coop.Res.Rep. No.92 (1980); paras. 48-51, 1980 ACMP Report, Coop.Res.Rep. No. 103 (1981)), recalling also that it had during its meeting on 11 October 1980 reviewed the Overall Conclusions of this document and, after making some amendments, approved them. Members of the Joint STWG (Scientific-Technological Working Group of the Helsinki Commission) /ICES ad hoc Group of Experts had met in Helsinki on 1 - 2 December 1980 and recommended some linguistic amendments which were acceptable to ICES. The whole document "Assessment of the Effects of Pollution on the Natural Resources of the Baltic Sea" (Part A-1, Overall Conclusions; Part A-2,

Summary of Results; Part B, Scientific Material) had been presented to the second meeting of the Helsinki Commission (HELCOM) on 16 - 19 February 1981. The HELCOM had been informed that the Overall Conclusions had been approved by the ACMP on behalf of ICES. The HELCOM on its part approved the Overall Conclusions, taking note of the scientific background material (Part B) and its summary (Part A-2) and noting their evident value for future work in this field. The HELCOM, emphasizing the importance of the assessment document, had adopted a recommendation to the Contracting Parties to the Helsinki Convention to carefully consider the document and to take into account the results of this assessment when taking measures towards the abatement of pollution of the Baltic Sea. The HELCOM, following the recommendation by the ACMP and the STWG, also decided that the entire assessment document should be published in the Baltic Sea Environment Proceedings, and efficiently and rapidly distributed.

78. In conclusion, the ACMP, noting that the project was now in principle finalized, expressed its appreciation to the Editor and the Editorial Board for the valuable work they had conducted and to their collaborators for their keen interest and their valuable contributions to the project.

ISSUES RELATED TO DUMPING

Considerations Relevant to the Selection and Monitoring of Dumping Grounds

79. The ACMP noted that the ICES Observer at the fourth meeting of the *ad hoc* Scientific Group of the London Dumping Convention (LDC) had recommended to ICES that if the LDC *ad hoc* Scientific Group decided to proceed with the development of guidelines for LDC Annex III, the ICES paper "Considerations Relevant to Selection and Monitoring of Dumping Grounds" (contained in Coop.Res.Rep. No. 76 (1978), Annex I) could be updated with more recent information in mind. It was suggested that the revision be restructured to correlate more closely with the LDC Annex III text and that it should take into account the comments of a proposal presented by Australia.

80. The ACMP then considered a revised and updated version of the portion of the above-mentioned ICES paper concerned with dumping site selection criteria. This revision had been carried out intersessionally and had (1) included points made in LDC Annex III, (2) taken the Australian proposals into consideration, and (3) included, where applicable, other factors and examples. In view of the comprehensive consideration of dumpsite selection criteria currently being taken by a GESAMP Working Group which is reviewing and revising the GESAMP report "Scientific Criteria for the Selection of Sites for Dumping of Wastes into the Sea" (Reports and Studies No. 3), the revision of the ICES paper had been based mainly on relevant ICES reports and the Australian proposals.

81. The ACMP agreed that work should continue intersessionally on the revision of the ICES paper on dumpsite selection criteria and that a new draft should be considered at the October ACMP meeting.

Biological Effects of Dumping of Wastes from TiO_2 Production

82. In 1975, the ACMP formulated advice on the disposal of wastes from TiO_2 production, among others, into the marine environment. Because

new scientific information on possible effects of the wastes on marine organisms is gradually becoming available, the ACMP re-opened the discussion on this question. It was agreed that because the 1975 advice was very general, it remained valid.

83. During the discussion, it became obvious that the scientific basis for advice in relation to dumping was rather limited. It was also realised that scientific information is available which could be interpreted as an indication that the dumping of wastes from the TiO_2 industry produces harm to certain components of the marine ecosystem.

84. The ACMP noted that the conclusion that no effects occur in TiO_2 dumping areas is based on only a limited number of studies on those compartments of the ecosystem which are particularly sensitive towards exposure to the wastes. Some of these studies do indicate that effects can be detected. Since this information often either lacks statistical significance or the ecological effects indicated are relatively unspecific, this information is not usually considered as proof of effects.

85. The ACMP recommended that new information on possible biological effects of TiO_2 wastes in the marine environment be collected and reviewed. Older information should be reconsidered in the light of the knowledge obtained during the Beaufort Workshop on biological effects of marine pollution. Studies such as those on plankton, heavy metals in plankton and benthos, and increased numbers of chromosomal aberrations in mackerel embryos in the New York Bight, and the work on pathology in the German Bight should be repeated or intensified and new studies of biological effects should be initiated. In the meantime, caution should be exercised in the disposal of TiO_2 wastes to the marine environment.

Concept of "Significant Amounts"

86. A brief report was presented to the meeting on the interpretation of the term "significant amount", as used under Annex II of the London Dumping Convention. The quantitative limits currently associated with this concept could result in adverse biological effects. After a general discussion, the meeting concluded that, from a scientific standpoint, concepts such as "trace" and "significant amounts" should take into consideration such factors as the quantity (volume) and time scale associated with dumping rather than arbitrary concentration limits.

Incineration at Sea

87. The ACMP recalled that, following its discussion concerning advice requested by the Oslo Commission on fisheries factors to be considered in the selection of a common site for incineration of wastes in the North Sea, the Marine Chemistry Working Group (MCWG) had been asked to provide information on the composition of exhaust gases resulting from incineration at sea. The ACMP took note of a review prepared at the request of MCWG on this subject and of the relevant discussions at the 1981 MCWG meeting. Based on this information, the ACMP noted that this subject is reasonably well covered by other international groups and that a good deal of research is being done on the composition of stack gases and their possible deposition into the sea. Nonetheless, the ACMP wished to follow the trends and problems in the use of incineration of wastes at sea and to be assured that it is being carried out under the proper operating conditions.

PLANKTON BLOOMS

88. The Chairman opened the discussion by stating that there had been no follow-up of the suggestions agreed upon at the last meeting. However, a few papers on plankton blooms had been presented at the Statutory Meeting in 1980 following the initiative of the ACMP. The Chairman noted further that there still had been no follow-up of the recommendations of the Working Group on Red Tides and Eutrophication from 1976. In the following discussion, it was mentioned that the Working Group might have been too academic in its approach, as several of the recommendations seemed not applicable for ICES action.

89. A report from a seminar on red tides, held in Dublin in 1979, was presented which stressed the implications of red tides on fisheries, mariculture, and public health and suggested that research was needed, among other things, to provide a means of prediction of blooms. Recent observations in Scotland and Ireland on mortality in fish cages and ponds during plankton blooms and the recent dissolved oxygen problems in the United States suggested that algal blooms are becoming an increasing problem in fisheries management. Offshore observations of discoloured water/plankton blooms are made in the United States by remote sensing, which was suggested as a useful technique in monitoring the occurrence of blooms. The need for precise identification of the species causing blooms was also noted.

90. It was suggested that the Chairman of the Biological Oceanography Committee should arrange invited papers and, if time permits, a small special session on plankton blooms at the Statutory Meeting in 1981. It was agreed that ACMP would continue to consider aspects of this problem related particularly to hypertrophication and pollution and would refer other aspects to groups within ICES concerned with fisheries management and mariculture.

OIL DISPERSANTS

91. In the discussion of the report on Scientific Studies in Response to an Oil Pollution Incident, it had been noted that new types of dispersants and new methods of application are now being used. The possibility of a more extensive use as well as a greater toxicity to marine organisms was discussed. In regard to this, the ACMP agreed that information should be collected on the types of organisms which may be affected by the dispersants and the degree of toxicity. A brief report was presented to the meeting on oil spill dispersants.

92. During the discussion, it became obvious that a good deal of research is being carried out in different countries on the approval and use of dispersants. It was further noted that this subject is followed up by other international organisations, especially IMCO. In order to avoid overlapping of work and to get better information on the work which IMCO is undertaking in this field, the ACMP asked the ICES Secretariat to contact the IMCO Secretariat and to report to the next ACMP meeting.

93. It was generally felt that there was an interest in the ICES member countries in this problem area and the ACMP, therefore, wished to follow the trends in using new types of dispersants and, if appropriate, to discuss this at a later stage.

ACTIVITIES IN THE MARINE CHEMISTRY WORKING GROUP OF INTEREST TO ACMP

94. It was reported that at the Marine Chemistry Working Group meeting in February 1981 several members had described studies which they were undertaking to investigate the uptake, distribution and effects of pollutants in marine organisms. A considerable amount of interest had also been expressed in compounds which are not yet the subject of monitoring. In order to keep these under review, the Marine Chemistry Working Group proposed to commission brief reviews on the state of the art for several compounds. Polychlorinated terphenyls (PCTs), polynuclear aromatic hydrocarbons, and phthalate acid esters were mentioned as three probable candidate groups of substances.

95. It was noted that no new intercalibration exercises had been planned in detail. However, there were plans to conduct new exercises for both organochlorine compounds and metals in biological materials, once the intersessional work to develop techniques to the stage of collaborative testing was complete. There were also tentative plans for a further exercise on petroleum hydrocarbons. The ACMP was accordingly asked to take this statement as the advance warning which the Council had stipulated as being necessary for intercalibration exercises. In relation to both new substances and investigations on oil, it had been noted that a very wide range of substances were being used in the course of offshore oil exploration and exploitation in the North Sea oil fields. This was considered to be of interest on a wider scale than simply the North Sea, e.g., in relation to developments on the east coast of North America (Georges Bank) and in the Channel between England and France. Among the materials being used in very substantial quantities were diesel oil in drilling works, some of which is discharged with drill cuttings; biocides of various types are also used fairly extensively.

96. Finally, it was mentioned that plans were well in hand for the production of leaflets on methods of sampling, storage and analysis for various pollutants in different substances. Several leaflets had been promised and editorial boards had been established to consider the drafts during the intersessional period.

97. The ACMP noted all these points and indicated that it looked forward to receiving the state-of-the-art reviews and other reports. It noted with approval the progress being made on the production of the leaflets on methods of sampling, storage and analysis, which it was felt would have a value beyond the immediate ICES circle. It was also noted with approval that the range of topics to be covered by the leaflets would extend beyond those which are usually considered as matters of interest in a purely pollution context.

OTHER MATTERS FROM THE WORKING GROUP ON MARINE POLLUTION BASELINE AND MONITORING STUDIES IN THE NORTH ATLANTIC

98. It was noted that in relation to the choice of contaminants for the monitoring programme, the Working Group was seeking information on national priorities and had briefly discussed the need for further information on a number of "new" pollutants (phthalates, PCTs, Toxaphene and organosilicons). The Working Group hoped to complete the North Atlantic input study by the next session; it had briefly discussed atmospheric inputs and reiterated a call for further information. Discussion on the effects of pollution on marine mammals was postponed pending the outcome of discussions at the 1981 Statutory Meeting. The ACMP discussed the relation

between the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic and certain other ICES Working Groups (e.g., Marine Chemistry, Marine Sediments, Baltic and others) and agreed that joint or "back-to-back" meetings were often useful and appropriate, but no rigid rule should apply.

ANNEX 1

TABLES OF COEFFICIENTS OF VARIATION OBTAINED IN THE ICES INTERCALIBRATION EXERCISES FOR ANALYSES OF TRACE METALS AND ORGANOCHLORINE RESIDUES IN BIOLOGICAL MATERIALS

For a discussion of these tables, see paragraphs 11 to 19 of the body of the ACMP Report. Full details and results of the individual intercalibration exercises are reported as follows:-

> First, second and third trace metal and first and second organochlorine intercalibrations published in Coop.Res.Rep. No. 80 (1978).
>
> Fourth and fifth trace metal and third organochlorine intercalibrations published in Coop.Res.Rep. No. 108 (1981).
>
> Sixth trace metal intercalibration in Coop.Res.Rep. (in prep.).
>
> Fourth organochlorine intercalibration (in prep.).

Table 1. Coefficients of variation between analysts for heavy metals.

Residue	Exercise	Year	No. of values submitted	Accepted concentration range (μg/g)	Mean (μg/g)	s.d.	c.v.	Qualification
Cu	2	1973	7	8.3 - 10.1	9.25	0.72	7.8	None
	3	1975	20	2.69 - 5.68	3.76	0.67	17.9	None
	5	1978	36	0.4 - 4.0	1.84	0.71	38.7	< 0.4 as 0.4
Zn	2	1973	7	23 - 32	27.2	3.3	12.0	None
	3	1975	21	27.8 - 52.7	37.5	6.0	16.0	None
	5	1978	36	12.8 - 37.3	22.6	4.4	19.6	None
Hg	2	1973	8	0.60 - 0.83	0.70	0.07	10.7	None
	3	1975	16	0.74 - 0.94	0.85	0.06	7.0	One high value omitted
	5a	1978	33	0.047 - 0.370	0.207	0.066	32.0	None
	5b	1978	34	0.019 - 0.131	0.056	0.030	53.0	All (2) <values and 2 high values omitted
Cd	3	1975	17	0.020 - 0.177	0.075	0.056	74.7	All (4) <values and 3 high values omitted
	4	1977	13	0.022 - 0.060	0.041	0.014	35.0	Two high values omitted
	5	1978	36	0.005 - 0.100	0.033	0.027	80.7	All (5) <values and 4 high values omitted
	6	1979	49	0.53 - 1.11	0.800	0.136	16.9	None

...cont'd.

Table 1 cont'd.

Residue	Exercise	Year	No. of values submitted	Accepted concentration range (µg/g)	Mean (µg/g)	s.d.	c.v.	Qualification
Pb	3	1975	21	0.16 - 3.00	1.10	0.88	77.3	One high value omitted
	4	1977	13	0.03 - 1.51	0.67	0.40	60.3	One high value omitted
	5	1978	33	0.018 - 0.707	0.211	0.152	71.7	All (7) < values and 2 high values omitted
	6b	1979	46	0.22 - 4.5	2.56	1.11	43.2	One high value omitted
	6c	1979	32	0.11 - 3.20	0.87	0.72	82.5	None
As	5	1978	16	5.27 - 20.7	14.71	4.17	28.2	3 low values omitted
Mn	5	1978	15	0.54 - 1.60	0.90	0.28	31.6	One high value omitted
Fe	5	1978	15	5.7 - 15.6	10.81	3.5	32.2	None
Se	5	1978	8	0.95 - 2.21	1.63	0.38	23.4	One < value omitted

Table 2. Coefficients of variation between analysts for organochlorines.

Residue	Exercise	Sample[a)]	Year	No. of values submitted	Accepted concentration range (µg/kg)	Mean (µg/kg)	s.d.	c.v.	Qualification
HCB	2	3B	1974	7	14 - 70	46	18.8	40.6	None
	3	4	1978	22	34 - 116	67	21.9	32.7	None
	4	5	1979	15	13 - 70	36	14.5	41	None
α-HCH	2	3B	1974	7	29 - 50	41	6.4	15.5	None
	3	4	1978	23	10 - 131	49	21.3	43.5	One low value omitted
	4	5	1979	11	7 - 99	62	28.0	46	None
γ-HCH	1	2A	1972	4	10 - 130	80	56	70	None
	1	2B	1972	8	630 - 890	750	101	13.5	One low value omitted
	2	3B	1974	8	42 - 85	52	14.6	27.9	None
	3	4	1978	20	1 - 25	11	8.1	71.1	One high value and 5 "less than" values omitted
	4	5	1979	11	5 - 50	21	18.1	89	None
Dieldrin	1	2A	1972	7	70 - 210	115	63	55	None
	1	2B	1972	8	1 300 - 1 600	1 440	98	6.8	One low value omitted
	2	3B	1974	9	53 - 120	93	22.7	24.3	None
	3	4	1978	17	12 - 129	79	29.5	37.4	None
	4	5	1979	10	14 - 140	58	36.5	63	None
pp-DDE	1	2A	1972	9	340 - 780	450	137	30	None
	1	2B	1972	9	4 100 - 6 300	5 260	1 037	19.7	None
	2	3B	1974	9	83 - 128	101	13.6	13.5	One low value omitted
	3	4	1978	27	32 - 139	80	30.2	38.0	One low, two high values omitted
	4	5	1979	17	21 - 343	221	57.7	26.0	None

.../cont'd.

Table 2 ...cont'd

Residue	Exercise	Sample[a)]	Year	No. of values submitted	Accepted concentration range (µg/kg)	Mean (µg/kg)	s.d.	c.v.	Qualification
pp-DDT	1	2A	1972	9	330 - 610	430	89	21	None
	1	2B	1972	9	4 500 - 5 900	4 990	530	10.6	None
	2	3B	1974	10	175 - 220	196	12.7	6.5	One low value omitted
	3	4	1978	25	30 - 220	113	49.9	44.1	One high, one doubtful value omitted
	4	5	1979	12	25 - 480	149	134.9	91	None
PCB	1	2A	1972	9	1 000 - 3 900	1 890	907	48	None
	1	2B	1972	9	8 300 - 11 800	9 960	1 060	10.6	None
	2	3B	1974	10	944 - 1 190	1 059	95.2	9.0	One low, one high value omitted
	3	4	1978	16	172 - 900	451[b)]	204.4	45.3	Two high values omitted
	3	4	1978	13	190 - 1 500	863[c)]	431.8	50.0	None
	4	5	1979	23	70 - 255	193	41	28	One high value omitted
	4	5	1979	23	48 - 181	107	33	31	One high value omitted

Notes

a) Sample 2A - unspiked fish oil
Sample 2B - spike in fish oil
Sample 3B - spike in corn oil
Sample 4 - unspiked fish oil

b) Without sulphuric acid treatment

c) With sulphuric acid treatment

ANNEX 2

STANDARDS AND ENVIRONMENTAL CRITERIA: AN IDEALISED FRAMEWORK FOR THEIR DERIVATION AND APPLICATION TO THE REGULATION OF MARINE ENVIRONMENTAL QUALITY AND THE CONTROL OF POLLUTION

by

A. Preston

PREFACE

In its 1978 report (Coop. Res.Rep. No. 84), the Advisory Committee on Marine Pollution presented a philosophy of monitoring. This forms one part of the basic scientific principles underlying various regulatory activities in relation to marine environmental quality. The next logical step has been to formulate principles for deriving criteria and setting standards applicable to the regulation of marine environmental quality and the control of pollution. This latter part has been carried out by an *ad hoc* group of the ACMP under the chairmanship of Mr A. Preston. A draft report, written by Mr Preston, was first discussed at the ACMP meeting in 1979 and, following amendments, at the 1980 meeting. The result of the deliberations is presented in the following paper. This has been composed by Mr Preston taking into account comments on the first draft given by members of the ACMP. The paper thus presents a consensus view of the 1980 ACMP, although it is here presented under the name of the main contributor.

INTRODUCTION

The marine environment receives toxic materials of all kinds either naturally or deliberately and accidentally through the activities of man. In the case of deliberate man-made introductions, its ability to receive such materials without suffering unacceptable degrees of damage requires careful examination and assessment in advance of the introduction. From a scientific point of view, the aim of this assessment should be to define maximum safe rates of introduction and to set necessary controls, including where appropriate the monitoring of rates of input and of environmental levels and effects. The selection of actual rates of introduction will be a matter of the regulatory authorities concerned, and they will need to take account of factors which lie outside those of a strictly scientific nature. The aim of this particular paper is to expose the main scientific principles and the guidelines which should be followed wherever possible. It is assumed that a major aim of any regulatory framework will be to keep marine environmental contamination to a practical minimum.

When toxic materials are introduced to the environment, damage may be caused to many components, living and non-living, and the possibilities are manifold. However, in practice only a few, and more usually only one or two, modes or types of damage will be really dominant so that their control to satisfactory levels should ensure that all other forms of effect are controlled at levels well below those likely to present unacceptable situations. This approach, where especially sensitive or "critical" targets are singled out as those requiring the most stringent degrees of protection, has come to be known, by analogy with similar programme evaluation and review techniques used in industry, as the critical pathway approach, in which after careful review of the whole situation a particular sequence, or sometimes particular sequences, of events has been selected as posing the most serious set of consequences and as providing a basis of control which will ensure adequate control of all other combinations of circumstances. The sequence of events leading to exposure of the "critical target" is known as the "critical pathway" and typically includes initial dilution, dispersion, reconcentration by physical, chemical and biological processes and, where appropriate, synergism, degradation, or other changes which may either promote or reduce the initial toxicity of the introduced material.

The ability to set safe rates of introduction does of course necessitate the definition of appropriate standards of exposure for the critical target(s) and then, via the critical pathway approach, their application to individual environmental situations. In the definition of such standards, it will of course be necessary to ensure that they provide a degree of protection necessary to avoid unacceptable degrees of risk to public health or of environmental damage. However, it will not be possible, or justifiable, to eliminate risk altogether, and in principle a balance will have to be struck between the cost of reducing the risk of damage and the value of the reduction in damage which would ensue.

These factors then, taken together, constitute the necessary elements of an idealised framework for the effective application of standards to the regulation of environmental quality. It will not be possible of course to apply them in all cases, and urgent actions of a more direct kind may often be called for. Nevertheless, they constitute a set of principles and guidelines within which to consider regulatory action to promote research for the more effective application of the principles.

THE DERIVATION AND APPLICATION OF STANDARDS

The essential steps in the derivation and application of standards can be stated as :-

1. the criterion of dose/response (exposure/effect): this relationship is usually taken to be linear and without threshold because of the difficulty of unequivocally demonstrating the presence or absence of thresholds at the low doses applicable to properly managed environmental situations. For those situations where a threshold does exist, linearity assumptions will provide an additional margin of safety.

2. the setting of primary protection standards based on the relationship derived, or assumed, in 1;

3. derived working limits, or environmental quality standards (secondary or tertiary protection standards) based on the primary standard but interpreted, for example, in the light of data on the metabolism or behaviour of the critical target organism, or the environmental quality objectives it is desired to achieve;
4. the derivation of discharge standards based on 3 but taking account of the characteristics of the particular receiving environment and of national policy and/or international obligations, and including as appropriate the considerations of cost/risk and cost/benefit.

DOSE/RESPONSE CRITERIA AND SOME OF THEIR IMPLICATIONS FOR EXPOSURE STANDARD SETTING

Definition of an acceptable degree of exposure requires quantitative assessment of the relationship between dose and response. The response in question, when applied to the living resources of the marine environment, may be death, or a degree of impairment of function which carries with it a lower probability of survival than would otherwise be expected. This latter category of effect would include sub-lethal effects, that is, effects determined experimentally which are of sufficient severity as to carry with them a high probability of death or reduced reproductive capacity which, in the struggle for survival amongst and within natural populations, would have a similar significance for the exposed population as a whole as relatively prompt direct lethal effects to substantial numbers of individual members of that population.

The dose/response relationship should be established if possible for different rates or levels of exposure. However, the relationship is only likely in most cases to be established from effects observed at relatively high doses and dose rates, and it may never be possible to develop the relationship at low dose rates from direct observation of effects, even under experimental conditions. It will therefore usually be necessary to assume the form of the relationship at those low doses and low dose rates. The response curve in this lower dose regime may be assumed to be one of two basic types (see Figure 1). The curve which exhibits a threshold will in most cases, for practical purposes, at low dose rates be indistinguishable from the linear response curve, and a standard for acceptable exposure set on the basis of the linear response hypothesis will afford an added degree of protection. There will be a few cases where the threshold itself can be determined and, where this is possible, then clearly there is the option of setting a standard below the threshold, that is, a no-effect level. Even when this is practicable, however, care should be taken to see that the implied costs of so doing are justified by the advantages to be derived.

In the absence of data positively demonstrating a threshold, and this will be the more usual case, the dose/response relationship is assumed to be linear and without threshold. This is a very pessimistic assumption, and attempts to establish effects at low dose rates will probably fail to demonstrate any detectable effect. It is possible therefore that estimates of effect based on such assumptions will, in some cases, be overestimates of actual effects, and will lead to the establishment of primary standards (exposure or dose limits) which may contain substantial margins of safety.

There are two immediate consequences of this type of dose/response hypothesis which are important when applying standards derived from it to environmental situations. One is that since any dose carries with it some finite, even if very low, risk of effect, dose or exposure should not only be below the standard selected but as far below as is practicable. The second consideration, again since all doses carry at least an implied risk of effect, is that the collective dose to the whole of the exposed population should at least in principle be assessed in order to estimate the total risk of detriment. These collective dose considerations will not often be of overriding importance in human populations where limitation of risk to the individual will more usually be the aspect of major importance, but they will usually be the aspects of primary importance in the context of other organisms. This concept of collective dose has been well developed in respect of radiation to take account of its mutagenic or carcinogenic properties when human populations are exposed. It has not as yet been applied in the context of other animal populations, or other toxic materials, though it has a potential relevance for those carcinogens, mutagens and teratogens which are not readily degraded in the environment.

However, the use of collective dose concepts, though in principle requiring the summation of all per capita doses however small, needs a great deal of care in its application and interpretation, since the summation of extremely low per capita doses delivered at very low dose rates over large populations may give a very false picture of the risks actually being run. In natural populations, subject to a large and variable natural mortality, such considerations in relation to the costs of reducing a very large number of extremely low doses will seldom if ever be justified by the benefits to be gained by so reducing the exposure. There is therefore an implied lower limit beyond which the cost of reducing doses may be prohibitive.

In the absence of adequate data at the low dose rates applicable to the environment, the linear dose hypothesis should provide a basis for setting conservative primary standards and permit the derivation from them of sensible environmental quality standards sufficient to achieve reasonable control until better data are available. Such environmental quality standards of course will need to reflect the caution proper to safety and environmental protection considerations, but on the other hand should not demand large and unrealistic margins of safety for every uncertainty.. Furthermore, they should be treated with some flexibility and not regarded as rigid lines of demarcation below which there is no effect and above which effects automatically become manifest.

The crucial question therefore when setting the primary standard is, what level of effect, implied by the choice of a particular point on a dose/response curve, is acceptable? It has already been suggested that due to cost, when using the linear response hypothesis, zero effect will seldom be a practicable objective, and we know that in the majority of cases we are dealing with experimentally derived data whose relevance to real-life environmental considerations is questionable. In human health terms, as for example with radiation, the choice has been exercised on the basis of prevention of threshold effects in the individual, i.e. those whose severity is a function of dose, and reduction of the risk of stochastic effects, i.e., those whose frequency of occurrence is a function of dose, e.g., carcinogenesis, to an acceptable rate of occurrence in the exposed population as a whole. It is unlikely in the case of marine organisms that we would be unduly concerned with the protection of a few individuals but rather with the health of the population as a whole, that is stochastic effects. It might thus be possible to consider setting standards at a level where the probability of occurrence of effects is so low as to render them undetectable in the environment against the background of spatial and temporal variability or the effect of some other imposed stress such as fishing mortality. If, however, judgements on the effectiveness of environmental quality control are to be made in part on the results of environmental monitoring, and since, except under accident conditions, it is unlikely that actual effects will be demonstrable in unequivocal terms, alternative methods of monitoring and interpretation of the results of monitoring must be sought.

For the time being, it seems most realistic to approach this problem of environmental monitoring, and related toxicity and standard setting, on the basis of chemical residue monitoring in the critical target. Value judgements on the data obtained will have to be made by comparison with environmental quality standards, which in turn are based on a primary protection standard derived from a dose/response relationship built up from toxicity testing. This will mean that toxicity testing will have to be concerned with the establishment of body-burden data and the metabolism of pollutants in relation to the end-points selected for the test. The identification of critical organisms and organs and their associated pollutant burdens will be necessary in order to ensure that the monitoring effort is properly directed and the data from it interpretable.

Experimental work therefore needs to be directed to the more common pollutants to establish responses at a series of exposure levels and to associate these responses with the related pollutant concentrations in the relevant critical organ in a representative selection of marine organisms of demonstrated sensitivity and ecological relevance.

THE DERIVATION OF SAFE RATES OF INTRODUCTION

Standards once developed can be used to control specific environmental situations by deriving limits to the environment's ability to safely receive wastes which are based upon them. The upper limit to the safe rate of introduction of a pollutant is that rate which at equilibrium will result in a rate of exposure of the critical target(s) per unit time equal to that defined by the primary standard.

The preferred method for deriving this maximum rate of introduction should be based on critical path techniques and seek to estimate the equilibrium levels in critical materials resulting from unit rates of introduction of the pollutant in question (see Figure 2). The assessment will require a careful environmental study to obtain some idea of the pollutant's pattern of behaviour and general distribution after release, especially in relation to those uses, or intended uses, of the receiving environment which will set the basis for environmental quality objectives. These studies are a prerequisite to the establishment of acceptable rates of introduction and they will also indicate whether there is a need for environmental monitoring and, if so, will permit its planning and execution in the most effective way.

The aim is thus to establish an empirical relationship between discharge rate and level in critical targets so as to provide a basis, by comparison with a standard for protection of the target, for setting a permissible rate of introduction. The scale of investigations required will vary enormously from one sitation to another, according to the amount and toxic nature of the material requiring disposal, the physical and dispersal characteristics of the receiving environment to which it is to be introduced, and the uses made of that environment. It is therefore essential to conduct investigations on a case-by-case basis and to take into account significant variations between seasons and years. Where the major effect is to cause a change in the physical conditions of the environment, or an accumulation of undesirable substances in the food chain leading to man, the selection of critical materials presents no serious problems. But where the major effect may be on the stability of populations or whole ecosystems, substantial investigations may be required to establish the critical routes and materials.

During the conduct of these environmental surveys, those segments of the exposed populations or ecosystems likely to receive the greatest exposure need to be identified and they will usually be small segments. However, in a few instances the populations exposed may be large and it will then be necessary to establish, for a representative sample of the population, those factors with respect to their behaviour which will influence the degree of exposure, for example, human consumption habits, migratory patterns, life-stages and life-span of other organisms, etc. It will then normally be possible to isolate a group whose behaviour or life cycle makes them liable to receive the greatest exposure. Maximum rates of introduction of the pollutants may then be calculated such that the average exposure of this group does not exceed the primary standard. In the case of animal or plant populations, the death of or damage to a few individuals will not normally be regarded as of paramount importance, and the need will be rather to protect the population of an area and to maintain the stability of the ecosystem, the productivity of exploitable resources or the amenity characteristics of the environment.

It should always be the practice of regulatory authorities to set rates of introduction well below those compatible with the primary standard, i.e., well below the maximum rate, and during the early history of discharges to take the opportunity to check the accuracy of the original assessment through the monitoring of effluent compositions and the levels or effects of the pollutant in the receiving environment.

MONITORING*

Once acceptable rates of introduction have been set, the control framework within which continuing discharges are made may require some monitoring. Monitoring is here used to mean the measurement of a pollutant or its effects, for reasons related to the assessment, or control, of exposure to that pollutant of either man or specified components of the natural environment. Two categories of monitoring - the rate of input and the levels or effects in the environment - may be distinguished; the former, in any case, should normally be a regulatory requirement.

Monitoring of the levels of pollutants in the environment might in some cases start with a baseline survey to establish existing levels, possibly to be followed by some form of regular monitoring. A baseline survey will be of particular importance where previous introductions of the pollutant have not been preceded by an environmental assessment or accompanied by any necessary controls, e.g., PCBs, DDT. The objectives of environmental monitoring should wherever possible be related to the assessment of the actual or potential exposure of the critical target(s) resulting from the introduction of the pollutant, or, in some cases, estimation of the probable upper limit of such exposure. It may be possible on occasion to look for the actual effects of pollution - so-called "biological" or "ecological" monitoring. The full and proper implementation of environmental monitoring programmes envisages a much better quantitative understanding of the toxicity, effects and associated body burdens of many pollutants than we presently have.

The pursuit of monitoring operations for their own sake, without the ability to interpret the significance of the data obtained, i.e., by comparison with derived environmental quality standards, will seldom be a profitable use of resources except possibly to establish spatial and temporal trends, in which case the frequency of survey can be substantially reduced compared with that of a routine regulatory monitoring programme. In any case, all monitoring programmes should be subject to periodic review, particularly from the point of view of the environmental implication of releases.

Thus, all surveillance operations should be considered as two-stage processes. The first phase, the monitoring of discharges, should be mandatory; the second, environmental monitoring, needs only to be established where it is justified in relation to the nature and scale of the discharge. In general terms and for the majority of pollutants, there has in fact been more effort on environmental monitoring than on input monitoring and this has led to the situation where observed levels in the environment cannot be sensibly related to rates of input. This is a regrettable loss of opportunity to establish a basis for sensible regulation of input.

DERIVED WORKING LIMITS OR ENVIRONMENTAL QUALITY STANDARDS - SECONDARY AND TERTIARY STANDARDS IN RELATION TO THE CONDUCT OF MONITORING OPERATIONS AND ENVIRONMENTAL QUALITY CONTROL

Direct measurement of the exposure of targets to pollutants is seldom possible as part of a monitoring operation, and resort has to be made to measuring exposure indirectly by using measurements of contamination in conjunction with environmental survey data, such as food consumption rate

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*See also ICES Coop.Res.Rep. No. 84 (1979).

or occupancy factor. The method employed is to calculate Derived Working Limits (DWLs), sometimes referred to as environmental quality standards. These are based on primary standards but do not have either their validity or wide applicability since they usually only relate to a case study for a particular segment of the environment for which the assessment was carried out. The outline methodology applicable to the derivation of these secondary standards for internal and external exposure of an organism to pollutants is given in Figures 3 and 4. The figures also demonstrate how they are used in a monitoring operation, that is, to derive estimates of exposure to the critical individuals or population groups. The second important use of monitoring data is the quantitative post-operational reassessment of the maximum safe rate of introduction (see Figure 5) where both details of effluent composition and environmental monitoring data are required.

It is important to remember that primary standards are based on criteria developed in relation to particular targets, and are derived on the basis either of a linear response type hypothesis as a basic protection level or where a threshold in the dose/response relationship can be demonstrated, sometimes set immediately below that threshold as a no-effect level (see Figure 6). In the case of basic protection level, that is, where a target is not exposed to unacceptable risk, an element of cost/risk and cost/benefit is involved in the judgement as to what constitutes an acceptable risk. This implies some flexibility of approach and is contrary to the inflexible use of arbitrarily derived exposure or concentration standards, which are based on primary standards but which take no account of individual environmental circumstances. There can be no uniform value for quality standards; rather, there should be uniform application of primary standards with due interpretation to fit the conditions of the wide range of receiving environments. Since in practice the majority of environmental situations will be different, and the values of the variables which will determine the ultimate exposure of a target will differ, a wide range of actual values for environmental quality standards will result, each related to a particular environment, but each observing the primary standard and thus maintaining the overall objective of protecting the target to the same extent, that is, the extent determined by the original selection of the primary standard.

Thus, primary standards are derived against accepted dose/response criteria in order to ensure so far as is reasonably achievable that there is no undue exposure of a target. Derived standards based on these primary standards (that is, secondary, tertiary, etc., standards) are set so as to ensure that in particular sets of circumstances, where compliance with the primary standard cannot be directly shown, there is reasonable assurance that it cannot be exceeded. Provided that it is not exceeded, the derived standard based on the primary standard should not seek to impose unnecessary further safety factors. This will be the case, however, if uniform values for quality standards are adopted, since in some environments the factors determining the exposure of the target will be such as to lead to very much smaller exposure than will be the case in other more restrictive environments. Unnecessary degrees of either over or under protection will thus be imposed possibly at considerable cost, depending on whether the quality standard is set for the more or the less restrictive situation. It is for these reasons that each environmental situation requires some degree of separate consideration and may even require separate detailed evaluation to enable quality standards for a particular environment, appropriate to the desired quality objective(s), to be derived. What is required, therefore, and what regulatory activity should be directed to, is the establishment and adoption of a common approach to environmental assessments which will permit a reasonably uniform application of basic or primary standards.

CRITERIA, PRIMARY STANDARDS, ENVIRONMENTAL QUALITY STANDARDS (DWLs) AND QUALITY OBJECTIVES - RADIATION : AN OUTLINE CASE STUDY

It has been stressed that in applying standards to the environment it is essential to take due account of those environmental variables which will determine the actual degree of exposure experienced by a target. The best developed example for the uniform application of standards is probably that of the limitation of exposure of humans to ionizing radiation, where the primary standards are the acceptable degrees of human radiation exposure recommended by the International Commission on Radiological Protection (ICRP) and widely adopted within national regulatory bodies (see Figure 7).

To apply these primary standards for human radiation exposure to the radiation from internally deposited radionuclides, a metabolic model of a 'standard man' has been arrived at, and human organ or body burdens of individual radionuclides have been established from this model such that the resulting radiation exposure does not exceed these standards. These burdens are secondary standards and, in so far as individual metabolism will vary from that of the 'standard man', a range of exposures will be experienced in any actual population of individuals exposed to such levels.

These body or organ burdens are in turn related to rates of intake sufficient to establish and maintain the burden. These rates of intake are tertiary standards. They may in turn be translated into concentrations in air or water based on the simplifying assumption that humans have a uniform intake of air and water. These concentrations in air or water are quaternary standards and they will clearly be another source of variation within any real exposed population. In the case of intake from food, no such simplifying assumption can be made about intake, and individual food consumption rates for particular foods in particular circumstances have to be established in order to set up quaternary standards for various foods, many of which will be so closely related to local circumstances as to be site specific.

In the context of, for example, marine foods the establishment of standards for concentrations in sea water which will lead to the acceptable concentration in foods such as fish and shellfish, that is, the establishment of quinary standards, requires a host of other variables to be taken into account, including the chemical and physical states of radionuclides which will determine their entry into plants and animals used as foodstuffs. Thus, the establishment of such standards introduces another set of variables leading to an even wider variation of exposure in a real exposed population of consumers.

Thus, a common methodology for application of standards has been largely met in the case of human radiation exposure from environmental contamination by radioactive materials by the application of critical path techniques to the evaluation of individual environmental situations. ICRP (1966) has recommended the identification and establishment of a critical group of exposed individuals the control of whose radiation exposure will set acceptable limits to environmental contamination. Clearly, the value of specific variables determining the degree of exposure of such groups will vary from critical group to critical group and specific case studies will sometimes be required for each environment. It is thus evident that the establishment of widely applicable environmental quality standards could not be met in this type of situation except as already noted in the case of drinking water or air. Furthermore, it would defeat the basic concepts of radiation protection that, since exposure cannot be zero, it should be held to a practicable minimum taking due account of cost/risk and cost/benefit considerations. Individual consideration of risks and benefits is required to implement such a philosophy, and thus specific case studies of each situation are often required. Similar considerations will apply to metal contamination and many other pollutants, not only in the context of human health but also in the context of environmental damage.

What is required, therefore, is the establishment of a sensible rationale or framework which will permit a meaningful and reasonably uniform application of primary standards to specific situations or cases. Such a framework seen against the background of environmental quality objectives will have to take due account of many environmental variables as well as those associated with human habits. The application of critical path techniques probably affords the best opportunity to provide such a framework.

CONCLUSIONS

Regulation of the introduction of potential pollutants to the environment clearly demands the identification of critical targets, the definition of exposure standards to protect these targets, and a rational application of these standards to real environmental situations.

The standards themselves may, if necessary, have to be developed on a purely empirical basis, using a hypothesis such as that of linear dose/response, unless theshold phenomena can be clearly shown to exist. The application of standards to individual situations may be based on critical path techniques in order to define acceptable rates of introduction and associated environmental concentrations. Monitoring of situations should include the monitoring of discharges and, where appropriate, the environment, using Derived Working Standards (Environmental Quality Standards) as the field criteria demonstrating compliance with standards.

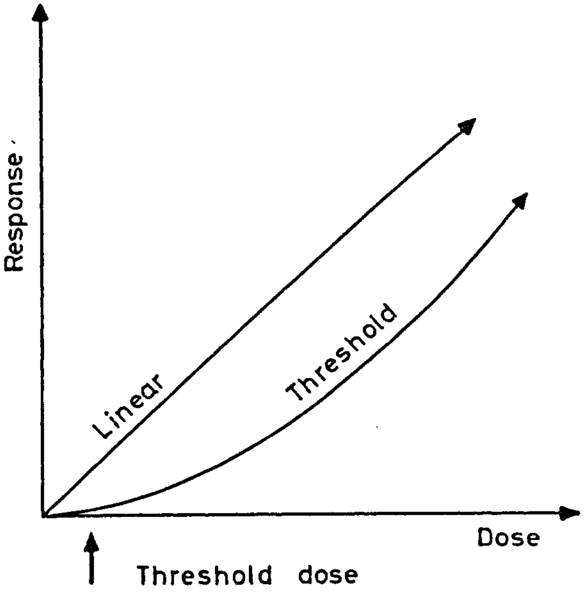


Figure 1 Possible dose/response relationships at low doses.

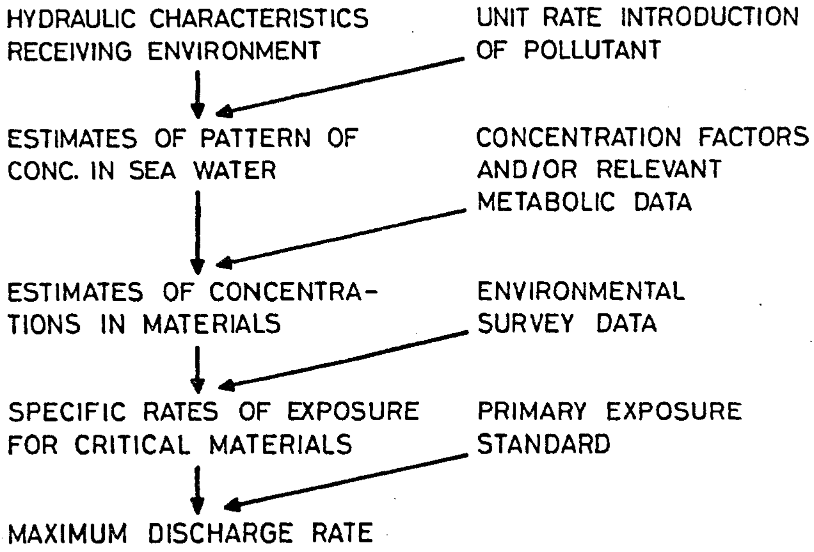


Figure 2 Diagram of principal stages in pre-disposal assessment of maximum discharge rate.

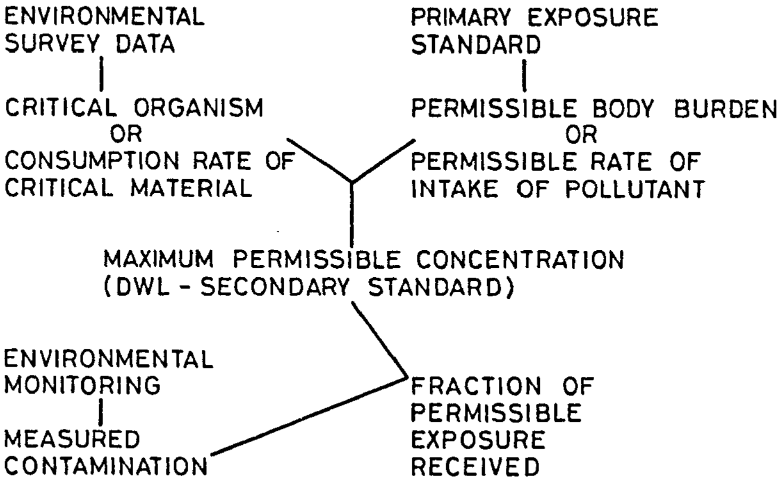


Figure 3 Derivation and use of DWLs for internal exposure.

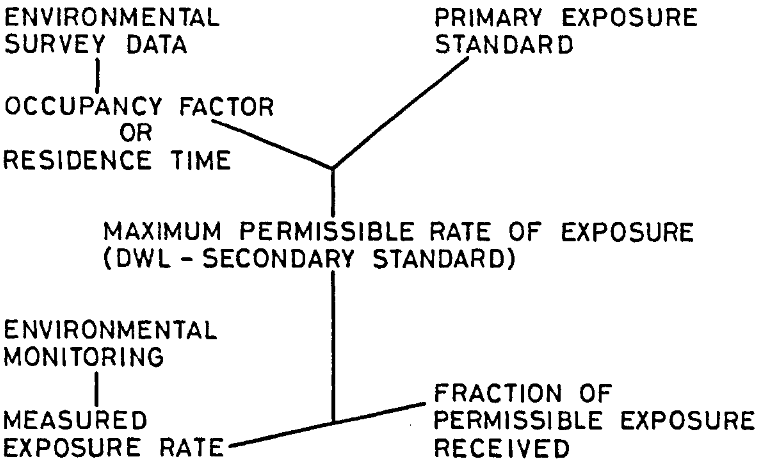


Figure 4 Derivation and use of DWLs for external use.

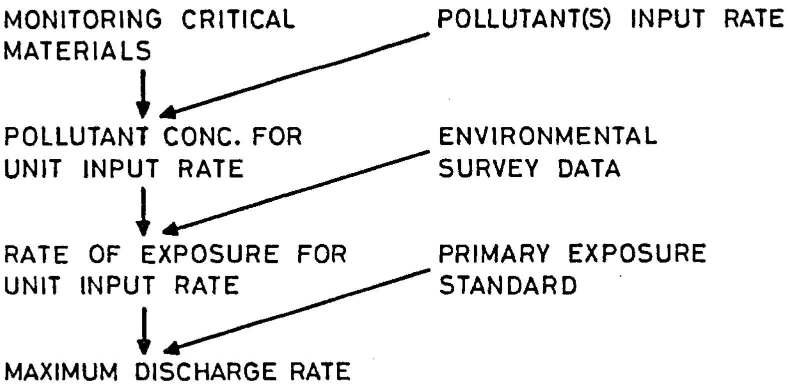


Figure 5 Diagram of principal stages in post-disposal reassessment of maximum discharge rate.

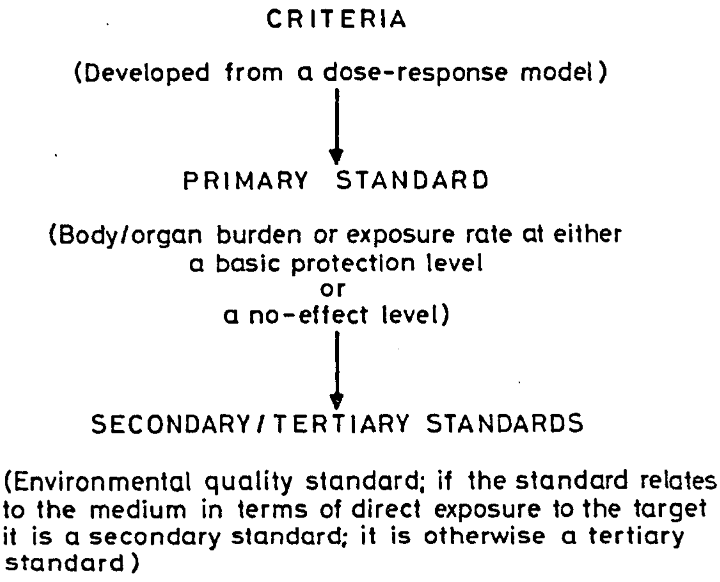


Figure 6 EEC Environmental Programme terminology.
Note: Environmental quality standards are regarded as one method of helping to construct and reach environmental quality objectives.

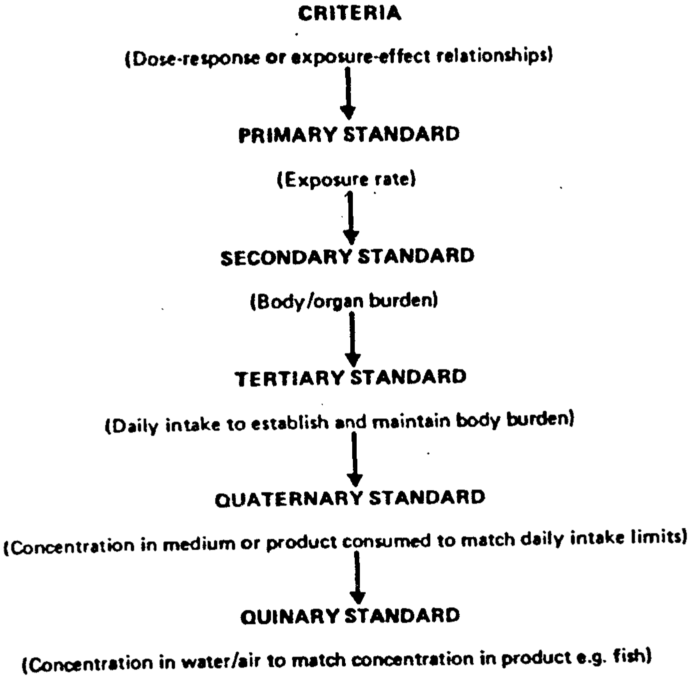


Figure 7 Ionizing radiation - critical pathway terminology.

ANNEX 3

THE CURRENT STATUS OF "MUSSEL WATCH" TYPE MONITORING PROGRAMMES

The value of using living organisms for the detection of environmental contamination has long been recognised, and in the marine environment bivalve molluscs have received particular attention. In 1967 a working group of the US National Academy of Sciences discussed indicator species and concluded that the blue mussel, Mytilus edulis, had much to offer on the basis of a comprehensive monitoring network. A so-called "mussel watch" programme was initiated in the United States in 1976 (1), using three bivalve molluscs (two species of blue mussel and one species of oyster) and analysing for trace metals, transuranics, petroleum hydrocarbons and organochlorines. The results identified a number of hot spot areas, but were also useful in indicating "no-problem" areas. In the United States, several government agencies and academic investigators are using the mussel watch approach, and programmes of this type are reported from Canada, the United Kingdom, Netherlands, Sweden, Denmark, Greenland and Northern Ireland, while plans are underway to encourage a more global coverage.

An examination of these programmes indicates that as well as the extension of geographical range, there is also an increasing scientific content, since many of the programmes are no longer directed only at the detection of hot spots. The Canadian work, for example, highlights the possibility of trend analysis and several other countries utilise the hardy nature of mussels by transferring specimens from known stocks to study areas where they can be exposed in cages. The widespread scientific interest in mussels makes their use particularly appropriate and new studies have been generated in the light of questions raised in mussel watch projects, for example, on the mechanisms of contaminant accumulation, on synergistic effects and on a range of other factors which may influence the condition of the mussel.

Further, the initial concept of simply using the integrating ability of the mussels' filtering activity is now being extended by adding observations on the well-being of the animals and correlating this with both the environmental concentrations and the body burdens of contaminants. Thus, studies of lysosomal stability, taurine/glycine ratios, oxygen/nitrogen ratios and scope for growth (2) are included in mussel watch programmes, thereby adding a biological component to the purely chemical analyses so that the extended mussel watch can be used at several points in the overall monitoring strategy (3), linking the detection of a hot spot to an evaluation of its significance.

Although the early work focussed on bivalves and particularly on Mytilus, other organisms are being used. In Canada, the lobster was found useful in one study and amphipods are used in Sweden, eels in the Netherlands and several species of seaweed in Greenland. This gives a flexibility which is desirable because mussels may not be always available and, even when they are, they may not necessarily be the most suitable organism for a particular pollutant.

To summarise accumulating experience, it may be said that the mussel watch approach has proved useful in indicating hot spots of contamination over wide areas of coast. It is considered that extensive surveys need not be repeated at intervals of less than 3-5 years, but that, having completed one wide-scale mussel watch programme, it may be useful to repeat it in limited hot spot areas and to include histological and biological measurements at that stage.

REFERENCES

1. Goldberg, E.O. *et al.*, 1978. The mussel watch. Environ.Cons. 5:101-125.

2. McIntyre, A.D. and Pearce, J.B., 1980. Biological effects of marine pollution and the problems of monitoring. Rapp.P.-v. Réun.Cons. int.Explor.Mer, No. 179.

3. GESAMP, 1980. Monitoring biological variables related to marine pollution. Reports and Studies, No. 12.

ANNEX 4

ICES

MARINE CONTAMINANT OVERVIEWS

The overview documents prepared by members of the ICES Working Group on Marine Chemistry, for the provision of advice to both ICES and the Joint Monitoring Group of the Oslo and Paris Commissions, are intended to constitute a summary of contemporary understanding of the distribution, behaviour and transport of particular contaminants in the marine environment. They are prepared for a general scientific and administrative audience. It should be recognized that in order to keep the documents concise and readily understandable, emphasis is placed upon generalized statements and the use of conditional clauses is minimal. The quantitative information is largely based upon global mass balances and consensus estimates of contaminant concentrations in marine, terrigenous and atmospheric reservoirs. Consequently, these overviews must be treated with some caution since the quantitative information is generally subject to large uncertainties and behavioural understanding is rapidly developing.

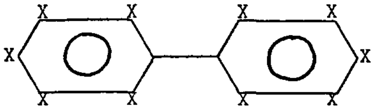
PCBs IN THE MARINE ENVIRONMENT - AN OVERVIEW

PREFACE

At the 1978 meetings of the Oslo and Paris Commissions, a request was made that ICES should provide advice on the behaviour of cadmium, mercury and PCBs in the marine environment. This paper on PCBs was originally intended to be a rather more comprehensive review, but following discussion at the 1980 meeting of the Marine Chemistry Working Group a much shortened paper has been prepared. The material which follows is therefore a summary of existing knowledge on the form and probable behaviour of PCBs in the marine environment. The overview drew upon a number of recent papers and follows the same general format adopted for the mercury overview (in Coop.Res.Rep., No. 103, Annex 2 (1981)). The original draft was prepared by Dr. J. E. Portmann, MAFF Fisheries Laboratory, Burnham-on-Crouch, with assistance from a colleague, Mr. Hampson; the text which follows incorporates a number of amendments agreed by the Marine Chemistry Working Group.

INTRODUCTION

Of the three substances on which the Oslo and Paris Commissions sought advice, two are metals, which although present in different ionic or complex forms in the marine environment are essentially the same naturally occurring substances and, provided a non-selective method of analysis is employed, will each report as a total metal figure. In contrast, PCBs are industrially produced mixtures of a chlorinated biphenyl molecule in which chlorine may be present at any one or a combination of the sites labelled X.



Structure of PCBs

It will be readily appreciated that a wide range of molecular formulae and isomers thereof are possible and that different batches will contain different combinations. In fact, 209 chlorinated biphenyl compounds are theoretically possible, although in practice only about 100 occur in commercial products. Because several different formulations with different degrees of chlorine substitution are manufactured by at least four major chemical companies in the western world, and because different compounds and isomers are degraded at different rates, the residues found in the environment usually do not match precisely any known commercial formulation. This casts a substantial uncertainty over precise quantification as the concentration will differ according to the standard used.

practice until recently has been to use as the standard a commercial formulation which happens to match the sample reasonably closely. This can cause errors of at least two-fold and perhaps, in extreme cases, as high as an order of magnitude, depending on how well the formulation used matches the sample and the exact method of quantification applied. The trend now is to use capillary column gas chromatography and single peak identification and quantification or, using the same technique, to integrate all peaks. The overall result of this uncertainty is that much of the information in the literature is of doubtful comparability in absolute terms and of debatable accuracy in quantity terms. No single organisation has ever attempted its own quantification with a view to a major budget assessment, although at least two attempts have been made on a local scale (Duinker and Hillebrand, (1979) and Osterroht and Smetacek (1980)). Thus, most of the figures which follow for concentration or budget values may be adjustable by as much as an order of magnitude either way. They do however represent a consensus value as far as the Marine Chemistry Working Group is concerned.

FORM OF PCBs IN THE ENVIRONMENT

PCBs are strongly hydrophobic and as a consequence are found in association with particulate material in the water column and especially in surface films, where the concentration may be as high as 10^6 times greater than that found in water immediately below (Ofstad and Lunde, 1978). Additionally, they are readily accumulated by marine organisms, as in plankton where the phenomenon may be purely surface adsorption although in some cases lipid solubilisation also plays a role, or in fish and marine mammals where there is a clear association between lipid content and body burden (Portmann, 1975).

Although metabolism by animals has been demonstrated, it is usually assumed that the only significant method of degradation is microbial (IRPTC (1978), EPA (1979)) and that this is much more effective for compounds containing 4 or less chlorine atoms. Thus, although a wide range of isomers are likely to be present in the environment, there will be a tendency for there to be an accumulation of higher chlorinated isomers relative to lower chlorinated isomers. The higher chlorinated compounds are less soluble in water and likely to adsorb even more readily and strongly to particulates or to be absorbed by biota or in surface films. Very recent evidence (Phelps, pers.comm.) suggests that certain forms of biota may discriminate against the higher isomers.

PRODUCTION AND USE OF PCBs

PCBs have found a very wide variety of applications in the past. However, production has now ceased in a number of countries and the use of PCBs is now restricted in many countries to those which limit the possibility of their ready escape to the environment. As a consequence, world-wide production has declined since 1971 when controls on use and manufacture began to be applied. Production began around 1930 and by 1970 US production alone amounted to 33 000 tonnes annually (Nisbet and Sarofim, 1972), but by 1971 production by OECD countries as a whole amounted to only 48 000 tonnes (USA 18 000 tonnes). 1978 production in Europe amounted to 18 000 tonnes, which was roughly the same as in 1971. Overall production has been estimated as at least 10^6 tonnes; the maximum total quantity is probably about 2×10^6 tonnes, of which about half is expected to have reached the marine environment by one route or another (NAS, 1977). Although production patterns have altered, both in terms of geographic location and the formulation produced, annual production worldwide probably still amounts to at least 50 000 tonnes. However, it is probable that as a result of more controlled use, much less than half of this will ever escape to the marine environment. Allowing for the controlled methods of disposal after use (incineration), a reasonable estimate seems likely to be between 10 and 25%.

PATHWAYS TO THE MARINE ENVIRONMENT

Although PCBs have a low vapour pressure, it is fairly certain (EPA, 1979) that volatilisation and aerial transport is an important route by which PCBs enter the marine environment. It is thought that the evaporation of PCBs results from the entrainment of the molecule in the stream of water vapour molecules rising from soil or water surfaces and is, as a consequence, higher than the vapour pressure alone might suggest. It is considered that only atmospheric transfer could explain the very widescale distribution of PCBs and their presence at quite measurable concentrations in areas far from sites of production or use.

PCBs have been reported to be present in several major rivers of the northern hemisphere and this route of input to the marine environment must be quite important, at least in relation to coastal waters. Typical figures which have appeared in the literature are 1 tonne/year for the Rhine (Borneff, 1978), and 800 kg/year in the Los Angeles Basin (EPA, 1979). Direct sewage inputs may also be considerable, e.g., 19.4 tonnes/year from Los Angeles in 1971; although this had been reduced to 5.4 tonnes/year by 1974 (Young *et al*., 1976). However, the overall contribution from this source is probably less than that from atmospheric sources by a factor of 10:1 (Kalmaz and Kalmaz (1979) and Beeton *et al*.(1979)).

CONCENTRATIONS OF PCBs IN ENVIRONMENTAL COMPARTMENTS

The following table gives concentration ranges for PCBs in various aquatic environment compartments. It should be noted that the concentrations quoted represent typical values; concentrations well outside these may well be encountered in particular areas.

Phase	Concentration Range
Rainfall	85 ng/l or 100 - 10 000 ng/m^2
Rivers/Estuaries	1 - 100 ng/l
Coastal Seawater	2 - 20 ng/l
Oceanic Seawater	0.1 - 1 ng/l
Plankton*	0.1 - 1 mg/kg dry weight
Fish	0.01 - 1 mg/kg wet weight
Sediments	< 0.001 - 1 mg/kg depending on distance from land

*The measurement of PCBs in plankton samples is fraught with particular difficulties and the results may be markedly influenced by the presence of other particulates or by contamination from surface films.

PROCESSES WHICH MIGHT AFFECT THE TRANSFER OF PCBs IN THE MARINE ENVIRONMENT

In a frequently cited paper, Harvey et al. (1974) suggest that up to 20 000 tonnes of PCBs might be transferred annually to the deep ocean on sedimenting particulates. It is generally recognised that much of the PCBs entering the marine environment via rivers is, at least temporarily, deposited in the estuarine sediments although it has been suggested that up to 50% of this is likely to be remobilised by biological activity and transfer through the food chain (Weiniger, 1978).

On the basis of the table of concentrations provided above and using the figures for area and volume, etc., used by Topping and Windom in their overview paper on mercury, the range of total quantities of PCBs likely to be present in any one compartment has been calculated.

It will be noted from these figures that the riverine input appears small by comparison with that possible from rainfall. Data for inputs from the atmosphere range from 100 - 10 000 ng/m^2/year (Södergren, 1973) and, for example, for the North Sea were estimated to average 3 500 ng/m^2/year (Holden, 1976). Assuming 1 000 ng/m^2/year worldwide, this would amount to 36 000 tonnes/year. This is identical to the estimate obtained using the rainfall concentration figure and probably represents a reasonable compromise estimate.

Compartment	Annual production or Quantity in Compartment	Total Quantity of PCBs involved (tonnes)
Phytoplankton	100 g/m^2/year	3 600 - 36 000
Fish	240 x 10^6 t/year	240 - 24 000
Seawater	1370 x 10^6 km^3	137 000 - 1 370 000
Sediments	360 x 10^6 km^2 (1 mm thick)	360 - 360 000
Rivers	3.2 x 10^{16} litres	32 - 3 200
Rainfall	4.2 x 10^{17} litres or 100 - 10 000 ng/m^2	36 000 3 600 - 360 000

Since the scale of atmospheric input is of the same order as the present annual production rates, it can be regarded as realistic only if a considerable amount of recycling sea to air to sea occurs. As it is known that PCBs are concentrated in surface films and that they are readily lost from wet surfaces along with water vapour, this appears quite possible. The probability of recycling seems even more likely if one considers that much less than 50% of the PCBs produced now is likely to escape to the environment and yet there are other inputs which must be of a scale similar to that from rivers, e.g., that via sewage.

There is considerable doubt about the accuracy of the very few measurements that have been made of PCBs in deep ocean sediments. It should also be recognised that the 1 mm overall deposition figure is an estimate for the average deposition; in some areas it will be much less and in others much more. Nevertheless, since the upper end of the range calculated for sediments assumes a concentration typical only of estuarine sediments (1 mg/kg), it can be seen that the quantity of PCBs transferred to sediments world wide must be relatively small, probably no more than 3 000 tonnes/year. Even allowing for a thicker layer of sediments than the 1 mm assumed, the total quantity must be small and much of what is present in the sediments must be concentrated in the coastal sediments of the world's seas. Even assuming that the same rate of transfer to sediments has occurred annually more or less since production began, and that no degradation or recycling takes place, the total quantity of PCBs in marine sediments is unlikely to exceed 100 000 tonnes.

As far as concentrations in the deep water are concerned there are comparatively few data, but the information available does suggest a fairly uniform depth profile distribution (Harvey et al. (1974) and Elder and Villeneuve (1979)). In order to explain this distribution, Harvey et al. postulated a rate of transfer of up to 20 000 t/yr. This value appears possible only if one assumes that a significant proportion of the PCBs present in or on phytoplankton sinks through the water column as the plankton die or are grazed on by zooplankton which in turn excrete the PCBs in faecal pellets. There is evidence from recent work off Bermuda (Knap, personal communication) that transfer by plankton-derived material may be quite rapid, at least in some areas. However, assuming the rate of plankton production already quoted, a euphotic zone of 100 metres and a concentration factor water to plankton of 10^4 and a concentration of PCBs in sea water of 1 ng/litre, the amount of PCBs removed annually from a 1 m^2 water column would be 1 µg. This represents only 1% of the amount of PCBs present in the water column, which suggests that certainly no more than 10% of the PCBs in the water column could be adsorbed and removed per year by this route. Thus, the annual quantity cited above as present in the phytoplankton must represent a significant element of recycling. Additionally, it is known that a substantial proportion of the PCBs present in an estuarine environment is removed by sedimentation within the estuary. Osterroht and Smetacek (1980) estimated that up to 95% of the PCBs was present on the sediments in the Kiel Bight and that sedimentation was removing annually between 1/3 to 2 times that instantaneously present in the water column, i.e., inorganic particulates must be important.

The quantity of PCBs in sea water at the highest concentration assumed would account for more than the total quantity of PCBs produced, which is obviously unrealistic. The figures do however suggest that much of the PCB which has actually been released to the water column is still present in the water, a conclusion which was also reached by Beeton et al. (1979). The data for quantities present in the sediments tend to suggest that this probably is the case.

CONCLUSIONS

Since PCBs are wholly of man-made origin, they offer a unique opportunity to calculate a budget for the oceanic system. Unfortunately, most of the data relate to a relatively small part of the world's seas, the quality of the analytical results is not uniform and some of the higher concentrations assumed produce quantity figures for single compartments which approach the total quantity manufactured, a situation which clearly cannot exist in reality. The following conclusions represent a reasoned interpretation of the results discussed above and offer best estimates of the quantity in each compartment.

1. The largest single source of input of PCBs to the marine environment appears to be via atmospheric deposition (probably about 30 000 tonnes/yr). However, this quantity is of the same order of magnitude as the annual rate of production, which gives considerable weight to the theory that considerable sea ⟶ air ⟶ sea cycling of PCBs takes place: probable "new" input is 5 000 - 10 000 tonnes/yr.

2. On the basis of known inputs for a few major European rivers, it seems likely that the input via rivers and direct sewage inputs amount to a further 500 - 1 000 tonnes/yr. Bearing in mind that the data available are for the northern hemisphere only and concentrations must be lower elsewhere, this must be an upper estimate.

[illegible]. Within estuaries there is considerable transfer of PCBs to sediments, but the total quantity of PCBs in the sediments of the world's sea areas is relatively small (maximum ca 100 000 tonnes) in relation to the quantity which has escaped to the environment as a whole (probably not more than 1 000 000 tonnes, of which probably not more than about one-half to two-thirds has yet reached the marine environment). This suggests that a considerable amount of remobilisation occurs subsequent to deposition in the estuary.

4. Although the amount of PCBs fixed by plankton could in theory account for transfer to the deep ocean, this would assume no loss en route and no recycling. Concentration factor considerations in relation to planktonic crop show that this route of deposition cannot account for more than 10% of the loss, say 1 000 tonnes/yr. Some transfer on inorganic particulates must take place.

5. The fish compartment represents a true removal from the ocean system since it is based on the quantity of fish landed for food or fertiliser use. However, a proportion of this removed quantity returns almost immediately as fish-processing waste. Consequently, the amount removed by this means is unlikely to be more than 10 000 tonnes/yr (assuming 0.5 ppm in fish), i.e., it is less than that entering as "new" input from the atmosphere.

6. The total quantity of PCBs present in the water column of the seas (probably no more than 200 000 - 500 000 tonnes) appears to account for most of that which has so far escaped to the marine environment.

7. Assuming that controls do lead to a reduction in inputs to coastal regions, the various recycling processes will probably lead to a gradual evening out of distribution. This in turn should lead to reductions in the peak concentrations found in biota from coastal seas. However, unless degradation occurs on a more rapid scale than appears to have been the case hitherto, contamination seems likely to persist for a considerable time.

8. It should be noted that although an apparent decline may occur in PCB concentration based on total PCB quantitation, there may be a build-up in relative and absolute terms of the more persistent compounds or isomers. Some of these may be among the more toxic components of commercial PCB formulations.

REFERENCES

Beeton, A.M. et al., 1979. Polychlorinated Biphenyls. US Nat. Acad. Sciences, Washington, D.C.

Borneff, J., 1978. Occurrence of Carcinogens in Surface Water and Drinking Water. In Aquatic Pollutants and Effects. Eds. Hutzinger, O. et al. Publ. Pergamon Press, pp125-133.

Duinker, J.C. and Hillebrand, M.T.J., 1979. Behaviour of PCB, pentachlorobenzene, hexachlorobenzene, α-HCH, β-HCH, γ-HCH, dieldrin, endrin and pp-DDD in the Rhine - Meuse Estuary and the adjacent coastal sea. Neth. J. Sea Res., 13 (2) : 256-281.

Elder, D.L. and Villeneuve, J.P., 1977. Polychlorinated biphenyls in the Mediterranean Sea. Mar. Poll. Bull., 8 : 19-22.

Harvey, G.R., Steinhauer, W.G. and Miklas, H.P., 1974. Decline of PCB Concentrations in North Atlantic Surface Water. Science N.Y., 252 : 387-88.

Holden, A.V. , 1976. Input of organochlorines to North Sea via atmospheric deposition. ICES C.M. Doc. 1976/E:46 (mimeo).

IRPTC, 1978. Data profiles for chemicals for the evaluation of their hazards to the environment of the Mediterranean Sea. UNEP, IRPTC, pp 67-128.

Kalmaz, E.V. and Kalmaz, G.D., 1979. Transport, distribution and toxic effects of polychlorinated biphenyls in ecosystems: Review. Ecological Monitoring 6 : 233-251.

National Academy of Sciences, 1977. Drinking Water and Health. Washington, D.C.

Nisbet, I.C.T. and Sarofim, A.F., 1972. Rates and routes of transport of PCBs in the environment. Environ. Hlth. Perspect. 1 : 21-38.

Ofstad, E.B. and Lunde, G., 1978. A comparison of the chlorinated organic compounds present in the fatty surface film of water and the water phase beneath. In Aquatic Pollutants and Effects. Eds. Hutzinger, O. et al. Publ. Pergamon Press, pp 461-2.

Osterroht, C. and Smetacek, V., 1980. Vertical transport of chlorinated hydrocarbons by sedimentation of particulate matter in Kiel Bight. Mar. Ecol. Prog. Ser. 2 : 27-34.

Portmann, J.E., 1975. The bioaccumulation and effects of organochlorine pesticides in marine mammals. Proc. Roy. Soc. Lond. B. 189 : 291-303.

Södergren, A., 1973. Chlorinated hydrocarbon residues in airborne fallout. Nature, Lond. 236 : 395-397.

USEPA, 1979. Water-related environmental fate of 129 priority pollutants. Vol. 1, 36-1 to 36-18.

Weiniger, 1979. Accumulation of PCBs by lake trout in Lake Michigan. Thesis. University of Wisconsin. Madison, Wis.

Young, D.R., McDermott, D.J. and Heeson, T.C., 1976. Marine inputs of PCBs off Southern California. In Criteria Document for PCBs. US EPA. Doc. No. 560/6-75-004.

CADMIUM IN THE MARINE ENVIRONMENT - AN OVERVIEW

PREFACE

The Oslo and Paris Commissions, at their 1978 meeting, requested advice from ICES on a number of topics related to marine pollution matters. These requests were considered by the ICES Marine Chemistry Working Group at its meetings in Lisbon, May 1979, and Copenhagen, February 1980.

One of the requests for advice concerned the fluxes and behaviour of cadmium in the marine environment. This note has been formulated as a means of providing such advice. It takes the form of a summary of existing knowledge with regard to the dissemination and behaviour of cadmium in the ocean and is based upon several recent reviews as well as the primary scientific literature. The overview was prepared by Dr. J. M. Bewers, Bedford Institute of Oceanography, Dartmouth, N.S., Canada, and was approved by the Marine Chemistry Working Group.

FORMS OF CADMIUM IN THE AQUATIC ENVIRONMENT

In fresh water, cadmium can exist as Cd^{2+} ion, $Cd(OH)_2^o$ complex and in various organic complexes depending upon pH and the prevalence of soluble organic material. As salinity increases, cadmium complexation with chloride also increases until, in normal sea water, cadmium exists almost entirely as $CdCl_2^o$ and $CdCl^+$ complexes. There is no strong evidence for major cadmium chelation in sea water.

Adsorption of cadmium on inorganic particulate material in sea water is relatively unimportant. The only phases that greatly adsorb cadmium in both fresh water and marine environments are hydrous manganese oxides. Thus, cadmium may be scavenged from solution during the precipitation of Mn^{2+} as MnO_2 and may be released with manganese from sediments during early diagenesis in which reducing conditions occur close to the sediment/water interface.

CONCENTRATIONS OF CADMIUM IN NATURAL ENVIRONMENTAL PHASES

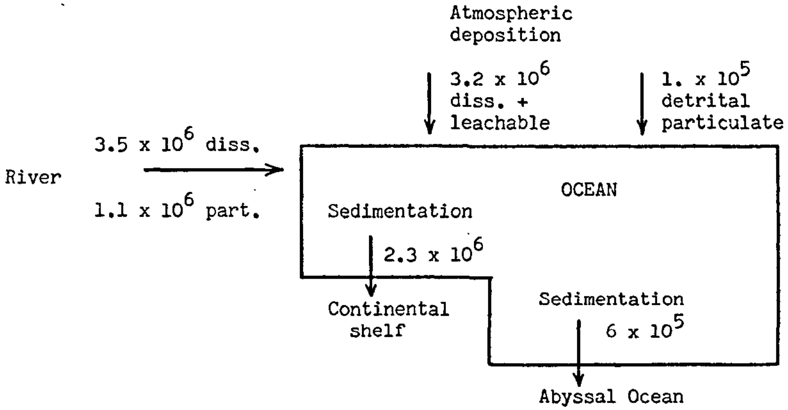
The following table gives concentration ranges for cadmium in various geological, fresh water and marine constituents.

Phase	Concentration Range	Comments
River water*	10 - 100 ng/l	Considerable variability expected
Coastal sea water*	10 - 200 ng/l	
Oceanic water*	1 - 100 ng/l	Covariant with phosphate
Rain/Snow	10 - 1000 ng/l	Upper part of this range probably reflects pollution or sample contamination
Marine sediments	0.2 - 2.0 μg/g Average 0.4 μg/g	
Igneous Rocks	0.1 - 0.3 μg/g	
Sedimentary Rocks	0.04 - 4 μg/g	Excepting phosphorites that are heavily enriched in cadmium

*denotes dissolved.

FLUXES OF CADMIUM THROUGH THE MARINE ENVIRONMENT

The following diagram shows contemporary estimates of the annual fluxes (kg/y) of cadmium into and out of the ocean.



As can be seen, total inputs (7.9×10^6 kg/y) exceed outputs (2.9×10^6 kg/y) by more than a factor of two. This implies that the ocean is not in steady state balance as far as cadmium is concerned. It is, therefore, not easy to estimate the residence time for cadmium in the ocean. It should have a value between residence times calculated on the basis of streamflow (~5 000 years) and sedimentation rate (~100 000 years) and is probably closer to the latter figure.

FLUXES OF CADMIUM ARISING FROM ANTHROPOGENIC ACTIVITY

The rates at which cadmium is being mobilized through industrial activity, particularly cadmium and zinc mining and refining operations, are comparable with the natural fluxes of the element through the atmosphere and runoff. Approximately half a million tonnes of cadmium have been produced for commercial applications in the 20th century. There are few 'permanent' end-uses for cadmium that remove the metal from the natural cadmium cycle for extended periods. Invariably most of yesterday's production winds up as tomorrow's waste. Furthermore, the amount of cadmium that is mobilized to the environment during the production of 1 tonne of cadmium in industrial products is nearly 2 tonnes. Considerable quantities of cadmium are thereby released to the natural weathering and hydrologic cycles of the earth. As an example, some 7 300 tonnes of cadmium were released to the atmosphere by United States industrial activities in 1975. Since the distance scales for atmospheric transport of cadmium released from industry are relatively short, most of this material is washed out into soils and is subsequently leached slowly into runoff.

It has been estimated that the current global flux of cadmium from anthropogenic sources is 1.6×10^6 kg/y through the atmosphere and 2.6×10^6 kg/y through river discharge to the ocean. Thus, 53% of the total cadmium influx to the ocean (7.9×10^6 kg/y) is probably derived from anthropogenic activities (4.2×10^6 kg/y). This proportion will increase as the industrial use of cadmium increases - the industrial use of cadmium in the last two decades of this century is expected to equal the production of cadmium during the previous eight decades - and the wastes arising from previous production grow in volume.

MARINE TRANSPORT AND CYCLING OF CADMIUM

The natural sources of oceanic cadmium are runoff and atmospheric deposition. The majority ($\sim$90%) of the suspended particulate material in continental runoff is sedimented on the continental shelves and therefore only about one-tenth of the cadmium that is tightly bound within weathered mineral lattices reaches the deep ocean basins. It appears that about 15% of the cadmium in river runoff is removed within the coastal zone. This result has been obtained by two groups of workers independently investigating two very different river/estuarine environments.

Thus, it seems that the vast majority of riverborne dissolved cadmium reaches the deep ocean and that remobilization of cadmium from the exchangeable phases of nearshore sediments occurs as it does for manganese. In view of the large amounts of cadmium that are being mobilized by anthropogenic activity, the concentrations of cadmium in the dissolved and exchangeable particulate phases in river water might be expected to show considerable geographic and temporal variability. A very large proportion of the cadmium brought down to the ocean in wet and dry atmospheric precipitation is solubilized in oceanic surface waters.

The distribution and transport of cadmium in the ocean is greatly influenced by marine biological activity. Cadmium is released from marine biogenic detritus in direct proportion to the regeneration of the labile nutrients phosphate and nitrate. Thus, the surface mixed layer of the ocean, in which photosynthesizing primary producers predominate, generally exhibits characteristic vertical distributions of both labile nutrients and cadmium, as depicted in Figure 1 on next page.

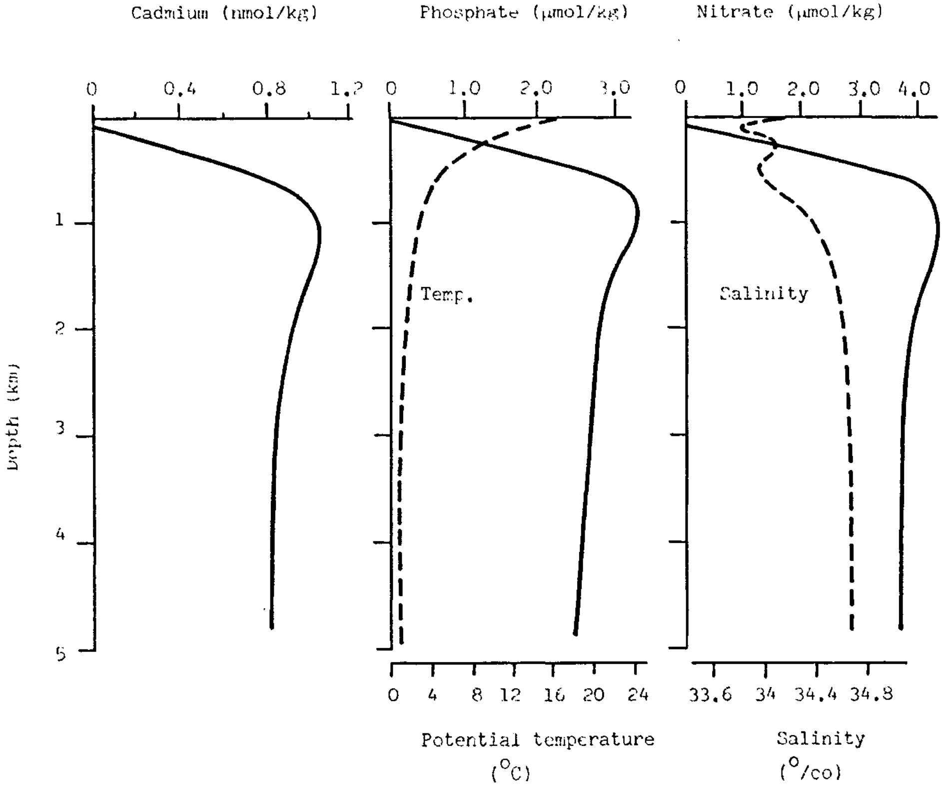
The magnitude of such vertical gradients in the mixed layer depends upon the physical oceanographic conditions in the area, particularly the intensity of vertical mixing and the presence or absence of vertical convection. Nevertheless, a remarkably strong relationship is often found between dissolved cadmium, dissolved phosphate and dissolved nitrate. Recent work in the Pacific Ocean gave the following relationship between these constituents:

$$\Delta Cd : \Delta P : \Delta N \text{ (atom)} = 3.5 \times 10^{-4} : 1 : 15.2$$

On a mass basis this becomes:

$$\Delta Cd : \Delta P : \Delta N = 1.3 \times 10^{-3} : 1 : 6.9$$

Figure 1. Cadmium and nutrient profiles in the eastern Pacific.



This relationship reflects the removal of cadmium in the surface layer from the dissolved phase into particulate organic material within phytoplankton and its subsequent regeneration at greater depths both within and below the mixed layer. For every cadmium atom passing through this cycle, there exist a corresponding 300 000 atoms of carbon acting as a carrier. Thus, the internal biogeochemical cycle of carbon, associated with the growth and decay of photosynthesizing organisms, dominates the vertical distribution of cadmium within the mixed layer and for some distance beneath it. The supply of cadmium and labile nutrients to primary producers in the surface layers is maintained by atmospheric inputs and vertical mixing - the latter process resupplying the regenerated constituents back to the euphotic zone. It appears that the residence time for cadmium in the mixed layer of the northeast Pacific is about 0.1 year. This is very short in comparison with the surface layer residence times of water and other metals.

Much of the cadmium settling within biogenic detritus is quickly regenerated and returned to the mixed layer by vertical mixing. Cadmium-containing particles that settle below the thermocline without complete regeneration constitute a source for deep water and sedimentary cadmium. Aside from fractions of phytoplanktonic detritus, such materials include zooplankton detritus and faecal materials. Dissolution and regeneration of such organic detritus continue below the thermocline but the faster settling particles, such as faecal pellets, may well succeed in carrying a significant fraction of the cadmium removed from the mixed layer to the abyssal sediments.

The removal of cadmium from the deeper layers of the ocean is less well understood. It seems likely that manganese chemistry plays an important role such that the removal of cadmium may be largely controlled by Mn^{2+} precipitation. Certainly, any exposed and accreting manganese oxide surfaces on suspended particles in the deep water or at the sediment/water interface will act as sites for cadmium removal. Since direct cadmium adsorption by other particulate phases is relatively minor, the vertical flux of other types of particles and particle aggregates is probably relatively unimportant as a vehicle for cadmium uptake and transport in the deeper layers of the ocean.

CONCLUSIONS

1. The flux of cadmium entering the ocean is greater than the rate of cadmium removal from the water column to the sediments. This implies that the ocean is not in steady state balance for cadmium.

2. The residence time for cadmium in the ocean is estimated, on the basis of sedimentation rate, to be around 100 000 years and a gradual increase in cadmium concentrations in the ocean can be expected.

3. The atmospheric deposition of cadmium is comparable to the riverine input of the element.

4. Only about 10% of the particulate cadmium in runoff reaches the deep ocean directly. The majority (~90%) of suspended particulate material discharged from rivers is sedimented on the continental shelves. A portion of the cadmium associated with particulate material sedimented on the continental shelves may be subject to remobilization in a similar manner to non-detrital manganese.

5. The majority of riverborne dissolved cadmium passes through estuarine and other near-shore mixing zones and its subsequent distribution and transport is largely controlled and mediated by marine biological activity.

6. Considerable heterogeneity in the concentration of cadmium in rivers can be expected as a consequence of anthropogenic activities.

REFERENCES

Simpson, W.R., 1978. A Critical Review of Cadmium in the Marine Environment. Internal Document No. 44, Institute of Oceanographic Sciences, Wormley, U.K.

Boyle, E.A., Sclater, F., and Edmond, J.M., 1976. On the Marine Geochemistry of Cadmium. Nature, 263: 42-44.

Bruland, K.W., Knauer, G.A., and Martin, J.H., 1978. Cadmium in Northeast Pacific Water. Nature, 271:74-743.

ANNEX 5

SUMMARY REPORT ON MINI-SYMPOSIUM ON TRANSPORT PROCESSES IN ESTUARINE AND NEARSHORE ZONES

This is a summary of the papers presented at C.M. 1980, based on extracts from the papers.*)

1. Introduction

Five papers were presented, see programme in Section 2. The paper by Dr Pearce discussed the conditions in several coastal areas along the east coast of the USA, identifying a number of problems where research is required and pinpointing why we are especially interested in the nearshore zone. It was, among other things, demonstrated that in some areas the environmental contamination is limited to very near the coast. A major problem is how much of the material flux to the coastal zone from land is retained in the nearshore zone and how much of it is transferred to the open sea, respectively, and on what time scales.

These questions were considered in the following paper by Dr Duinker, for the southern North Sea. He showed that a large amount of the suspended matter was retained in the nearshore zone and with it a large amount of metals. The importance of the size distribution and composition of the suspended matter was shown, the smaller size fraction being transferred offshore with a relatively higher portion of metals than the large size fraction. Correct information on the amounts can only be obtained by studying both the suspended and dissolved fractions.

This was also demonstrated in the subsequent paper presented by Dr Jeffries. The concentration distributions of ^{137}Cs in the Irish Sea were shown from observations over an 8-year period. The successive spreading from the source was shown, the concentrations however remaining 1-2 orders of magnitude larger very close to the source than in the southern entrance to the Irish Sea. Residence times of the water in various parts of the Irish Sea were calculated on the basis of these observations. The distribution of plutonium in the sediments was used to show deposition areas in the Irish Sea. The Cs observations were used to obtain an estimate of the amount of plutonium leaving the area, which together with the amount in the sediments and the known input gave a rough budget; this, however, did not account for all the input.

The paper presented by Dr Yeats gave an account of a series of box models which had been developed for the Gulf of St Lawrence area in order to study the budgets and fluxes of various metals. Physical oceanography observations were used to define boxes and flow rates. Fluxes of material into the area from rivers were known and the atmospheric input was estimated. It was clearly shown that very large parts (up to 95%) of suspended matter and certain metals are retained in the coastal zone. Estimates were given of the supply from the coastal zone to the pelagic sediments, giving results in reasonable agreement with observations for some metals. About 30% of the supply was estimated as atmospheric input to the open ocean.

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*) Composed by the Convener (G. Kullenberg)

The last paper, presented by Dr Peters, reviewed processes in a sequence of estuaries with different tidal ranges, fresh water run-off and morphology. The importance of the stratification and vertical mixing for the residence time of waters in the estuaries was shown and the retainment of suspended matter by the various processes in the estuarine zone was discussed. Large amounts of material supplied by the fresh water run-off will be retained and not reach the open ocean. The importance of events of large fresh water supply was discussed and it was shown how these can alter the conditions temporarily and also effectuate a pulse of large transfer of material further off-shore.

Short discussions after each presentation and a general discussion after the last paper brought up several points of interest, including the reliability of analytical techniques, the importance of the different morphological configurations of the areas discussed, making generalisations difficult, and the importance of events of meteorological origin (streams) which are difficult to study at the time of the event. The papers dealt mainly with chemical aspects, including some physics, but generally not biological processes. These could be considered at a later similar occasion. The session was very useful in showing that very active research in the area is going on, making considerable progress and addressing several important practical questions like that of retention of material in the coastal zone and transfer to the open sea. It was felt that the subject should be considered again in a few years' time, perhaps in the form of a special meeting.

Some of the important general points raised in the Mini-Symposium are presented.

2. Programme for the Mini-Symposium

1. J.B. Pearce "States of estuaries and coastal waters between Cape Hatteras and Maine: A review" (C.M.1980/E:56)
2. J.C. Duinker "Processes affecting the behaviour of contaminants during estuarine mixing and in coastal areas with particular reference for the southern North Sea" (C.M.1980/E:34)
3. D.F. Jeffries, R.J. Pentreath, J.W. Talbot "Transport processes in the Irish Sea as indicated by the measurement of radionuclides released from Windscale" (C.M.1980/Gen:5)
4. J.M. Bewers, D.A. Yeats "Transport of metals through the coastal zone" (C.M.1980/Gen:4)
5. R. Wollast, J.J. Peters "Results on material transports in estuarine zones" (C.M.1980/Gen:8)
6. General discussion: One point is feelings about an ICES special meeting or symposium in 3-4 years' time on estuarine and coastal zone processes considered interdisciplinary.

3. Physical description of different types of estuaries

The knowledge of hydrodynamic characteristics (advection and dispersion terms) of the system is of primary importance in order to understand the behaviour of substances in the estuary. These characteristics are, however, complicated because of the peculiar circulations induced by the mixing of fresh and salt water and the often intricate morphology of the estuarine zone.

The circulation patterns govern in turn the residence time and the transfer mechanisms through the estuary and important processes like the eventual accumulation of suspended matter by sedimentation.

In fact, only a limited number of master parameters is sufficient to distinguish between various estuarine types:

- morphological characteristics (width and depth, inner or outer estuary, delta, lagoon, fjord, etc.);
- fresh water inflow;
- tidal characteristics (range and propagation).

The study of the distribution of salinity is a powerful tool in order to approach qualitatively and quantitatively the hydrodynamic characteristics and thus to define the type of estuary. Salinity is a conservative variable and the source term may be introduced as a condition at the boundaries of the model. Furthermore, it is possible to accumulate easily and rapidly numerous salinity measurements.

Therefore, the actual classification of estuaries is mainly based upon the relative vertical and lateral stratification of the water masses identified by means of their salinities.

Most of the earlier efforts were devoted to the distinction between vertically homogeneous or stratified estuaries. The vertical mixing is essentially controlled by the relative influence of river flow and tidal action. The latter is governed by the tidal range at the river mouth and the geometry of the estuary. It must be noted that, because of the relatively small variations of the tidal range with respect to the generally large changes of fresh water inflow, a given estuary may present different stratification patterns during draughts or freshets. Furthermore, the vertical mixing increases rapidly with decreasing depth and stratification is therefore reduced in many shallow parts of estuaries.

The residence time of fresh water increases quickly with rising vertical mixing owing to its dilution in a large body of sea water. In perfectly stratified estuaries, the fresh water flows in a restricted surface layer without mixing with the underlying salt water wedge and thus quickly reaches the sea.

Simple calculations allow the estimation not only of the mean residence time, but also of the longitudinal and vertical dispersion coefficients. It is further possible to predict with a fairly good approximation longitudinal profiles of salinity and vertical gradients of salinity and velocity, which can be extended under certain conditions to the calculation of the transport of other material associated with the fresh water inflow (river discharge).

The geometry produces lateral velocity gradients which, in turn, induce and maintain a complex system of channels and tidal flats. A striking example is the existence in many coastal plain estuaries of flood and ebb channels.

The lateral salinity gradients reflect the local transport rates of the water masses and their residence times in different channels and tidal flats. The choice of the disposal sites of waste in such estuaries must take these critical parameters into account in order to avoid local accumulation of high pollutant concentrations.

4. Aspects of transfer through the coastal zone

Rivers are a major source of metals and other materials passing through the coastal zone, and mixing between continental runoff and marine waters is most pronounced in estuaries. However, it should be noted that as far as the net flux of material to the ocean is concerned, attention must also be given to conditions in the waters of the continental shelf in general. It cannot be assumed that the flux to the open ocean corresponds to the flux through the estuary. Estuarine processes continue in the continental shelf region.

The transport of chemicals through the coastal zone can be visualised in terms of a progression from the riverine environment through the estuarine and continental shelf environments to the deep ocean, as shown schematically in Figure 1. The coastal zone is here defined as the estuarine and continental shelf waters and sediments. The coastal zone exchanges metals with the overlying atmosphere and the adjacent continental and deep marine environments, although the net flow of metals is generally from the continent towards the deep ocean. Knowledge of these exchanges is of paramount importance in quantifying the fluxes of metals through the coastal zone. The fluxes of metals within continental runoff and atmospheric precipitation are relatively better quantified than the exchanges across the coastal zone/deep ocean interface.

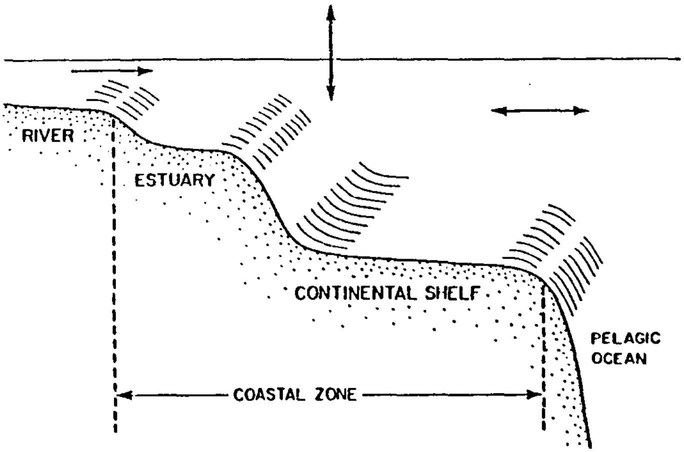

Figure 1 Schematic cross section through the coastal zone

Atmospheric deposition into the coastal zone is, at best, poorly known. In a global sense, there appears to be reasonable agreement as to the particulate matter flux through the atmosphere into the ocean. However, the concentrations of metals associated with particulate fallout in remote areas are much higher than would be expected from crustal weathering or the introduction of bulk sea water into the atmosphere. Whereas, for some elements, atmospheric deposition seems to be the dominant mechanism of their entry into the deep ocean, the situation in the coastal zone is far more ambiguous. Some estimates of atmospheric deposition of dissolved and particulate metals into particular coastal regions have been made. These studies show that the atmosphere is a major source of input of metals to the sea areas investigated.

Much speculation on the loss of metals from surface ocean waters into the atmosphere has been advanced. The field is, however, in its infancy and a great deal more research on air/sea exchange processes needs to be conducted before much can be said, in a quantitative sense, about the balancing transport of marine metals to the overlying atmosphere.

The exchanges at the coastal zone/ocean basin boundary are undoubtedly the largest unknown in the mass balance equation. Whilst the composition of the marine end-member of nearshore mixing becomes an increasingly stable quantity with distance from fresh water sources, the actual discrimination between the marine (landward flowing) source water and the mixed (seaward flowing) water becomes increasingly difficult. In many cases it will not be possible to identify these individual water flows on the continental shelf. Marine source water may only appear on the shelf as a complicated and varying mixture of oceanic water masses or intermittently, e.g., as a result of periodic upwelling. Mixed water may be flowing predominantly along the coast rather than perpendicular to it. Only where environmental conditions are suitable and reliable physical oceanographic information is available can any attempt be made to distinguish between these two counterflows. In general, as one approaches the estuarine zone, this distinction becomes easier, but, as stated earlier, it is important that some estimate of the cumulative effect of processes in both estuarine and continental shelf environments be gained, and this in turn demands that we examine the composition of landward and seaward flowing waters as remotely as possible from fresh water sources.

5. Removal of material by sedimentation and aspects of trace metal geochemistry in the coastal zone

Most of the particulate matter, organic or inorganic, transported by rivers is negatively charged. The increase in ionic strength during the mixing of fresh and sea water neutralizes the surface charges by adsorption of cations. As a consequence, the particles, often colloidal, are flocculated and thus more able to settle.

Many pollutants are, in fact, transported as particulate matter by rivers. For example, the mean global river flux of organic matter is equally distributed between the dissolved and the particulate phase. In polluted rivers, the fraction of particulate organic matter is still more important and reaches for instance 80% of the total load in the Scheldt.

The distribution of heavy metals between the aqueous and solid phase is a characteristic of the metals considered. It has been estimated that 30-45% of the total discharge of zinc and cadmium is usually associated with particles, and 60% to more than 80% of metals like copper, mercury, chromium and lead is transported by particulate material.

The increase in salinity also induces the flocculation of dissolved organic matter of high molecular weight. The precipitation of humic acids by this process has been the most extensively studied. As humic compounds are also able to form strong complexes with metals, these mechanisms may transfer them from the aqueous phase to the solid phase and favour their possible removal from the water column by sedimentation in the estuary or in the adjacent coastal zone. It has been shown that the terrestrial humic material can account for up to 25% of the total organic material in coastal zones.

On the other hand, it has been shown that humic substances contain a sizeable portion of copper and zinc found in the sediments. Flocculation is however not sufficient to prevent the transport of the material to the sea and the hydrodynamical characteristics must be encountered to allow the flocculated material to settle and accumulate in certain zones. Again, the latter process depends strongly on the type of estuary, but generally all estuaries are areas of intensive sedimentation. This is not only due to their geomorphology but also to the density currents induced by the salinity gradients. The net effect of these currents is a predominantly landward flow of estuarine bottom waters, even in very well-mixed estuaries like the Scheldt. River-borne sediment is trapped to a certain extent by this net non-tidal current near the toe of the salt wedge. In well-mixed or partially stratified estuaries, the circulation caused by the density structure is also the critical factor influencing the occurrence of a turbidity maximum which usually corresponds to the accumulation zone of bottom sediments.

Figure 2 summarizes schematically, as an example, the interrelations between flocculation and transport processes on the accumulation and entrapment of sediments in the case of the Scheldt.

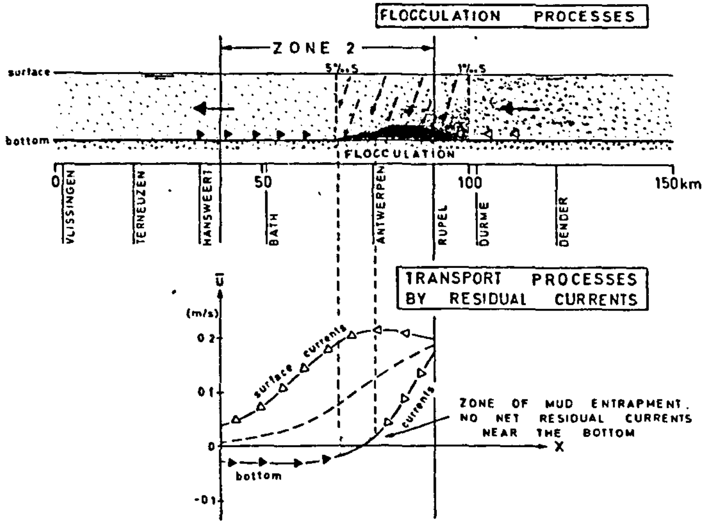

Figure 2 Mechanism of mud accumulation in the Scheldt

In the case of well or partially mixed estuaries, the removal of suspended matter is very efficient. An annual budget based on measurements of the turbidity and the sedimentation rate shows that in the Scheldt estuary 80% of the suspended matter is removed in the zone corresponding to a salinity range of 2-10‰. On the basis of long-term sedimentation, it has been demonstrated that 85% of the river-borne sediment is permanently trapped in the Gironde estuary and never reaches the coastal zone.

The major portion of our present understanding of metal behaviour in the coastal zone has been gained through the study of metal distributions in estuaries. A great deal of use has been made of the relationships of metals with salinity or chlorinity since the method provides a convenient mechanism of filtering out much of the purely physical hydrographic influences. Considerably greater attention has been paid to iron and manganese than to other metals. Dissolved iron exhibits a characteristic, and apparently universal, relationship with salinity that is indicative of loss of the metal from solution during the estuarine mixing. These losses are attributed to the precipitation of dissolved or colloidal iron introduced in fresh water during mixing with saline water. Particulate iron is produced by this process but the increased concentration of particulate iron may not be discernible against the background of the naturally high concentrations of detrital particulate material. The very dynamic nature of many well-mixed estuaries or partially mixed estuaries makes the study of particulate metal behaviour and adsorption and desorption processes very difficult. Nevertheless, since a high proportion of the suspended matter introduced to the ocean by rivers is sedimented within the coastal zone, only a relatively small amount of particulate iron, either introduced directly by rivers or generated by precipitation of dissolved iron during estuarine mixing succeeds in escaping to the deep ocean basins. In the case of manganese, the picture is rather more complicated. Dissolved manganese has shown a variety of relationships to salinity in estuaries. These differing features are due to the relative importance of particulate desorption and adsorption processes and the presence and strength of manganese releases from bottom sediments following early diagenesis. While manganese desorption from riverine particles during estuarine mixing has not been conclusively established, it seems very clear that both manganese precipitation from solution and widespread releases from nearshore pelitic sediments can occur.

Rather less is known about the universal aspects of the behaviour of other metals, either because of a paucity of consistent data or because the apparent behaviour of a particular element in some estuaries differs substantially from that in others. Probably the most important aspect of metal geochemistry in estuaries that needs continued attention is the exchange of metals between dissolved and particulate phases and the factors which control this exchange.

In polluted estuaries, the composition of the recent sediments denotes also the removal of various pollutants and especially the heavy metals associated with the sedimentation process. In the case of the Scheldt, annual mass balances for Zn, Cu and Pb were evaluated by dividing the estuary into two zones. The upper zone corresponds to a salinity range of 0-15‰ and is the preferential sedimentation and accumulation area. This part of the estuary is also generally oxygen depleted due to the high organic load.

It should be pointed out that in this case a large fraction of the heavy metals are introduced into the river as solid compounds or are rapidly precipitated if they are discharged in a soluble form. The percentage of Zn, Cu and Pb removed by sedimentation is around 75% for the three metals. As mentioned earlier, flocculation may affect dissolved substances when they enter the estuarine zone. The existence of oxydo-reduction and pH gradients also induces dissolution and precipitation reactions affecting the transport of material. The existence of an anoxic zone in heavily polluted estuaries complicates the behaviour and transport of many elements.

For instance, Mn and Fe are dissolved at the low oxydo-reduction potentials occurring in the anaerobic zone and are precipitated more downstream, when oxygen is restored. These elements, and especially the precipitated iron hydroxides, eliminate by scavenging dissolved heavy metals and other compounds like phosphates. On the other hand, copper is much less soluble in anaerobic conditions and the increase in the oxydo-reduction potential leads to solubilisation of particulate Cu.

It should be noted that anoxic conditions can also occur in the bottom water of stratified estuaries in the zone where organic matter tends to accumulate.

The above discussion refers to average conditions, but during river floods, the sediment load can increase drastically. For instance, the Potomac river carried about 70% of its sediment load during ten days in each year in 1961 and 1962. In the Delaware river, more sediment was carried in two days of record flooding than during a normal year. The increase in sediment load in the river is not only due to the increase in land erosion but also to the erosion and resuspension of the riverbed material.

A second effect of increasing river flow is the increasing stratification and the seaward movement of the two-layer circulation pattern which may be pushed completely out of the mouth, so that water moves predominantly seawards at all depths within the estuary. Under these conditions, most of the inflowing river sediment would be transported through the estuary and out to sea.

In the case of well-mixed estuaries like the Scheldt and the Gironde, the zone of net non-tidal movement remains in the river. The increased fresh water inflow carries larger amounts of suspended material which may be deposited near the mouth, in the river or even in the adjacent coastal zone. This transport is however temporary and in both estuaries the landward bottom transport of sediments brings part of them back to the accumulation zone of the estuary.

Definition and analysis of compounds in solution and in suspension

Water and particulates are subjected to different transport mechanisms, both in rivers, estuaries and the ocean. Also, biogeochemical processes are different for dissolved and particulate components. It is essential, therefore, to distinguish between dissolved and particulate fractions. From a practical point of view, this distribution is not defined unambiguously for sea water and other natural waters. The main reason is that the size of particles in sea water suspension covers a continuous range from colloidal up to sand grain size fractions.

The problems involved can be "solved" by filtration of samples, using filters with some arbitrarily selected nominal pore size (usually 0.45µm). Serious problems are associated with this operational definition because of the change of effective pore size during filtration, due to clogging. So, the average size of the particles collected on the filter may depend on the total concentration and on the size distribution of particles in suspension.

6. Elemental contents in particulate suspended matter as exemplified by studies in the southern North Sea

The technique of elemental ratio was used to investigate the degree of association of some metals (Fe, Mn, Al, K, Mg, Cn, Zn) with inorganic and organic constituents in the southern North Sea. Additionally, a study has been made of its dependence on the total suspended matter concentration. The distributions of salinity and seston concentration in transects off the Dutch coast show that seston concentrations are lowest (0.5-1.0mg/dm^3) in an area east of the axis of maximum salinity. The distribution of metal concentrations per water volume (µg/dm^3) is, at least qualitatively, similar to the distribution of total suspended matter, with values decreasing in transects from the coast towards the central part of the Bight.

However, the rate of change is distinctly different for the various elements. This can be observed from plots of the distribution of elemental contents in terms of seston dry weight (µg/g or %) : those of Fe, Al and K pass through a minimum and those of Mg, Cu, Zn and organic C through a maximum. Minima and maxima do not coincide with the axis of maximum salinity but rather with the minima in seston concentrations and maxima in organic C content.

Elemental contents of Fe, Al and K are higher at higher rather than lower seston concentrations, while those of Mg, Cu, Zn and organic C are higher at lower seston concentrations. A critical change occurs at about 5 mg/dm^3. The behaviour of Mn is different: its more complicated distribution pattern and the less regular relations of its content in seston with both salinity and seston concentrations result from processes that cause transitions between dissolved and particulate Mn species in the estuarine and coastal environment. Aluminium is closely related to total suspended matter; it may be considered as almost entirely associated with Al-silicates, mainly clay minerals. The elemental content of an element X in particulate matter is altered when varying amounts of components with low content of X (e.g. quartz) are mixed with fine-grained Al-minerals with higher contents of X. However, X/Al ratios are not altered. X/Al ratios in these data are practically constant at seston concentrations above 10-20 mg/dm^3. This applies to the plots of all elements considered here. In addition, the X/Al ratios increase strongly with decreasing seston concentration below 5 mg/dm^3. This is obvious for Mg, Cu, Zn, and organic C, and it also applies to Fe, Mn and K.

A seston fraction consisting of low density small-sized particles that resist settling dominates at low seston concentrations. Another fraction, derived from the bottom, dominates at high seston concentrations. These fractions have different settling properties and different contents of metals and organic matter. Thus, relatively high contents of Fe, Al and K occur in material present at high seston concentrations, while high contents of Mg, Cu, Zn and organic C occur in material present at low seston concentrations. The X/Al ratios above 10-20 mg/dm^3 for the major elements Fe, Mn, K and Mg are very similar to the values reported for fine-grained sediments. This supports the idea that suspended matter at high seston concentrations contains a relatively high fraction of bottom-derived material.

The metals studied here are partitioned over organic matter and minerals. The strong increase in the X/Al ratios at low seston concentrations suggests that the elemental contents in the continuously suspended fraction are determined primarily by mineral components such as Fe and Mn hydrous oxides rather than by Al-silicates.

The contents of particulate Mg, Cu, and Zn co-vary with the organic carbon content; a negative correlation is observed for Al, Fe and K. No such conclusion can be drawn for Mn. Therefore, Mg, Cu and Zn may be associated with organic matter or, alternatively, with mineral fragments, such as oxide coatings, occurring in association with organic matter. An attempt has been made to determine the role of living phytoplankton as a possible site for trace elements. Practically pure samples of dinoflagellates and diatoms were obtained at some stations at low seston concentrations off the Dutch coast in April 1979. The contents of Cu, Zn, Fe, and Mn were found to be far below the levels found in total suspended matter at low concentrations. The relatively unimportant role of living phytoplankton in the Southern Bight has also been reported in earlier work. A strong correlation has also been reported between trace metals and organic matter in bottom sediments of the North Sea. These results, in combination with the strong correlation between the contents of several elements and organic C in seston, suggest that detrital organic matter rather than living phytoplankton should be considered as a potentially significant site for the metals in these data.

However, mineral components such as Fe and Mn hydrous oxides, co-varying with organic matter, possibly as aggregates, may also be important sites for trace metals, in particular at low seston concentrations.

7. The influence of biological activity on the transfer of material

Two main characteristics of the estuaries from a biological point of view must be taken into account in order to discuss the role of organisms in the transfer of matter.

It has already been shown that terrestrial organic matter has a tendency to accumulate either in the zone of turbidity maximum for well-mixed estuaries (Scheldt), or in preferential bottom water masses in the case of stratified estuaries (Zaire). The detrital organic matter is submitted to degradation by heterotrophic bacteria with consumption of the available oxidants. Due to the residence times, the water often becomes anoxic.

The mineralization of terrestrial organic matter by this process depends to a large extent on the "refractoriness" of the substrate. For instance, in the case of the Scheldt, it has been estimated that 25% of the organic load carried by the river is decomposed by this process. In the case of the Zaire, only 1% of the organic load is respired in the water column before it settles.

This process has more drastic effects on substances able to be used as oxidants by bacteria. The case of Mn and Fe oxides and hydroxides, which may be reduced and dissolved by bacteria, has already been mentioned. Nitrate and nitrite are also rapidly transformed into N_2 when oxygen is no longer available.

Except during the winter, when the heterotrophic activity is low, all the nitrate present in the fresh water of the river Scheldt is reduced to N_2 and transferred to the atmosphere in the anoxic part of the estuary. On the other hand, nitrate is produced in the lower part of the estuary, when aerobic conditions are restored, by nitrification of ammonia resulting from the mineralisation of organic matter.

On the other hand, estuaries are also productive areas and the contribution of organic matter synthesized in the water column or salt marshes and swamps associated with the estuaries may become predominant within the material transported to the sea. The high nutrient content of estuarine waters promotes the development of high productivity zones as soon as the turbidity caused by the terrigenous suspended matter drops by flocculation and sedimentation.
