

ERRATA TO C.M.1981/C:2 - Third Report of the Marine

=====
Chemistry Working Group
=====

page 3 - para. 4.9 - add:

The six PCB compounds are as follows:

<u>Peak no.</u>	<u>Structure</u>
28	2, 4 - 4'
52	2, 5 - 2', 5'
101	2, 4, 5 - 2', 5'
138	2, 3, 4 - 2', 4', 5'
153	2, 4, 5 - 2', 4', 5'
180	2, 3, 4, 5 - 2', 4', 5'

page 3, para. 4.12, in second line, delete: "on humans".

page 5, para. 5.2.4, change first sentence as follows:

"The Group agreed that these investigations should continue intersessionally. The scientists participating are listed in Annex 8."

page 6, para. 6.4, add the underlined words:

"compare data from different areas from different laboratories ..."

page 7, para. 6.7.2, change first two sentences to read as follows:

"The 5th ICES organochlorine intercalibration exercise has demonstrated that with oils containing 1 or 2 µg PCB/g inter-laboratory coefficients of variation of 31% and 28%, respectively, are found among the 23 participating laboratories. Results on other organochlorine compounds demonstrated much higher variance than for PCB results in general, presumably due to the low levels present (see the values given in Table II)."

page 12, para. 6.9, add at the end of paragraph:

"This contribution by ICES had been duly recognised by the organisers of and participants in the exercise."

page 15 - para. 8.4, add the following: "It was stressed that it would be useful for the Group to have in the future similar short presentations on subjects of interest to its activities because of the wide diversity of interests of the members. The Chairman accepted this proposal and agreed to consider it when planning the next meeting."

New annex - ANNEX 8

PCB STUDIES

The following participants in the 5th organochlorine intercalibration exercise are investigating the possibility that analyses of individual PCB compounds would yield a lower interlaboratory variance in results:

Dr. J. Luc Charlou
Centre Nat. pour l'Exploitation des Oceans
Centre Océanologique de Bretagne
BP 337, 29273 Brest Cedex
France

Dr J. Portmann
M.A.F.F.
Burnham-on-Crouch
Essex - U.K.

Mrs. dr. M.A.T. Kerkhoff
Netherlands Institute of Fishery Investigations
Postbus 68, 1970 AB LJ muiden
Holland

Dr. L.G.M. Tuinstra
Rijks-Kwaliteitsinstituut voor hand-en
Tuinbouwprodukten, Postbus 230
6700 AE Wageningen
Holland

Mr. J.C. Duinker
Nederlands Instituut voor Onderzoek der Zee
Postbus 59, Texel
The Netherlands

Dr. Bjarne Bøe
Fiskeridirektoratets Sentrallaboratorium
Møllendalsveien 4, P.O. Box 185
5001 Bergen, Norway

Mr. K.H. Palmork
Fiskeridirektoratets Havforskningsinstitutt
Nordnesparken 2, PO Box 1870-72
5011 Bergen-Nordnes, Norway

Ms. E. Baumann Ofstad
Sentralinstituttet for Industriel Forskning
Forskingsveien 1, PO Box 350
Blindern, Oslo 3, Norway

Dr. Ross Norstrom
Environment Canada
National Wildlife Research Center
Canadian Wildlife Service
Ottawa, Ontario
K1A OE7

This Report not to be quoted without prior reference to the Council^{x)}

International Council for the
Exploration of the Sea

C.M.1981/C:2

Hydrography Committee
Ref. Marine Environmental Quality
Committee

THIRD REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Nantes, 16-19 February 1981

This document is a report of a Working Group of the International Council for the Exploration of the Sea and does not necessarily represent the views of the Council. Therefore, it should not be quoted without consultation with the General Secretary.

x) General Secretary
ICES,
Palægade 2-4
DK 1261 Copenhagen K, Denmark

TABLE OF CONTENTS

	<u>Page</u>
1. Opening of Meeting and Adoption of Agenda.....	1
2. Report of the 68th Statutory Meeting.....	1
3. International Activities of interest to the Group.....	1
3.1. ICES/SCOR Working Group on the study of the Pollution of the Baltic.....	1
3.2. Joint Monitoring Group of Oslo and Paris Commissions.....	2
4. Reports on Projects and Studies from Working Group members.....	2
5. Reports of the Intercalibration Studies for Heavy metals and Organochlorines.....	4
5.1. Cd and Pb in Biological Material.....	4
5.2. PCBs and other organochlorines in Fish Oil.....	5
6. Future Activities Following Intercalibration Exercises.....	6
7. Studies on Petroleum Hydrocarbon Analysis.....	12
7.1. Report on the Intercomparison Study.....	12
7.2. Report on the Questionnaire on Sampling and Analysis of Sea Water, Sediments and Biota for Trace Organic Compounds.....	13
7.3. Reports on Other National or International Intercomparison Studies	13
7.4. Future Activities.....	14
8. Carbon Dioxide Cycling in the Oceans.....	15
9. The Use of Tracers for the Study of the Movement of Substances in the Marine Environment.....	15
10. Methods for Primary Production as an Alternative to the ^{14}C Method - Techniques and Concepts.....	16
11. Programme for the Publication of Leaflets on "Techniques in Marine Chemistry".....	16
12. Possibilities of further Work on Problems Related to Incineration at Sea.....	17
13. Overviews on Fluxes and Transport of Pollutants in the Marine Environment.....	17
13.1. Cadmium.....	17
13.2. PCBs.....	17
14. Methodology for the Measurement of River Inputs.....	19
15. Development of Standard Samples with Pollutants at Ambient Levels.....	19

....cont'd

	<u>Page</u>
16. Any Other Business.....	19
17 Approval of Recommendations and Deadlines.....	19
18. Closure of the Meeting.....	19
Annex 1 Agenda.....	20
Annex 2 List of Participants.....	21
Annex 3 5th Round Intercalibration on Trace Elements in Sea Water.....	24
Annex 4 Determination of Primary Production from changes of CO ₂ , O ₂ , and Nutrients in the Open Water.....	26
Annex 5 Recommendations.....	29
Annex 6 Action List.....	30
Annex 7 The CO ₂ Problem.....	31

REPORT OF THE THIRD MEETING OF THE MARINE CHEMISTRY WORKING GROUP

Nantes, 16-19 February 1981

1. OPENING OF MEETING AND ADOPTION OF AGENDA

- 1.1. The Chairman, Dr (Ms) M de Barros, opened the meeting at 10.00hrs on 16 February 1981 and welcomed the participants.
- 1.2. Professor C. Maurin, Director of the Institut Scientifique et Technique des Pêches Maritimes, Nantes, which hosted the meeting, welcomed the participants to his Institute and to Nantes. He provided some information about the Institute and the region in which it is located.
- 1.3. The Working Group then considered and adopted the agenda, which is attached as Annex 1. The list of participants is attached as Annex 2. The ICES Environment Officer acted as Rapporteur.

2. REPORT OF THE 68th STATUTORY MEETING

- 2.1. The Working Group was informed that the Report of the Second Meeting of the Working Group had been considered at the Joint Session on Marine Chemistry at the 1980 Statutory Meeting. The recommendations had been discussed and the following were accepted: (a) the recommendations that the report of the sixth intercomparison exercise on trace metals in biological materials (C. Res. 1980/1:7), and the reports of the intercalibration exercises on mercury and cadmium in sea water (C. Res. 1980/1:6) be published in the Cooperative Research Report series, (b) the recommendation that a new series of leaflet publications entitled "Techniques in Marine Chemistry," be established (C. Res. 1980/1:3), (c) the recommendation that ad hoc intercalibrations of nutrient analyses be conducted and results reported to ICES (C. Res. 1980/4:8), and (d) the recommendation for the third meeting of the Working Group (C. Res. 1980/2:7).
- 2.2. Two recommendations had not been accepted: the recommendation on the publication of the report of the intercalibration exercise on PCBs because the final report was not available at the time of the meeting, and the recommendation on the publication of the results of the first intercomparison exercise on petroleum hydrocarbons because the Committees felt that the report should be discussed by MCWG given that it was the first report on this subject.

3. INTERNATIONAL ACTIVITIES OF INTEREST TO THE GROUP

3.1. ICES/SCOR Working Group on the Study of the Pollution of the Baltic

- 3.1.1. The MCWG was informed about the major relevant activities of the ICES/SCOR Working Group: (1) the work on evaluation of the results of the Baltic Open Sea Experiment (BOSEX) was nearly finished, (2) plans are being developed for a study of patchiness in the distribution of physical, chemical and biological parameters in the Baltic Sea, and (3) a study is being planned on the biogeochemical cycling of substances in the Baltic Sea and relevant modelling aspects.
- 3.1.2. The Group was also informed that an assessment of the effects of pollution in the Baltic Sea, prepared under the auspices of the Helsinki Commission with the assistance of ICES, was nearly completed. The document contains a review of the basic information on the physical, chemical and biological characteristics of the Baltic Sea as well as data on the pollution level.

3.1.3. Information was also provided concerning a workshop on the determination of petroleum hydrocarbons in sea water which will be held in March 1981 in Kiel in the framework of the Helsinki Commission.

3.2. Joint Monitoring Group of Oslo and Paris Commissions

3.2.1. Dr Weichart summarized the recent activities of the Joint Monitoring Group (JMG), noting that the contribution of ICES to the work of this Group was appreciated.

3.2.2. The MCWG was further informed that the report on the results of the JMG intercalibration exercise on the analyses of certain trace elements in sediments would be available soon. The Environment Officer was requested to ensure that MCWG members without normal access to this report would be able to receive a copy.

3.2.3. The MCWG also noted that the European Economic Community has funded the conduct of an intercalibration of PCB analyses in sea water for the JMG. The results of this exercise will not be available for several months.

3.2.4. In closing discussion on this topic, the MCWG stressed that it would like to see close links between ICES and the Oslo and Paris Commissions in all areas under study by MCWG.

3.3. Others

Dr Jensen reported that Denmark will sponsor a biological intercalibration workshop in May 1982 under the framework of the Helsinki Commission. Nutrient analyses may possibly also be intercalibrated in this workshop.

4. REPORTS ON PROJECTS AND STUDIES FROM WORKING GROUP MEMBERS

4.1. Dr Topping reported on studies which were conducted to determine the route of uptake of cadmium by crabs. The results of the study show that the cadmium distribution observed occurs via uptake through food as opposed to water. Further studies are under way to identify which food items are the most important sources of cadmium. In another investigation, good correlations have been found between the concentrations of mercury, methyl-mercury, and carbon in settlement material.

4.2. Dr Harms informed the Group about two studies being conducted in his Institute. In one study, tank experiments had been used to determine the uptake and effects of mercury on fish. The results showed that natural sea water must be used to obtain valid information. In the second investigation, a reliable means of determining lead concentrations in marine organisms is being developed. Radioisotopes are used to determine the critical steps in the analysis.

4.3. Dr Windom provided information on an experimental programme using sediment microcosms to determine the uptake of metals in sediments by worms. It has been determined that the nutritional quality of the bottom deposit is an important factor in the amount of metals absorbed, with increased amounts of metals being absorbed in areas with poorer food values of deposits.

4.4. Dr Portmann reported the results of a survey of the distribution of HCB and HCBD, in which HCB was found in virtually all samples of fish from areas where inputs of HCB were expected. In contrast, HCBD was only detected in mussel samples from one estuary.

4.5. Dr Law informed the Group that a small survey has been carried out in England to determine the concentration of phthalate esters in water, sediments and certain fish and shellfish. In another investigation, the inputs of petroleum hydrocarbons to the North Sea from cuttings from drilling operations are being studied.

- 4.6. This latter topic brought up a discussion of the types of additives which are put into drilling muds, including diesel fuels and biocides. Although the exact nature of some of these additives is difficult to determine, the Group felt that the Advisory Committee on Marine Pollution should be made aware of this issue.
- 4.7. Dr Berman reported on a programme under the National Research Council of Canada to develop reference materials for trace elements in sediments and sea water. This topic is covered in detail under Agenda Item 15.
- 4.8. Dr Uthe provided information on two studies the results of which were reported at the 1980 Statutory Meeting: (1) a study of phthalate ester concentrations in finfish (C.M. 1980/E:11) and (2) a determination of petroleum hydrocarbons in lobster digestive glands (C.M. 1980/E:10).
- 4.9. Dr Kerkhoff described recent Dutch studies to develop a better method to quantify PCBs in various samples when using high resolution glass capillary columns. Her colleagues Tuinstra *et al* (C.M. 1980/E:14) described earlier the large variations in values of total PCBs obtained by using different calculation procedures. She then presented a paper on her own work to identify which individual PCB compounds would be best to use in quantifying PCBs in several types of samples. She identified four criteria on which the selection of appropriate PCB compounds should be made:

- 1) the selected PCBs should be representative of all industrial PCB mixtures,
- 2) they should be representative of all compartments of the marine environment,
- 3) they must be well separated on a glass capillary column, and
- 4) they should be the most important compounds in terms of their toxicity.

However, because the information about the toxicity of individual PCB compounds is insufficient, only the first three criteria can be used to select the PCB compounds to be used in quantitation. Dr Kerkhoff then proposed six specific PCB compounds to be used for routine analyses intended for monitoring purposes.

- 4.10. In the discussion of this subject, it was stressed that there is a great need for biological data on the toxicity, metabolism, sub-lethal effects, etc. of individual PCB compounds, so that the chemists can learn whether they are measuring the substances of real biological significance. In view of the new possibility of being able to analyze the components of a PCB mixture, toxicity information on individual compounds can now be used.
- 4.11. Thus the Group felt that the biologists should be asked to study the toxicity of individual PCB compounds and determine which are the most toxic. These should then be subjected to study and monitoring. The Group recognized that this is a difficult task, requiring a great deal of work, but it felt that without such information, it was not possible to interpret fully the meaning of the analytical data now being produced.
- 4.12. Dr Farrington added that, in addition to the need to study the toxicity of individual PCB compounds on humans, such compounds should be studied in terms of the transfer of PCBs from the coastal zone to the oceans. He noted that, if the background levels of PCBs in sea water can be determined very soon, PCB compounds can be used as tracers to study the movement of organic compounds in the sea, mixing processes in the ocean. etc. The issue of PCBs should be looked at not only in terms of pollution; but also in terms of how we can use them to understand ocean processes.

5. REPORTS OF THE INTERCALIBRATION STUDIES FOR HEAVY METALS AND ORGANOCHLORINES

5.1. Cd and Pb in biological material

- 5.1.1. Dr Topping, as Coordinator, reported on the results of the 6th intercalibration exercise on trace metals in biological materials, which had the objective of determining the degree of comparability of results among laboratories at the concentrations of cadmium and lead which are found in shellfish. He informed the Group that two samples, one consisting of the white meat of edible crab and the other of commercial fish meal, had been distributed to all participants, while a more limited distribution had been made of the third sample, lobster liver. In all, 52 participants had taken part in the exercise.
- 5.1.2. The results of the analyses for cadmium showed a coefficient of variation of 17% at its level in shellfish (ca. 1µg/g(dry weight)). Dr Topping felt that this was probably the best result possible with so many participants. For lead, however, the results were still very poor, even for the sample with a high concentration (ca. 2.5 µg/g dry weight) of lead (CV 47%). On the basis of these results, Dr Topping proposed that no further intercalibrations should be conducted at the present time, but that an agreed method of analysis should be developed.
- 5.1.3. The MCWG approved the report on the results of this intercalibration exercise for publication, subject to minor modifications and additions, which Dr Topping agreed to make. The additional material included the preparation of a summary table comparing the results of analyses obtained according to each method and an annex stating the methods used by each laboratory. The Group expressed its great appreciation to Dr Topping for his excellent work in coordinating the exercise and evaluating the results.
- 5.1.4. The question was raised concerning what ICES should advise on the possibility that lead may be included in the Joint Monitoring Programme of JMG. The Group agreed that, as the results for lead vary from laboratory to laboratory within an order of magnitude, they could not encourage the establishment of a monitoring programme with lead.
- 5.1.5. In order to advance the state of the art of lead analyses, a small sub-group met to prepare a proposal for experiments to identify problems in the determination of lead in biological materials. The sub-group consisted of Dr Harms (Chairman), Dr Berman, Dr Jensen, Mr Olafsson, Dr Topping and Dr Windom. They proposed that a set of experiments be carried out by a small number of laboratories (about 6) with planned overlap in order to ensure valid corroboration. The surplus supply of sample "B" from the sixth trace metal intercalibration will be used, as it contains a concentration of lead high enough to promise relatively good accuracy and precision. The main method of measurement will be atomic absorption spectrometry (flame or graphite furnace) because over 90 % of the participants in the recent intercalibration exercise used this method. However, the application of anodic stripping voltammetry will also be examined. The topics of investigation will include: (1) dissolution of the sample, (2) direct determination by atomic absorption spectrometry, (3) solvent extraction of lead from the matrix, (4) calibration, and (5) the blank. The exchange of information among participating laboratories will take place by correspondence but the sub-group requested that it be authorized to meet the day before the next meeting of MCWG to discuss the results of their work.
- 5.1.6. The Chairman reminded the Group that the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic had requested that information be provided on the degree of comparability of data among laboratories for each metal at a given concentration which is being studied in the Coordinated Monitoring Programme. It was agreed that this subject would be taken up under Agenda Item 6.

5.2. PCBs and other organochlorines in fish oil

- 5.2.1. Dr Uthe, Coordinator of the fifth intercalibration exercise on the analysis of PCBs and other organochlorine compounds in biological materials, presented the report on the results of this exercise to the Group. He stated that data had been received from 23 out of 24 participants. The results showed that there is still a large variation in the values obtained for PCB analyses by different laboratories. The exercise had also examined the results obtained using a common PCB standard or a common method of calculation versus those obtained using the laboratory's own standard or own method of calculation. Dr Uthe stated that he had been unable to find any difference in values 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. It appeared that systematic error contributed significantly to the variance in results. The results of the exercise had also revealed other differences in results depending on the type of column used and whether Florisil or alumina is used in the clean-up step.
- 5.2.2. It was agreed that members with comments on the report should send them to Dr Uthe so that they arrive by 1 April 1981. The Working Group accepted the report as may be slightly amended, and recommended that it be published in the Cooperative Research Report series (Recommendation 1). The Group expressed its great appreciation to Dr Uthe for his excellent work in coordinating this exercise.
- 5.2.3. Dr Uthe further reported that the responses from the laboratories participating in the 5th ICES organochlorine intercalibration study had included two replies in which the analysts had determined the concentrations of certain individual polychlorinated biphenyl (PCB) isomers in the two fish oils. The overall agreement between these two laboratories was good, surpassing the usual level of agreement found among laboratories reporting results based upon a certain commercial mixture, such as Aroclor 1254. In order to investigate the possibility that analysis of PCB isomers would yield interlaboratory results with a much lower variance than that found in the 5th exercise, Dr Uthe had requested that a number of laboratories analyse newly prepared kits of the stock oils as well as Aroclor 1254. Two additional sets of results were received during the meeting. Dr Uthe noted that a preliminary variance is lessened by this approach, especially if only isomers common to each participant are considered. Five of these nine common isomers (IUPAC No 52, 101, 153, 138, and 180) are also on Dr Kerkhoff's list of PCB isomers recommended for future study. A study of the highest and lowest reported values for each oil showed that none of the laboratories reported consistently high or low results.
- 5.2.4. The Group was informed that these investigations will continue interessionally. When all the results are available, a full assessment will be made. If the work is completed in time, Dr Uthe agreed that he and his collaborators would submit a report on the results to the 1981 Statutory Meeting. It was further agreed that, following the interpretation of the results of this study, Dr Uthe in consultation with Drs Kerkhoff and Palmork should prepare a draft protocol for a sixth PCB intercomparison study. This document should be based on the likelihood of improved performance being obtained as compared to the previous intercalibration studies. The plans should reflect the recommendation made in Dr Uthe's report on the fifth organochlorine intercalibration exercise as well as the information resulting from the PCB isomeric composition study. The intercalibration should include (1) the use of a standard analytical method and calculation procedure, (2) a comparison of results using Florisil versus alumina, and (3) the determination of individual PCB isomers. Based on this outline proposal, the Working Group recommended that the intercalibration exercise be conducted in 1982 with Dr Uthe as Coordinator (see Recommendation 2) and looked forward to reviewing the detailed protocol for the exercise at its next meeting. Dr Kerkhoff asked to be put on record that she had expressed doubts as to whether the new intercalibration could result in improvements in the comparability of PCB results.

6. FUTURE ACTIVITIES FOLLOWING THE INTERCALIBRATION EXERCISES

- 6.1. It was noted that Document C.M. 1980/E:45 had been discussed at the 1980 Statutory Meeting and had been referred to the Working Group with the request that it be considered by the marine chemists who should advise the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic on the implications for coordinated monitoring.
- 6.2. Dr Topping introduced the paper, which he had co-authored with Dr Holden. In doing so, he explained that the intention had been to draw attention to certain short-comings and to provoke discussion. However, they had been unable to avoid the conclusion that the agreement among laboratories on the results of the analysis of single samples did not warrant the compilation and comparison of data from numerous laboratories. This conclusion applied equally to metals and organochlorine compounds. He also mentioned that after suitable revision, they would like to publish the conclusions they had reached in the open literature.
- 6.3. There was general support for the idea that considerable caution should be exercised in the comparison of the results obtained by different laboratories on different samples from different areas. Some members indicated that they welcomed the idea of open publication of this paper as a means of warning other organisations that it is not yet appropriate to attempt large-scale compilations of data from multiple sources. However, other members of the Group pointed out that the general tenor of the paper was one of almost extreme pessimism. As such, it was open to misunderstanding, particularly by administrators, but also by scientists who were not fully aware of the details of ICES activities. These members indicated that mention should be made of, and emphasis placed on, the advances that had been made and what it is now possible to achieve as a result of the work done to date. It was pointed out that, as a result of the work in ICES, it had been possible to show that certain areas were more contaminated than others, that controls ought to be applied to the use and input to the marine environment of certain pollutants, and that it was desirable that data for these pollutants and areas should be collected on an on-going basis.
- 6.4. While there was general agreement that it probably was not possible to compare data from different laboratories, it was pointed out that the ICES coordinated monitoring reports did not do this and, in fact, specifically cautioned against reading too much into apparent differences of two- or three-fold. In addition, based on the results of the intercalibration exercises, the coordinated monitoring reports did not include all data submitted to the ICES Secretariat; some data, e.g., on lead and cadmium, were rejected.
- 6.5. Finally, it was pointed out that the exercises conducted within the ICES framework have produced better results than most other similar exercises. They have also allowed positive statements to be made on what concentrations of a number of pollutants were really likely to be present in fish or shellfish.
- 6.6. Dr Topping indicated that he had taken note of all these points of view. He and Dr Holden would take them into consideration, along with a number of written comments which they had received, when they considered revising the paper for open literature publication. He also indicated that they would offer those members who had expressed their views particularly strongly an opportunity to see the final paper prior to publication.
- 6.7. The Working Group then turned to the question of what positive advice could be offered to the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic concerning which substances may be studied in a monitoring programme and with what limitations. There was a great deal of discussion on the value of presenting the information on the basis of what coefficient of variation (CV) has been obtained for which metal at which concentration. As analysts, Working Group members did not feel that the CVs for the metals were acceptable. However, it was finally agreed that the CVs should be listed which had been obtained in the trace metal intercomparison exercises so that persons involved in monitoring programmes can better

evaluate the information obtained. Ultimately, it was up to the scientists running monitoring programmes to define what level of CV is needed. Thus the Working Group agreed to the following statement concerning the comparability of analytical results:

- 6.7.1. On the basis of the results reported in the second through sixth ICES trace metal intercomparison exercises for biological tissues, as summarised in Table 1, it would seem that
 - a) the majority of participants in these exercises are capable of producing data for Cu, Zn, Hg, and Cd 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 CVs 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 CVs are higher,
 - c) although there are a small number of participants who have little difficulty in analysis of tissue containing 0.02 - 0.3 µg Pb/g (dry weight), the majority of participants are only capable of producing data with a CV <50% at a concentration of > 2 µg Pb/g.
- 6.7.2. The 5th ICES organochlorine intercalibration exercise has demonstrated that with oils containing 1 or 2 µg PCB/g, interlaboratory standard deviations of 28% and 31 %, respectively, are found within the twenty-three participating laboratories. Results on other organochlorine compounds demonstrated much stronger variance than PCB results in general, presumably due to the low levels present (see the values given in Table II). The Working Group on Pollution Baseline and Monitoring Studies in the North Atlantic should decide whether this degree of precision is sufficient for their coordinated monitoring studies. A number of papers, e.g., ICES Documents C.M. 1980/E:14, E:22, E:35, have indicated that improvement may be achieved by quantitation of individual peaks. This is being investigated further and it is expected that, at least for PCBs, a significant improvement will be possible for those laboratories which employ the new methodology.
- 6.7.3. It should be noted that, taken as a group, the laboratories which contribute data to the Coordinating Monitoring Programme are not significantly better than the participants of the intercalibration exercises taken as a whole. The results do appear to indicate that the CV is lower at higher concentrations of most residues.
- 6.7.4. As analysts, the Group does not consider the results achieved to be satisfactory. However, the acceptability of the coefficients of variation can only be judged in relation to the use which it is intended should be made of the data, or the concentrations which are judged as being cause for concern.
- 6.8. The Working Group then turned to a consideration of intercalibration exercises for analyses of contaminants in sea water, in particular the plans for the ICES fifth round intercalibration exercise on trace elements in sea water. The Chairman reported that although there had been hopes that this exercise could have been performed during 1981, this will not be possible as no firm offers for ship time have been received. She reported, however, that a standing offer had been received for the use of land-based laboratory facilities from the Institut Scientifique et Technique des Pêches Maritimes. It was agreed that the Coordinating Group for the exercise should meet again during the week to re-evaluate the design of the experiment, taking into account the results of the recently completed report of the IOC Bermuda intercalibration exercise (PANCAL - 80).

TABLE I

COEFFICIENTS OF VARIATION BETWEEN ANALYSTS FOR HEAVY METALS

Residue	Exercise	No. of Values Submitted	Accepted Concentration Range ($\mu\text{g/g}$)	Mean ($\mu\text{g/g}$)	s.d.	c.v.	Qualification
Cu	2	7	8.3 - 10.1	9.25	0.72	7.8	None
	3	20	2.69 - 5.68	3.75	0.67	17.9	None
	5	36	0.4 - 4.0	1.84	0.71	38.7	< 0.4 as 0.4
Zn	2	7	23 - 32	27.2	3.3	12.0	None
	3	21	27.8 - 52.7	37.5	6.0	16.0	None
	5	36	12.8 - 37.3	22.6	4.4	19.6	None
Hg	2	8	0.60 - 0.83	0.70	0.07	10.7	None
	3	16	0.74 - 0.94	0.85	0.06	7.0	One high value omitted
	5a	33	0.047 - 0.370	0.207	0.066	32.0	None
	5b	34	0.019 - 0.131	0.056	0.030	53.0	All (2) < values and 2 high values omitted
Cd	3	17	0.020 - 0.177	0.075	0.056	74.7	All (4) < values and 3 high values omitted
	4	13	0.022 - 0.060	0.041	0.014	35.0	Two high values omitted
	5	36	0.005 - 0.100	0.033	0.027	80.7	All (5) < values and 4 high values omitted
	6	49	0.53 - 1.11	0.800	0.136	16.9	None

TABLE I (Contd.)

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

TABLE II
 COEFFICIENTS OF VARIATION BETWEEN ANALYSTS FOR ORGANOCHLORINES

Residue	Exercise ^a	No. of Values Submitted	Accepted Concentration Range ($\mu\text{g}/\text{kg}$)	Mean ($\mu\text{g}/\text{kg}$)	s.d.	c.v.	Qualification
HCB	3B	7	14 - 70	46	18.8	40.6	None
	4	22	34 - 116	67	21.9	32.7	None
	5	15	13 - 70	36	14.5	41	None
α -HCH	3B	7	29 - 50	41	6.4	15.5	None
	4	23	10 - 131	49	21.3	43.5	One low value omitted
	5	11	7 - 99	62	28.0	46	None
δ -HCH	2A	4	10 - 130	80	56	70	None
	2B	8	630 - 890	750	101	13.5	One low value omitted
	3B	8	42 - 85	52	14.6	27.9	None
	4	20	1 - 25	11	8.1	71.1	One high value and 5 "less than" values omitted
	5	11	5 - 50	21	18.1	89	None
Dieldrin	2A	7	70 - 210	115	63	55	None
	2B	8	1300 - 1600	1440	98	6.8	One low value omitted
	3B	9	53 - 120	93	22.7	24.3	None
	4	17	12 - 129	79	29.5	37.4	None
	5	10	14 - 140	58	36.5	63	None
pp-DDE	2A	9	340 - 780	450	137	30	None
	2B	9	4100 - 6300	5260	1037	19.7	None
	3B	9	83 - 128	101	13.6	13.5	One low value omitted
	4	27	32 - 139	80	30.2	38.0	One low, two high values omitted
	5	17	- 343	221	57.7	26.0	None

TABLE II (contd.)

Residue	Exercise ^a	No. of Values Submitted	Accepted Concentration Range ($\mu\text{g}/\text{kg}$)	Mean ($\mu\text{g}/\text{kg}$)	s.d.	c.v.	Qualification
pp-DDT	2A	9	330 - 610	430	89	21	None
	2B	9	4500 - 5900	4990	530	10.6	None
	3B	10	175 - 220	196	12.7	6.5	One low value omitted
	4	25	30 - 220	113	49.9	44.1	One high, one doubtful value omitted
	5	12	25 - 480	149	134.9	91	None
PCB	2A	9	1000 - 3900	1890	907	48	None
	2B	9	8300 - 11800	9960	1060	10.6	None
	3B	10	944 - 1190	1059	95.2	9.0	One low, one high value omitted
	4	16	172 - 900	451 ^b	204.4	45.3	Two high values omitted
		13	490 - 1500	863 ^c	431.8	50.0	None
	5	23	70 - 255	193	41	28 %	1
	23	48 - 1-81	107	33	31 %	1	

Notes. a. Exercise 2A - unspiked fish oil

2B - spike in fish oil

3B - spike in corn oil

4 - unspiked fish oil

b. Without sulphuric acid treatment

c. With sulphuric acid treatment

- 6.9. Concerning the IOC intercalibration, Dr Bewers informed the Working Group about the results of the trace element investigations, for which he had served as Coordinator. He reported that three types of samples had been tested : (1) Niskin, (2) Go Flo and a modified Go Flo, and (3) Hydrobios, and three types of sampling wires had been used: (1) Kevlar wire, (2) plastic-coated steel, and (3) stainless steel. The samples had been taken in open ocean waters off Bermuda at a depth of 1300 m, where homogeneous distributions had been found for most trace elements. He reported that many laboratories from the ICES member countries had participated and that the plans developed by the MCWG for the ICES fifth round had been invaluable in developing the plans for PANCAL - 80. Thus, although ICES had not formally participated in the programme, its work had provided a strong contribution to the planning and execution of the IOC exercise.
- 6.10. Dr Bewers stated that the results of the exercise indicated that for many metals a modified Go Flo sampling bottle gives the best results, followed by a modified Niskin. The overall results seemed to indicate that sampling introduces very little variance in the results, in contrast to the earlier anticipation that the use of different sampling methods would introduce a source of variance.
- 6.11. Dr Palmork provided information on the results of the PCB programme of PANCAL-80, for which he had served as Coordinator. He stated that, although it had been possible to analyse total PCBs and individual PCB compounds down to a very low concentration (as low as 9pg/l), a number of problems had been identified. These involved not only variance introduced by the sampling and sample treatment procedures, but also problems in terms of distinguishing between dissolved and particulate-associated PCBs. On the basis of this investigation, Dr Palmork recommended that no monitoring programmes concerning PCBs in sea water should be developed until the various problems associated with this type of work have been resolved.
- 6.12. After considering the above items, the Coordinating Group for the ICES fifth round intercalibration of trace metals in sea water met and reconsidered the plans for this exercise. Dr Windom, Chairman of the Coordinating Group, presented the results of this meeting (attached as Annex 3) to the Working Group. He noted that, although the outline plans for this exercise are well developed, it will take six months' time to prepare the final plans for this exercise after a firm offer of a research vessel has been received. Thus, it would be necessary to receive an offer by the 1981 Statutory Meeting if the exercise is to take place in 1982.
- 6.13. The Working Group thanked the Coordinating Group for its efforts on this project and emphasised the need for carrying out this intercalibration exercise in order to advance the requirements of the ICES programmes, which are mainly carried out in nearshore waters. It was noted that, although the Bermuda intercalibration PANCAL - 80 had provided much useful information, this had been conducted in open ocean waters where the conditions were quite different from those in the coastal areas, where ICES member countries were conducting most of their programmes. It was agreed, however, that if no firm offers are made to permit the conduct of the exercise in the near future, the Working Group would consider other ways of obtaining the needed information at its next meeting.

7. STUDIES ON PETROLEUM HYDROCARBON ANALYSIS

7.1. Report on the intercomparison study

- 7.1.1. Dr Law informed the Working Group about the results of the first ICES intercomparison exercise on petroleum hydrocarbons, which he and Dr Portmann had coordinated. He reported that 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, was only sent to analysts speci-

fically requesting it. Thirty-six sets of samples had been distributed and results had been received for 26 of these, 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 a reasonable agreement was obtained among laboratories for broad fraction analysis, but the concentrations determined for specific hydrocarbons showed greater variation. Better inter-laboratory agreement had been attained for analyses of the sediment sample than for the sample of biological materials, but it had not been possible to determine whether the problems with the biological materials were due more to sample variability or to greater analytical difficulties associated with biological tissues. Dr Law concluded his presentation by summarizing the recommendations for future work on this subject based on the experience gained in this first exercise.

- 7.1.2. In the discussion of this report, several members suggested that the conclusion concerning the good level of agreement achieved by the UV fluorescence method should note the fact that all participants had used the same standards and similar wavelengths in this exercise. It was agreed that equally good results would probably not be obtained for different sediment samples as had been found for the particular sediment sample used in this exercise.
- 7.1.3. Based on this discussion, Dr Law and Portmann were requested to include some additional information in their report, stating what was meant by the term "total hydrocarbons" and preparing an annex showing the types of methods used by each participant and the problems associated with those methods. Dr Farrington agreed to assist in the preparation of this annex. It was agreed that any further comments should be sent to the coordinators so that they arrived no later than 1 April 1981.
- 7.1.4. Noting that this was the first overall intercalibration exercise on petroleum hydrocarbon analyses, which is a very complicated subject, the Working Group expressed its great appreciation to Dr Portmann and Dr Law for their excellent work in coordinating the exercise. The Working Group then recommended that the report on the results of the intercalibration be published in the Cooperative Research Report series, with the results of the questionnaire on sampling and analysis of petroleum hydrocarbons (see next section) attached as an Annex (Recommendation 3).
- 7.2. REPORT ON THE QUESTIONNAIRE ON SAMPLING AND ANALYSIS OF SEA WATER, SEDIMENTS AND BIOTA FOR TRACE ORGANIC COMPOUNDS
- 7.2.1. Dr Portmann presented the report on the responses to this questionnaire, which had been developed to supplement the intercomparison exercise by determining the range of techniques available to analysts studying organic compounds, especially petroleum hydrocarbons. Completed questionnaires had been received from 29 analysts, most of whom had participated in the intercomparison exercise. After summarizing the responses to each point on the questionnaire, Dr Portmann indicated that two of the problem areas identified by the responses were detection limits and sampling techniques.
- 7.2.2. The Working Group agreed that this report contained very valuable information and felt that it would be useful if a table could be presented containing a summary of the methods used by each respondent. Dr Portmann agreed to prepare such a table. The Working Group expressed its appreciation to Dr Portmann for his excellent work and recommended that this report be annexed to the report on the results of the first intercomparison exercise on petroleum hydrocarbons and published in the Cooperative Research Report series (see para. 7.1.4.).
- 7.3. REPORTS ON OTHER NATIONAL OR INTERNATIONAL INTERCOMPARISON STUDIES
- 7.3.1. Dr Osterroht informed the Group that an intercalibration workshop on petroleum hydrocarbon analyses would take place in Kiel during the last two weeks of March 1981. The Workshop would be attended mainly by scientists from countries around the Baltic Sea. The major aim of the Workshop was to compare analytical

methods for the determination of petroleum hydrocarbons in sea water, particularly the UV fluorescence method as recommended by UNESCO (IGOSS).

7.3.2. Dr Farrington provided information about the following relevant activities in the United States:

- (a) The National Bureau of Standards (NBS) has sponsored two intercalibration exercises on the analysis of petroleum hydrocarbons using mussel samples. The main methods used were GC and GC/MS. Reports on the results are now available. NBS also has a small programme concerned with the preparation of reference materials.
- (b) The National Oceanic and Atmospheric Administration is presently carrying out intercalibration exercises on petroleum hydrocarbons, especially polynuclear aromatic hydrocarbons, in sediment samples.
- (c) The US Environmental Protection Agency has conducted an intercalibration exercise using the same mussel homogenate sample that had been used in the ICES intercalibration.

7.3.3. Finally, it was noted that there would be a meeting under the auspices of IOC in March 1981 to examine the advantages and disadvantages of analysing oil in sea water using UVP and GC. On the basis of the results of this meeting, it was hoped that a recommendation could be made concerning the best analytical method.

7.4. FUTURE ACTIVITIES

7.4.1. The Working Group considered the fifth conclusion in the report of the results of the first ICES intercomparison study of petroleum hydrocarbon analyses, in which Dr Law and Dr Portmann had proposed the outline for a second intercomparison exercise. The Working Group agreed that an exercise along these lines should be developed and regretted that Dr Portmann and Dr Law would not be in a position to coordinate it.

7.4.2. After some discussion, Dr Farrington and Dr Knap offered to serve as coordinators of the second exercise on the condition that they were able to obtain increased funding for the on-going intercalibrations concerning sediments and mussels in the United States. If this is possible, they agreed to prepare a paper for the 1981 Statutory Meeting giving a detailed proposal for the exercise on the basis of conclusion number 5 and discussions with other members of the Working Group.

7.4.3. The Working Group gratefully accepted this offer and passed Recommendation 4 on the conduct of this exercise.

7.4.4. As the second intercomparison exercise would only deal with petroleum hydrocarbons in sediments and biological tissues, the Working Group then discussed the means to advance the methodology for determinations in sea water. It was agreed 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. For one such study, the following proposal was drafted:

An examination of the capability of UVP methodology to detect different oils in sea water should be conducted. At least six oils of different aromatic character and composition should be spiked to coastal sea water samples and the IGOSSE or similar UVP methodology applied to the analysis of these samples. All results should be calculated using each oil as a standard for the UVP method. This should result in a series of six or more concentration values for a given sample. By comparison of these values for each of the spiked sea water samples, we should gain valuable insight into the advantages and disadvantages of the UVP methodology in preparation for an intercomparison exercise on the analysis of oil in sea water.

Dr Bowers indicated that he thought Dr Levy of his laboratory would be willing to undertake the proposed study and agreed to check whether this would

be possible.

8. CARBON DIOXIDE CYCLING IN THE OCEANS

- 8.1. The Chairman reminded the Group that this subject had been brought up by Professor K. Grasshoff at the first meeting of the Group with a view of determining whether ICES could make a contribution to other on-going studies of the role of the oceans in the global CO₂ cycle. Unfortunately, Professor Grasshoff had been unable to attend the meeting, but Professor Poisson from the University of Paris had agreed to attend the meeting for the discussion of this subject.
- 8.2. Professor Poisson gave a background description of the CO₂ cycle, indicating the order of magnitude amounts of carbon contained in the atmosphere, oceans, organisms etc. He stated that, by the end of this century the concentration of CO₂ in the atmosphere will double and this will influence the CO₂ cycle in the oceans. An important question in this regard is, thus, what is the capacity of the oceans to absorb this increase in CO₂ in the atmosphere? He then presented a description of the buffering capacity of the oceans and the factors affecting it. A summary of Professor Poisson's presentation is contained in Annex 7.
- 8.3. The Working Group then discussed the possible contribution that ICES could make to the studies on this subject. It was felt that perhaps the best area of study from the ICES standpoint might be a consideration of whether the increase in CO₂ may result in an increase in primary production. Noting that there were several studies in the Baltic Sea which might provide relevant information, the MCWG decided to pass the suggestion on to the ICES/SCOR Working Group on the Study of the Pollution of the Baltic that it may be interesting to look into the CO₂ cycle in the Baltic Sea in relation to primary production levels and relevant hydrographic and hydrochemical parameters.
- 8.4. In closing the discussion of this subject, the Working Group thanked Professor Poisson for his presentation and assistance in the consideration of this matter.

9. THE USE OF TRACERS FOR THE STUDY OF THE MOVEMENT OF SUBSTANCES IN THE MARINE ENVIRONMENT

- 9.1. The Chairman reminded the Group that at last year's meeting it had been agreed that members should prepare review documents on the use of radionuclide analogues in the study of the natural marine environment and send them to the Environment Officer for compilation. Only two members, Dr Weichart and Dr Jensen, had sent in papers before the meeting. Dr Weichart's paper had provided information on studies being conducted in the Federal Republic of Germany whereby measurements have been made of various environmental radionuclides to study the circulation and mixing of ocean waters, the air-sea transfer of soluble gases, and sedimentary processes. Dr Jensen had provided a summary of a study of environmental radioactivity in Denmark in 1979.
- 9.2. At the meeting, Dr Thibaud provided a paper with information on studies carried out in France using radioisotopes as tracers in the marine environment, i.e., a study using ³H and ¹⁴C to follow the movement of water masses, a study of turbulence in the Baie de Seine, and an investigation of the movement of trace metals in certain estuaries, e.g., the Gironde.
- 9.3. Finally, it was noted that, although Dr P.G.W. Jones had not yet been able to finish the review he had undertaken to produce on the use of tracers in the study of, e.g., water movements, it would be available at the next meeting of the Group. The Working Group looked forward to seeing this report and agreed that members with additional information on this subject should send it to Dr Jones in Lowestoft or to the ICES Secretariat for transmission to Dr Jones.

10. METHODS FOR PRIMARY PRODUCTION AS AN ALTERNATIVE TO THE ¹⁴C METHOD — TECHNIQUES AND CONCEPTS

- 10.1. The Chairman informed the Group that the ICES Working Group on Primary Production Methodology had asked the MCWG for advice on alternatives to the ¹⁴C method of measuring primary production. The Chairman had requested Dr Weichert to consider this issue and report his suggestions to MCWG.
- 10.2. Dr Weichert then presented a paper (attached as Annex) in which he suggested a method for the determination of primary production from changes in the concentrations of CO₂, O₂, and nutrients in the open water. He mentioned that this method had been used in the "Fladen Ground Experiment (FLEX'76)" in the North Sea in the spring of 1976. It had permitted an integration over about ten days and thus had provided longer term information on daily changes in primary production, which is not possible in incubation experiments using ¹⁴C.
- 10.3. The Working Group felt that this paper presented a valuable approach to the subject and asked the ICES Secretariat to forward it along with a report by Dr Weichert on results obtained in the Fladen Ground Experiment ("Chemical changes and primary production in the Fladen Ground area (North Sea) during the first phase of a spring phytoplankton bloom" Meteor Forsch. Ergebnisse A 22:79-86 (1980)) to the Chairman of the Working Group on Primary Production Methodology. It was further agreed that members with additional information on this subject should forward it to the ICES Environment Officer to arrive no later than 15 May 1981, for transmission to the other Working Group.

11. PROGRAMME FOR THE PUBLICATION OF LEAFLETS ON "TECHNIQUES IN MARINE CHEMISTRY"

- 11.1. The Chairman opened the discussion of this subject by reminding the Group that its recommendation from last year's meeting for the establishment of a new series of leaflet publications entitled "Techniques in Marine Chemistry" had been approved by the Council. It was now necessary to decide the format of these leaflets, the subjects to be covered in the near future and the persons who should assist in this work.
- 11.2. After some discussion, it was agreed that a draft format should be prepared by correspondence among a small number of persons and then distributed to all members for comment. The format drafting group will consist of: Dr de Barros, Dr Harms, Dr Fonselius, Dr Kerkhoff, Dr Palmork and the Environment Officer. Drafts of the first one or two leaflets should also be circulated to all members of the Working Group. After these have been accepted, new drafts will only be reviewed by an editorial board for the relevant subject. It was agreed that the editorial boards should consist of the following persons:

<u>Nutrients</u>	<u>Metals</u>	<u>Organics</u>
Dr S. Carlberg	Dr S. Berman	Dr M. Kerkhoff
Dr F. Koroleff	Dr U. Harms	Dr R. Law
Dr S. Fonselius	Dr Y. Thibaud	Dr K. Palmork
Dr B. Boutier	Dr G. Topping	Dr J. Portmann
		Dr J. Uthe
		Dr P. Michel

- 11.3. Concerning the topics of the first leaflets, the editorial board for nutrients agreed to prepare draft leaflets for several methods, beginning with dissolved orthophosphate. Dr Harms indicated that he would be willing to prepare a leaflet on trace metal analyses in biological tissues. Dr Kerkhoff offered a leaflet on the quantification of PCBs and Dr Palmork one on analysis of PCBs in sea water. It was agreed that the work should proceed intersessionally so that several leaflets will be ready before the next meeting of the Group.

12. POSSIBILITIES OF FURTHER WORK ON PROBLEMS RELATED TO INCINERATION AT SEA

- 12.1. The Chairman reminded the Working Group that at the last meeting it had been agreed that Dr Hoogweg should prepare a paper on the composition of exhaust gases from the incineration of organochlorine wastes at sea, for presentation to the Advisory Committee on Marine Pollution (ACMP) at its October meeting. This paper had been noted by ACMP, who remitted it to the Working Group for its comments and conclusions.
- 12.2. Dr Hoogweg presented this paper, "Incineration of Chemical Wastes at Sea, A Short Review," prepared by Dr H. Compaan at his Institute, to the Working Group. The results of this paper showed that when the correct conditions for incineration at sea are used, there are almost no uncombusted organochlorines. Nearly all studies have shown that organochlorines are destructed with an efficiency of 99.94%. No harmful effects on the marine ecosystem have been found.
- 12.3. Dr Hoogweg also noted that three papers had been presented at the meeting of the Standing Advisory Committee for Scientific Advice (SACSA) of the Oslo Commission in November 1980. Two of these papers were concerned with the air pollution aspects of incineration at sea and the third with destruction efficiency of incineration. These papers had also come to the same conclusion, that under proper operating conditions, only a very small amount of uncombusted organochlorines are released, mostly below or slightly above the detection limit.
- 12.4. The Working Group took note of this information and agreed to forward it back to ACMP, indicating that several other organisations are conducting work on this subject and MCWG feels that it cannot contribute more to this work at the present time.

13. OVERVIEWS ON FLUXES AND TRANSPORT OF POLLUTANTS IN THE MARINE ENVIRONMENT

13.1. Cadmium

- 13.1.1. Dr Bewers presented his paper "Cadmium in the Marine Environment: An Overview," which he had prepared as a result of the agreements made at the first Working Group meeting that reviews should be developed on the distribution, behaviour and transport of certain substances in the marine environment. He pointed out that the overview covered mainly the physical and chemical aspects of the transport and cycling of cadmium, but not the biological aspects nor ecotoxicity.
- 13.1.2. After some discussion, the Working Group approved the report for transmission to ACMP. It expressed its gratitude to Dr Bewers for his work in preparing the report.
- 13.1.3. In this connection, Dr Jensen drew the Group's attention to a report which had recently been published by the National Agency of Environmental Protection in Denmark on "The Ecotoxicity of Cadmium in Fresh and Sea Water and Water Pollution with Cadmium in Denmark." An important conclusion of this report is that cadmium is very toxic to organisms in fresh water ecosystems because cadmium exists in ionic form, while it is less toxic to organisms in marine ecosystems, where cadmium exists almost entirely in complexed form.

13.2. PCBs

- 13.2.1. Dr Portmann presented the paper he had prepared on "PCBs in the Marine Environment - An Overview." He noted the various difficulties that had been encountered in preparing this paper, especially in extrapolating information from the North Atlantic to the entire world oceans. The paper reviewed the structure and form of PCBs, their production and use, and the pathways by which they enter the marine environment. It then provided typical values for the concentration ranges of PCBs in the various compartments of the marine environment and estimates of the transfer of PCBs from one compartment to another.

- 13.2.2. There were a number of comments made on the paper. Several members requested that qualifying statements be made concerning the estimates of the quantity of PCBs contained in the sediments. Dr Portmann agreed to amend the paper in accordance with the comments made.
- 13.2.3. The MCWG approved the report, as will be amended, for transmission to ACMP. It expressed its gratitude to Dr Portmann for his work in preparing the paper.
- 13.2.4. In the discussion of these two overview papers, it became apparent that at least several members felt that there was a danger that the generalised statements and global estimates contained in the overviews could be misinterpreted by some of the persons reading them. Thus the Group agreed that Dr Bewers and Dr Portmann should draft a statement indicating the purpose and conditions of these overviews. This statement should be placed as a preface to these and future overviews when they appear in printed form.
- 13.2.5. The Working Group then noted that either the ACMP or the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMFNA) had added to the text of the overview on mercury which had been discussed and agreed by the MCWG at its second meeting. In particular, a fifth conclusion had been added. There was no dissent from the view that changes by ACMP were in order or that other groups should be able to pass comment on reports by MCWG. However, it was pointed out that unless the origin of such comments or changes were made clear, there was a danger that MCWG members might be embarrassed by the final text. It was agreed that this was a procedural difficulty which the ICES Secretariat should seek to avoid in the future. After some discussion on the actual words used in the added fifth conclusion, it was agreed that a more generally acceptable formulation of the wording as recorded in the annex to the 1980 ACMP report would have been as follows:
- "Although sediments represent the major site of accumulation of mercury in inshore and coastal waters, the monitoring of mercury in these waters is possible by the measurement of body burdens of mercury in some organisms which by careful selection will reveal the spatial and temporal (in the order of 6 months to a year) trends of the mercury concentration."
- 13.2.6. Finally, the point was raised that in some countries an impression has been formed that the MCWG is a sub-group of or subordinate to the WG MPNA, because the latter group has in the past discussed several reports prepared by members of MCWG. It was felt that one way of overcoming this impression would be if WG MPNA were asked to make any comments on MCWG overview papers (or any other papers) in the form of an additional paper which could be attached to the original paper. In this way, the work conducted under each group would be separate and identifiable.
- 13.2.7. The Group then discussed whether the work on the preparation of overviews should be continued by studying other substances. It was felt that this could be very useful and several substances were mentioned, including lead and PCTs. The speciation of metals was also considered to be a useful topic.
- 13.2.8. Dr Jensen agreed to prepare a paper on the production, uses and levels in the marine environment of PCTs. He stated that this would not include estimates of fluxes. Dr Nounou raised the issue of whether the Group should undertake studies of the marine chemistry of other substances, such as fluorinated hydrocarbons, silver, zinc, chromium and other metals. The Group requested Dr Nounou to prepare a paper on this subject to act as a basis for discussion at the next Working Group meeting. Finally, the Group agreed

that all members should prepare a list of priorities on which substances should be studied for consideration at the next meeting.

14. METHODOLOGY FOR THE MEASUREMENT OF RIVER INPUTS

It was noted that, owing to the illness of the coordinator of this project, a report was not yet available giving a sampling design to measure gross riverine export. The Group looked forward to seeing this report at its next meeting.

15. DEVELOPMENT OF STANDARD SAMPLES WITH POLLUTANTS AT AMBIENT LEVELS

Dr Berman informed the Working Group that the National Research Council of Canada has a programme to develop reference materials for trace metals in sediments and trace metals in sea water. For marine sediments, two reference materials have recently become available. Reliable values in these materials are known for the trace metals Be, V, Cr, Mn, Co, Ni, Cu, Zn, As, Sb, Cd, Hg and Pb, and for the matrix and minor constituents C, Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, S, Cl, K₂O, CaO, TiO₂ and Fe₂O₃. Concerning sea water reference materials, Dr Berman reported that storage experiments are now being conducted to determine whether the integrity of metals can be maintained in sea water. He indicated that this work has resulted in the development of improved analytical techniques for the separation, isolation, concentration, etc. of trace elements in sea water and sediments.

16. ANY OTHER BUSINESS

16.1 The Working Group took note of a report on the results of the first and third intercalibration exercises on trace metals in sea water, which had been prepared by the Coordinator, Dr. P.G.W. Jones. It was noted that this was the final report on this exercise and any comments should be sent to Dr. Jones in Lowestoft no later than 1 April 1981. The Working Group approved the report for publication and asked the UK members of the Group to express their gratitude to Dr. Jones for his work in coordinating these intercalibration exercises.

16.2 The Working Group took note of the "Extended Report on the Mini-Symposium on Transport Processes in Estuaries and Nearshore Zones", which had been composed by the Convener, Professor G. Kullenberg. This Mini-Symposium had taken place at the 1980 Statutory Meeting and considerations were now being given as to whether a full symposium should be held on the subject. The Working Group felt that it would be very valuable to hold such a symposium and recommended that it be multi-disciplinary in character, with a very broad approach taken to the subject.

17. APPROVAL OF RECOMMENDATIONS AND DEADLINES

The Working Group reconsidered and approved the first four recommendations discussed earlier and adopted Recommendation 5 on the next meeting of the Group. The Recommendations are attached as Annex 5. The tasks and deadlines agreed for the intersessional period appear in the Action List in Annex 6.

18. CLOSURE OF THE MEETING

The Chairman thanked the members for their good work during the meeting and, on behalf of all the participants, expressed appreciation to the host Institute for the excellent meeting arrangements and assistance during the meeting. She closed the meeting at 17.00 hrs on 19 February 1981.

ANNEX 1

MARINE CHEMISTRY WORKING GROUP

AGENDA

1. Adoption of the agenda.
2. Report of the 68th Statutory Meeting.
3. International activities of interest to the Group.
 - 3.1 ICES/SCOR Working Group on the Study of Pollution in the Baltic.
 - 3.2 Joint Monitoring Group of the Oslo and Paris Commissions.
 - 3.3 Others.
4. Reports on projects and studies from Working Group Members.
5. Reports of the intercalibration studies for heavy metals and organochlorines.
6. Future activities following the intercalibration exercises.
7. Studies on petroleum hydrocarbon analysis.
 - 7.1 Report on the intercomparison study.
 - 7.2 Report on the questionnaire on sampling and analysis of sea water, sediments and biota for trace organic compounds.
 - 7.3 Reports on other national or international intercomparison studies.
 - 7.4 Future activities.
8. Carbon dioxide cycling in the oceans.
9. The use of tracers for the study of the movement of substances in the marine environment.
10. Methods for primary production as an alternative to the ^{14}C -method: techniques and concepts.
11. Programme for the publication of the leaflets on "Techniques in Marine Chemistry".
12. Possibilities of further work on problems related to incineration at sea.
13. Overviews on fluxes and transport of pollutants in the marine environment.
 - 13.1 Cadmium.
 - 13.2 PCBs.
14. Methodology for the measurement of river inputs.
15. Development of standard samples with pollutants at ambient levels.
16. Any other business.
17. Approval of recommendations and deadlines.
18. Closure of the meeting.

ANNEX 2

PARTICIPANTS

<u>Name</u>	<u>Address</u>
Dr. Claude Alzieu	Institut Scientifique et Technique des Pêches maritimes rue de l'Ile d'Yeu B.P. 1049 44037 Nantes Cédex, FRANCE
Dr. (Ms) M. de Barros (Chairman)	Ministério do Agricultura e Pescas DGPRA Quinta do Marquês 2780 Oeiras, PORTUGAL
Dr. Shier Berman	Chemistry Division National Research Council Ottawa, Ontario CANADA K1A 0RQ
Dr. J. M. Bewers	Bedford Institute of Oceanography P.O.Box 1066 Dartmouth, Nova Scotia CANADA
Dr. Stig Carlberg	National Board of Fisheries Institute of Hydrographic Research P.O.Box 2566 S-403 17 Göteborg, SWEDEN
Dr. Marcel Chaussepied	Centre National pour l'Exploitation des Océans Centre Océanologique de Bretagne B.P. 337, 29273 Brest Cédex FRANCE
Dr. Daniel Cossa	Pêches et Océans Canada C.P. 15500, 901 Cap Diamant Québec (Qué), CANADA G1K 7Y7
Dr. John Farrington	Chemistry Department Woods Hole Oceanographic Institution Woods Hole, MA 02543, USA
Dr. Stig Fonselius	National Board of Fisheries Institute of Hydrographic Research P.O.Box 2566 S-403 17-Göteborg, SWEDEN
Dr. N. Gonzalez	Instituto Espanol de Oceanografia Muelle de Animas s/n La Coruna, SPAIN
Dr. Uwe Harms	Bundesforschungsanstalt für Fischerei Isotopenlaboratorium Wüstland 2 D-2000 Hamburg 55 Federal Republic of Germany

<u>Name</u>	<u>Address</u>
Dr. Pieter Hoogweg	RIZA P.O.Box 17 8200 AA Lelystad, NETHERLANDS
Dr. Arne Jensen	National Agency of Env. Protection The Marine Pollution Laboratory Kavalérsgaarden 6 2920 Charlottenlund, DENMARK
Dr. (Ms) Mia Kerkhoff	Netherlands Institute for Fishery Investigations Haringkade 1 1970 AB IJmuiden, NETHERLANDS
Dr. Anthony Knap	Bermuda Biological Station Ferry Beach Bermuda, USA
Dr. Folke Koroleff	Institute of Marine Research P.O.Box 166, 00141 Helsinki-14 FINLAND
Dr. Robin Law	MAFF Fisheries Laboratory Burnham-on-Crouch Essex CMO 8HA, UNITED KINGDOM
Dr. Claude Leroy	Institut Scientifique et Technique des Pêches maritimes rue de l'Ile d'Yeu B.P. 1049, 44047 Nantes Cédex FRANCE
Dr. P. Nounou	CNEXO 66, avenue d'Iéna 75016 Paris, FRANCE
Mr. John Ólafsson	Marine Research Institute Skulagata 4, Reykjavik, ICELAND
Dr. Vagn Olsen	Danish Institute of Fisheries and Marine Research Charlottenlund Slot 2920 Charlottenlund, DENMARK
Dr. C. Osterroht	Institut für Meereskunde an der Universität Kiel Düsternbrooker Weg 20, 2300 Kiel FEDERAL REPUBLIC OF GERMANY
Dr. Karsten Palmork	Institute of Marine Research P.O.Box 1870-72 5011 Bergen-Nordnes, NORWAY

<u>Name</u>	<u>Address</u>
Dr. (Ms) Janet Pawlak (Rapporteur)	International Council for the Exploration of the Sea Palægade 2 1261 Copenhagen K, DENMARK
Dr. A. Poisson	Laboratoire de Physique et Chimie Marines Université P. et M. Curie, Tour 24 4, Place Jussieu 75230 Paris, Cédex 05, FRANCE
Dr. John Portmann	MAFF Fisheries Laboratory Burnham-on-Crouch Essex CM0 8HA, UNITED KINGDOM
Dr. Yves Thibaud	Institut Scientifique et Techniques des Pêches maritimes rue de l'Ile d'Yeu, B.P. 1049 44037 Nantes Cédex, FRANCE
Dr. Fred Thurberg	National Marine Fisheries Service Milford Laboratory, Milford Connecticut, 06460, USA
Dr. Graham Topping	DAFS Marine Laboratory P.O.Box 101, Victoria Road Aberdeen AB9 8DB, UNITED KINGDOM
Dr. John Uthe	Fisheries & Env. Sciences Division Dept. of Fisheries and Oceans P.O. Box 550 Halifax, N.S. CANADA B3J 2S1
Dr. Carlos Vale	Instituto Nacional de Investigaçào das Pescas Avenida Brasilia, 1400 Lisbon PORTUGAL
Dr. Günter Weichart	Deutsches Hydrographisches Institut Bernhard-Nocht-Strasse 78 D-2000 Hamburg 4 FEDERAL REPUBLIC OF GERMANY
Dr. H. Windom	Skidaway Institute of Oceanography Savannah, Georgia 31406 USA

ANNEX 3

5TH ROUND INTERCALIBRATION ON TRACE ELEMENTS IN SEA WATER

The Coordinating Group for the 5th round intercalibration exercise on trace elements in sea water met on 17 February 1981. Present at the meeting were: H. Windom (Chairman), J. M. Bewers, J. Ólafsson, Y. Thibaud, G. Topping and G. Weichart.

This meeting was convened in response to the Working Group Chairman's request to re-evaluate the design of the fifth round, taking into consideration the results of the recently completed I.O.C. report on its Bermuda intercalibration exercise (PANCAL-80). The Coordinating Group discussed the location, design and logistics of the fifth round exercise.

Location

Because cooperative programmes involving trace element analyses among ICES countries are likely to be conducted in coastal regions, the fifth round should be carried out in European continental shelf waters. This would be logistically wise and would also provide an opportunity to consider problems associated with sampling in those waters that were not addressed in the PANCAL-80 exercise.

Design

In view of the results of PANCAL-80, the Coordinating Group feels that the fifth round could also be a training exercise for laboratories wishing to gain experience in trace element sampling and analysis of sea water. A number of ICES laboratories participating in the PANCAL-80 exercise showed their ability to perform high precision analyses of trace elements in sea water and three or four of these laboratories could serve as "expert or core laboratories". The results of analyses of samples by the less experienced laboratories could therefore be compared to those of the "core laboratories" as well as to each other. This would provide some basis for a consideration of the accuracy of the results.

The fifth round should also evaluate problems associated with sampling in shallow, nearshore waters. The following are some of the questions which the Coordinating Group feels should be answered:

1. Which method of sampling results in the least contamination?
It was felt that the best comparison would be between pumping (peristaltic pump using silicone tubing) and discrete sampling using modified Go Flo bottles on Kevlar or plastic-coated steel.
2. Are variations in trace element concentrations in shallow, nearshore waters larger than variations introduced by sampling and analyses by participating laboratories?
3. Can samples be filtered or centrifuged without introducing significant contamination?
4. What are the relative merits of different types of storage bottles and storage methods (i.e., acids, time, etc.)?

These questions may best be answered through a programme of analyses conducted by the "core laboratories".

Logistics

As was emphasised by the Coordinating Group in the Second Report of the Marine Chemistry Working Group (C.M.1980/C:1, Annex V), the logistics and details of the design of the fifth round cannot be carried further until commitments are made for the provision of a ship and the shore-based laboratory facilities necessary for the conduct of the exercise. At the present time, there is a standing commitment for land-based analytical laboratory facilities by the Institut Scientifique et Technique des Pêches Maritimes.

Once a firm commitment to provide a ship has been made, a new Coordinating Group should be formed following the recommendations given in C.M.1980/C:1, Annex V, Part 3.

ANNEX 4

Determination of primary production from changes of CO_2 , O_2 , and nutrients in the open water.

Dr. Günter Weichert

Remark: Alkalinity is not considered, because it is not changed by primary production.

Growing phytoplankton consumes CO_2 and nutrients and produces O_2 . So, primary production can, in principal, be determined by measuring the temporal changes of CO_2 , O_2 , or a nutrient in the open water.

The CO_2 uptake (CO_2 can readily be determined from pH, alkalinity, temperature and salinity) and the O_2 release by the phytoplankton are very closely related to the primary production itself, whereas the uptake of the nutrients is not always proportional to primary production. From this point of view the CO_2 and O_2 methods would be more appropriate. On the other hand, O_2 and, to a certain extent, also CO_2 are exchanged between the water and the atmosphere.

From the nutrients we consider phosphate and fixed N. Silicate is omitted, because its uptake by the phytoplankton is in many cases not proportional to primary production.

The changes of CO_2 , O_2 and nutrients in the water always

reflect the gross primary production minus the respiration of all organisms, i. e. a special sort of net primary production.

For the determination of primary production from the changes of CO_2 , O_2 , and nutrients in the open water, a number of conditions must be fulfilled at the same time:

- 1) The primary production must be relatively strong, so that the changes in the water are measurable and the exchange of CO_2 and O_2 with the atmosphere may be neglected.

If we consider e. g. a net primary production of $0,1 \text{ g C m}^{-3} \cdot \text{d}^{-1}$,

the daily change of pH in the open sea would be ca. +0,02 (e. g. at $T = 6 \text{ }^\circ\text{C}$, $S = 35 \text{ }^\circ\text{/oo}$, in the pH range 8,1 to 8,3 it would be +0,017),

the daily change of O_2 concentration would be +8 $\mu\text{mol/l}$ (+0,2 ml/l),

the daily change of P concentration would be -0,07 $\mu\text{g-at/l}$ (-2 $\mu\text{g/l}$),

the daily change of N concentration would be -1,0 $\mu\text{g-at/l}$ (-15 $\mu\text{g/l}$).

From these numbers and from the precision of the methods it is obvious that for a one day experiment the net primary production must be ca. $0,1 \text{ g C} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ or more. For an experiment of some days the primary production may be less than $0,1 \text{ g C} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$.

- 2) Water samples must always be taken from the same phytoplankton patch within the same water mass.
- 3) The phytoplankton patch, in which the temporal changes of CO_2 , O_2 , or a nutrient are observed, must be large enough, so that during the experiment the horizontal and vertical mixing with the surrounding and underlying water may be neglected.

In nature, the coincidence of all these conditions is rather scarce. So, the determination of primary production from the temporal changes of CO_2 , O_2 , or a nutrient in the open water is only limited. An example for the successful application of the CO_2 and nutrient methods is the determination of the net primary production in the North Sea (Fladen Ground) during the first two weeks of a phytoplankton bloom.

ANNEX 5

RECOMMENDATIONS

Recommendation 1

The Marine Chemistry Working Group recommends that the "Report of the fifth intercalibration exercise on analyses of PCBs in biological materials" by Dr. J. F. Uthe be published in the Cooperative Research Report series.

Recommendation 2

The Marine Chemistry Working Group recommends that a sixth intercalibration exercise on the analysis of PCBs in biological tissues be conducted in 1982 with Dr. J. F. Uthe (Canada) as Coordinator, with the aim of attaining a satisfactory level of agreement among analysts. The exercise should utilize two oils, one spiked and the other unspiked, and analysts should employ a standard method of analysis as well as their own method.

Recommendation 3

The Marine Chemistry Working Group recommends that the "Report of the first ICES Intercomparison Exercise on Petroleum Hydrocarbons" by Dr. R. J. Law and Dr. J. E. Portmann be published, along with the results of the questionnaire survey on methods, in a volume of the Cooperative Research Report series.

Recommendation 4

The Marine Chemistry Working Group recommends that a second intercomparison exercise on petroleum hydrocarbons in marine samples be conducted in 1982 under the coordination of Dr. J. Farrington and Dr. A. Knap (USA), with the aim of determining the level of interlaboratory comparability of analyses for total oil (or oil equivalents) and specified compounds in samples of marine sediments and biological tissues. Each participant will be required to report their results according to a standard protocol and to provide full details of their methodology.

Recommendation 5

The Marine Chemistry Working Group recommends that the next meeting of the Group be held for four days in mid-February 1982 at ICES Headquarters in order to consider:

- (1) progress in the development of analytical methods for determining lead in biological tissues;
- (2) progress in the development of methods for analysing and quantifying PCBs;
- (3) progress in the study of petroleum hydrocarbon analyses, and
- (4) the overview paper on PCTs in the marine environment and additional overviews.

ANNEX 6

ACTION LIST

1. Dr. Harms (Coordinator), Dr. Berman, Dr. Jensen, Mr. Olafsson, Dr. Topping and Dr. Windom to carry out intersessional work on the identification of problems in the determination of lead in biological materials (para 5.1.5).
2. Dr. Uthe, in consultation with Dr. Kerkhoff and Dr. Palmork to prepare a detailed protocol for a sixth intercomparison exercise on the analysis of PCBs in biological materials (para 5.2.4).
3. Dr. Farrington and Dr. Knap to explore the possibility of coordinating the second intercomparison exercise on analyses of petroleum hydrocarbons in sediments and biological materials and to prepare a paper for C.M.1981 giving detailed proposals (para 7.4.2).
4. Members with additional information on the use of radionuclide tracers to study the movement of substances in the marine environment to send this to Dr. P.G.W. Jones, Fisheries Laboratory, Lowestoft, Suffolk NR33 OHT, United Kingdom, or to the ICES Environment Officer no later than 1 September 1981 (para 9.3).
5. All members with additional information on methods for the measurement of primary production, especially the one presented in Annex 4, should send it to the ICES Environment Officer to arrive no later than 15 May 1981.
6. Dr. de Barros, Dr. Harms, Dr. Fonselius, Dr. Kerkhoff, Dr. Palmork and the ICES Environment Officer to prepare a draft format for the leaflets on "Techniques in Marine Chemistry" for distribution to all members. Thereafter, Dr. Carlberg, Dr. Fonselius, Dr. Harms, Dr. Kerkhoff and Dr. Palmork to prepare leaflets as indicated in para 11.3 (paras 11.2 and 11.3).
7. Dr. Jensen to prepare a paper for the next meeting on the production, uses and levels of PCTs in the marine environment (para 13.2.8).
8. Dr. Nounou to prepare a paper on the subject of whether the Group should undertake studies of the marine chemistry of such substances as fluorinated hydrocarbons, silver, zinc or chromium, to act as a basis for discussion at the next meeting (para 13.2.8).
9. All members to prepare a list of priorities on which substances should be considered for the preparation of overviews for discussion at the next meeting (para 13.2.8).
10. Dr. Duinker, in consultation with Drs. Windom and Bewers, to prepare a draft paper describing procedures by which river inputs might reliably be measured. The paper should be sent to the ICES Environment Officer by 31 August 1981 for distribution to MCWG members (para 14 and Report of Second Meeting of MCWG, paras. 10.2 and 10.3).

ANNEX 7

THE CO₂ PROBLEM.

The partial pressure of CO₂ in atmosphere before the beginning of the industrialization has been estimated to be between 285 and 305 10⁻⁶ atm. In 1974, it was about 331 ppm. The increase of annual average CO₂ concentrations in air has been estimated to more than 3% over the 1959-71 period and the rate of increase has accelerated to more than 1 ppm/year in the last decade. This leads to a provisional CO₂ atmospheric concentration around 380 ppm in 2000 and 534 ppm in 2025, with the more optimistic scenario. This is mainly due to combustion of fossil fuels, intensification of agriculture and destruction of part of the world forest.

The carbon content of natural reservoirs have been estimated by various authors. This estimations are not all in good agreement but it is possible to get an idea of these contents by the following (Skirrow, 1975):

- atmosphere (in 1973)	:	6.75 10 ¹⁷	g.C
- terrestrial biosphere	:	16.4	"
- ocean			
- inorganic Carbon	:	387.5	"
- above thermocline	:	7.5	"
- deep-sea	:	370.	"
- organic Carbon	:	10.	"
- calcareous tests+detrital carbonates	:	12.9	"
- organic C in sedimentary rocks	:	68200.	"
- carbonate rocks	:	183000.	"

The fluxes of carbon between the natural reservoirs have also been evaluated (Skirrow, 1975):

- atmosphere - sea	:	0.7	10^{17}	g.C/year
- industrial CO ₂ (ca.1970)	:	0.04	"	
- photosynthesis on land	:	0.5	"	
- photosynthesis in the sea	:	0.5	"	
- weathering of carbonate rocks	:	0.005	"	
- oxidation in the sea	:	0.45	"	

To be able to predict the evolution of CO₂ content in atmosphere in the next decade, the oceanographers have to answer to the fundamental question: what is the response of the ocean reservoir to the increase of pCO₂ in air. The main phenomena to understand are then the kinetic of the exchange of CO₂ between atmosphere and sea, and the kinetic of the transport of CO₂ by the different water masses. And for the long term evolution, the capacity of the ocean to absorb the increase of pCO₂ in the atmosphere must be known.



