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REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Rostock-Warnemünde  
German Democratic Republic

20-23 February 1984

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\*General Secretary  
ICES  
Palægade 2-4  
DK-1261 Copenhagen K  
Denmark



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REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Rostock-Warnemünde  
German Democratic Republic

20-23 February 1984

1. OPENING OF MEETING

- 1.1 The Chairman, Dr J M Bewers, opened the meeting at 9.45 hrs on 20 February 1984 and welcomed the participants.
- 1.2 Dr K Voigt, Director of the Institut für Meereskunde of the Academy of Sciences of the German Democratic Republic, welcomed the participants on behalf of the host institute. He wished the Group success not only in its on-going work on marine chemistry, but also in the development of long-term programmes to identify and understand changes in the chemical conditions in the oceans. In particular, in terms of the work on long-term changes in climate and oceanography, he noted the importance of having marine chemists select appropriate parameters for an early detection of changes in the ocean climate.
- 1.3 On behalf of the Working Group, the Chairman thanked Dr Voigt for his words of welcome and for the opportunity to meet in Rostock-Warnemünde.
- 1.4 Each participant introduced him- or herself, giving affiliation and main areas of scientific responsibility.

2. ADOPTION OF AGENDA

- 2.1 The Working Group considered the draft agenda and adopted it as proposed. The agenda is attached as Annex 1. The list of participants is contained in Annex 2. The ICES Environment Officer served as Rapporteur.

3. REPORT OF THE 71st STATUTORY MEETING

- 3.1 The Working Group took note of a list of relevant Council Resolutions which had been adopted at the 1983 Statutory Meeting and was informed of other items of interest from that meeting.

4. REPORTS OF OTHER RELATED ACTIVITIES

4.1 Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic

- 4.1.1 An overview was given of the results of the 1983 meeting of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA). In particular, it was noted that the WGMPNA had requested the MCWG to develop guidelines for sampling, pre-treatment, and analysis of sea water for trace metals based on the outcome of the Fifth

Round Intercalibration on Trace Metals in Sea Water (5/TM/SW), for use in a proposed baseline survey of trace metals in coastal and shelf sea waters. The MCWG agreed to discuss this request under Agenda Item 10.

4.2 Working Group on Marine Sediments in Relation to Pollution

4.2.1 Noting that there would be a joint meeting with the Working Group on Marine Sediments in Relation to Pollution (WGMS) on 22 February, the MCWG decided to defer consideration of that Group's work until the joint meeting.

4.3 ICES/SCOR Working Group on the Study of the Pollution of the Baltic

4.3.1 The main results of the 1983 meeting of the ICES/SCOR Working Group on the Study of the Pollution of the Baltic were considered. In particular, note was taken of the work to study the patchiness (inhomogeneity) in space and time in the physical, chemical, and biological conditions in the Baltic Sea. This work aims to describe and map the occurrence of patchiness in the Baltic Sea, to gain an understanding of the mechanisms and processes for the generation and dissipation of patchiness, and to determine the significance of patchiness in relation to the ecosystem of the Baltic Sea.

4.3.2 Other work included the development of biogeochemical cycles of substances in the Baltic Sea, the development of techniques to monitor the biological effects of marine pollution, and the conduct of a pilot sediment study in the Baltic Sea. It was noted that this latter project and the associated intercalibration exercise on analysis of Baltic sediments would be discussed in greater detail at the joint meeting with the WGMS on 22 February (see C.M.1984/E:3 for the report of the joint meeting).

4.4 Joint Monitoring Group of the Oslo and Paris Commissions

4.4.1 The Environment Officer summarized the outcome of the January 1984 meeting of the Joint Monitoring Group of the Oslo and Paris Commissions and mentioned the requests for work relevant to the MCWG. These requests included:

- (a) to provide advice on the methods of sampling to determine the input of contaminants to the marine environment via rivers, with particular reference to net inputs;
- (b) to report on the outcome of the Fifth Round Intercalibration on Trace Metals in Sea Water, concerning in particular methods of sampling and pre-treatment;
- (c) to report on progress towards the conduct of an intercalibration exercise on the measurement of petroleum hydrocarbons in sea water and the outcome of the on-going intercalibration on petroleum hydrocarbons and PAHs in biological tissues;
- (d) to produce, as soon as practicable, a method for the quantification of the concentration of PCBs in environmental samples based on capillary gas chromatographic techniques. If necessary, on an



interim basis, this advice should involve only a few selected isomers of PCBs. In this advice should be included the extent to which data provided by the new method of quantification will be compatible with the already available data produced by packed column gas chromatography techniques;

- (e) to consider the feasibility of conducting an intercalibration exercise for PCBs in sediments and to advise accordingly. If appropriate, to draw up plans for and conduct such an exercise, reporting on the results in due course;
- (f) taking account of the report of and the information available to the ad hoc group of the Paris Commission responsible for assessing the input of contaminants from the atmosphere to the sea, to review knowledge on the input of contaminants from the atmosphere to the sea and to advise on the most appropriate methodologies for quantifying inputs from this source;
- (g) to keep under review the question of new contaminants that may be of interest to JMG.

4.4.2 The MCWG agreed that detailed consideration of each of these requests should take place under the relevant items of the remainder of the agenda. However, in terms of the request for a method to quantify PCB concentrations in environmental materials, the MCWG felt that a clear summary of the present status of PCB analysis should be made available to the JMG via the Advisory Committee on Marine Pollution (ACMP). Accordingly, the Chairman of MCWG was requested to provide the ACMP with an appropriate summary of the status of PCB analysis, as well as summaries concerning any other relevant items of advice on the ICES work programme from the Oslo and Paris Commissions or advice to other groups, as necessary.

#### 4.5 IOC/GIPME/GEMSI

- 4.5.1 Dr Topping summarized the work being done by the Group of Experts on Methods, Standards and Intercalibration (GEMSI) under the Working Committee on the Global Investigation of Pollution in the Marine Environment (GIPME) of the Intergovernmental Oceanographic Commission. He reported that GEMSI has sub-groups on, inter alia, the analysis of dissolved/dispersed petroleum hydrocarbons, on the sea surface micro-layer, and on the measurement of chlorinated hydrocarbons in sea water. It has produced or is producing reports on river inputs, on mass balances, on the possibility of conducting a baseline study of trace metals in sea water, and on the use of biological indicators in monitoring. He also pointed out that the Second Intercalibration Exercise on Analysis of Petroleum Hydrocarbons in Biota (2/HC/ET) was to be held jointly with IOC.
- 4.5.2 In the discussion of the GEMSI work, it was reported that progress has been good so far in the work on analysis of organochlorines in sea water. It was also noted that, while the GIPME programme had begun with the aim of measuring contaminant levels in the ocean, GEMSI was also giving attention to the matter of interfaces and fluxes in this context. To this end, a new sub-group has been established on the fluxes of contaminants across the land-sea boundary.

4.5.3 Dr Perttilä informed the Group that the IOC's Working Committee on International Oceanographic Data Exchange (IODE) has a Task Team on Pollution Data Exchange, which is examining issues relevant to the exchange of data on contaminants in the marine environment. The IODE agreed, at its January 1984 meeting, to collaborate with ICES on the development of reporting formats for data on contaminants in various marine compartments and to collaborate with ICES and GIPME on data handling issues. Dr. Perttilä pointed out that a crucial problem in the exchange of chemical data is the quality of these data; accordingly, quality control criteria for chemical data should be developed.

#### 4.6 Integrated Global Ocean Monitoring (IGOM) Meeting

4.6.1 Dr Topping informed the Group about the first International Symposium on Integrated Global Ocean Monitoring (IGOM), that was held in Tallinn, USSR on 3-8 October 1983. This Symposium was sponsored by the USSR, with support from UNEP, WMO and IOC. The main aims of the Symposium were to review the scientific problems associated with ecological and physical aspects of ocean monitoring, to exchange relevant information, and to consider possible international scientific cooperation in integrated global ocean monitoring. Dr Topping reported that the Symposium had made a number of recommendations concerning future work and had particularly supported UNEP's Regional Seas Programme and other regional approaches to environmental research and monitoring.

#### 4.7 Other relevant activities of multilateral and international agencies

4.7.1 Dr Falkowski informed the Group about the 14th Conference of Baltic Oceanographers, which will be held on 27 September to 2 October 1984 in Gdańsk. The theme of the Conference is "Physical and Chemical Processes and their Ecological Significance." In addition to plenary sessions, two parallel sessions will meet, one on physical oceanography and sedimentology and the other on chemical oceanography, pollution and its biological significance.

4.7.2 Dr Brüggmann reported that work is underway in the Helsinki Commission to prepare a second assessment of the impact of pollution on the Baltic Sea environment. This is a follow-up to the earlier "Assessment of the Effects of Pollution on the Natural Resources of the Baltic Sea, 1980," published as Baltic Sea Environment Proceedings No. 5 B.

4.7.3 Dr Calder provided information on the U.S. National Oceanic and Atmospheric Administration's Quality Assurance Program for Marine Environmental Measurements. This programme has been developed to improve quality and comparability of data among laboratories in terms of five types of marine environmental measurements: (1) organic chemicals, (2) trace metals, (3) inorganic nutrients, (4) human pathogens, and (5) biological rate determinations. Dr Calder stated that it was intended that links will be established with other international groups dealing with intercalibration and quality control of data on contaminants in the marine environment.

#### 5. REPORTS ON PROJECTS AND ACTIVITIES IN ICES COUNTRIES

5.1 No written reports on projects or activities had been submitted to the ICES Environment Officer, however, it was agreed that the participants

from countries not previously represented at an MCWG meeting should have the opportunity to present their relevant programmes to the Group.

5.2 The marine research programme of the host laboratory, the Institut für Meereskunde in Warnemünde, was presented during a visit to the Institute on the afternoon of 23 February. Participants were given a tour of all the laboratories in the Institute, during which the programmes on physical oceanography, nutrient studies, and measurements of trace metals and organochlorines in various marine compartments were described. Ample time was provided for participants to discuss the details of specific programmes with individual scientists at the Institute and a film was shown describing a major project in the equatorial Atlantic Ocean.

5.3 The marine chemistry research programmes carried out in Poland were described by Dr. Palkowski as follows:

In Poland, the research on marine chemistry is carried out in two fields:

- (1) The development of knowledge on the marine environment - coordinated by the Polish Academy of Sciences (PAS).
- (2) The elucidation of pollution problems - coordinated by the National Agency for Environmental Protection (NAEP).

Regarding (1), the research performed under the supervision of PAS concerns:

- the distribution of radionuclides and stable elements (Po, Ra, Cs, Sr, Zn, Co, Pb) between the various compartments of the marine environment;
- studies of the influence of inputs from the Vistula River and the atmosphere on the distribution of these elements;
- investigations of the concentration, origin and properties of natural organic compounds in sea water, sediments and marine organisms (sterols, amino acids, fatty acids, humic acids);
- studies of the influence of the environmental (ecological) conditions on the composition of lipids in marine organisms;
- studies of interactions between organic compounds and some trace metals and the biological effects of these interactions;
- development of methods for the determination of volatile organochlorine and organosulphur compounds;
- elaboration of analytical procedures for the determination of trace metals, hydrocarbons, chlorinated hydrocarbons (sea water, sediments, organisms).

All these studies are carried out mainly in the Institute of Oceanology, Sopot, and the Institute of Meteorology and Water Management, Department of Marine Physics and Chemistry, Gdynia, and the Technical University, Chemical Department, Gdańsk.

Regarding (2), the monitoring programme (hydrography and chemistry), requested by the Helsinki Commission, is performed by the Institute of Meteorology and Water Management (Gdynia) and to some extent (primary production) by the Marine Fisheries Institute, Gdynia.

Most of this effort is connected with the Baltic Sea, however, some research is carried out in the Antarctic region, also.

The major obstacles in our work:

- insufficient instrumental equipment;
- slow information exchange.

Contact address: Polish National Scientific Committee on Oceanic Research,  
Polish Academy of Sciences,  
Jaškowa Dalina 31,  
80-286 Gdańsk.

- 5.4 A discussion arose as to how laboratories in other countries might assist institutes in Poland and the German Democratic Republic in overcoming some of their problems. It was agreed that all members should make an effort to provide scientific material, particularly abstracts of papers and symposium proceedings, to participants or other scientists from both countries for distribution to their colleagues. It was stressed that scientists experiencing difficulties in the acquisition of information and research materials should not feel reluctant to write to other scientists requesting assistance.

## 6. INTERCALIBRATION AND OTHER QUALITY CONTROL ACTIVITIES

### 6.1 Trace Metals

#### 6.1.1 Intercalibration 5/TM/SW

- 6.1.1.1 The Chairman reported that three papers on the results of the Fifth Round Intercalibration on Trace Metals in Sea Water (5/TM/SW) had been presented at the 1983 Statutory Meeting. The Administrative Report of the intercalibration was presented as Doc. C.M.1983/E:28, which gave a summary of the exercise comprising five major components.
- 6.1.1.2 Dr. Berman then summarized the results of Section 3, a round-robin intercalibration on analyses of cadmium, copper, nickel, zinc, lead, iron and manganese in sea water, as reported in C.M.1983/E:24. Sea water samples were sent to 63 laboratories, 50 of which responded with results. These results showed a general improvement in analytical ability in comparison with that achieved in 4/TM/SW, however, results for lead are still poor in many cases, results for zinc were scattered, and results for iron were very poor. The concentrations of the trace metals in the samples were similar to concentrations found in open ocean surface waters, despite the fact that the samples had been taken in coastal waters. The Chairman concluded by stating that this had been a very successful intercalibration, showing that a number of laboratories had achieved good results on the analysis of a number of trace metals in sea water. Nonetheless, many laboratories must still improve their techniques to achieve acceptable results.
- 6.1.1.3 In the discussion of this report, the Working Group agreed that the results of this intercalibration exercise had been very good. It was pointed out, however, that many of the laboratories which contribute data to the Joint

Monitoring Programme of the Oslo and Paris Commission had not participated or, if they had participated, had obtained poor results. It was felt that this emphasized the importance of the use of uncompromised samples, i.e., samples for which the concentrations of trace metals or organic contaminants are not known to persons conducting the analyses, in joint or coordinated monitoring programmes. To assist laboratories in the development of their techniques, it was felt that sea water standards such as NASS-1, NASS-2, etc., were very useful. Accordingly, the Working Group requested the ICES Environment Officer to send information on the relevant sea water reference standards available from the Canadian National Research Council to the Oslo/Paris Commissions Secretariat for transmission to appropriate JMP laboratories.

- 6.1.1.4 Furthermore, in terms of an apparent question by the Joint Monitoring Group as to whether this intercalibration exercise is only relevant to the analysis of open ocean waters, given the low concentrations of trace metals in the intercalibration samples, the Working Group stated that the concentrations of trace metals found in the intercalibration samples were typical of coastal waters. Accordingly, this intercalibration exercise is very relevant to the Joint Monitoring Programme. While higher levels of trace metals may be found in estuaries, the conditions in estuaries are different from those in coastal waters and the situations are not generally comparable.
- 6.1.1.5 The Chairman then reviewed the results of Section 1 of 5/TM/SW, a comparison of sea water filtration procedures, as reported in C.M.1983/E:18. Six laboratories had taken part in this section of the exercise: (1) Netherlands Institute for Sea Research, Texel, The Netherlands; (2) Skidaway Institute of Oceanography, Skidaway, Georgia, USA; (3) Chalmers Institute, University of Göteborg, Göteborg, Sweden; (4) Deutsches Hydrographisches Institut, Hamburg, Federal Republic of Germany; (5) National Research Council of Canada, Ottawa, Ontario, Canada; and (6) Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada. This part of the intercalibration exercise had been carried out on the hypothesis that filtration of sea water resulted in a good deal of contamination of the filtrate. The results, however, have showed that comparatively little contamination occurs during the filtration procedures to separate suspended particulate matter from the sea water, given that appropriate precautions are taken. Only a few problem areas were identified by this experiment.
- 6.1.1.6 During the discussion of these results, the question arose as to whether the particulate matter left on the filter should also be analysed to determine trace metal concentrations in the particulate phase. It was generally agreed that it is important to analyse the particulate matter because (a) when estimating mass balances, one wants to know the relative amounts of substances on particles and in the dissolved phase, and (b) some contaminants adhere to particles which are ingested by organisms, and this may be a major source of contaminants to some organisms. The Group agreed to discuss the issue of particulate matter in greater detail later on in the meeting.
- 6.1.1.7 Turning to Section 4 of 5/TM/SW, a round-robin intercalibration exercise on analysis of mercury in sea water samples, the Chairman presented a summary of a draft paper by Dr. D. Cossa and Dr. P. Courau giving the results of this section. The Chairman reported that the first run of this part of the exercise had not been successful, owing to inadvertent contamination of the

intercalibration samples. Dr. Cossa had thereafter collected a second set of sea water samples from the Saint Lawrence estuary in Canada during September 1983. One set of samples contained the natural concentration of mercury, while the other set was spiked with methyl-mercury chloride. Samples were sent to 37 laboratories and results were received from 20 of them. Twelve laboratories reported reliable quantitative results for the natural level (unspiked) sample and fourteen for the spiked sample. The Chairman reported that the final report on this section of the exercise would be presented at the 1984 Statutory Meeting. Comments on the draft report should be addressed to Dr. Cossa. The Chairman agreed to carry out a thorough review of the report and forward comments and suggestions to Dr. Cossa within two weeks of the meeting.

- 6.1.1.8 Having considered all the available reports on the results of 5/TM/SW, the Working Group agreed that an enormous amount of work had been done on this exercise. The Working Group expressed its special appreciation to all the participants and particularly to those who had organized the work on the various sections and to the institutes which had provided the facilities: the Netherlands North Sea Directorate for the research vessel and the Institut Scientifique et Technique de Pêches Maritimes for the land-based facilities.
- 6.1.1.9 The Working Group recommended that the results of the Fifth Round Intercalibration on Trace Metals in Sea Water, comprising the administrative report, the report on the comparison of filtration procedures, the report on the round-robin intercalibration on analysis of general trace metals and the report of the round-robin intercalibration on analysis of mercury, should be published in the Cooperative Research Report series. The Working Group, having reviewed drafts of all these reports, approved their contents for publication, with the proviso that the final report on the mercury intercalibration would need to be considered and approved by the Marine Environmental Quality Committee. (See Recommendation 1, Annex 6.)
- 6.1.2 Intercalibration 7/TM/BT
- 6.1.2.1 Dr. Berman, Coordinator of the Seventh Intercalibration Exercise on Trace Metals in Biological Tissues (7/TM/BT), presented an interim evaluation of the results of the first phase of this exercise. Three samples had been distributed: A-lobster hepatopancreas, B-scallop, and C-plaice muscle. Sets of samples had been shipped on 30 August 1983 to 57 laboratories and results had been received from 41 of these, to date. The respondents had generally been cooperative, providing the details requested on methods used to analyse the samples. The results showed that good data were obtained for copper and zinc and, when analysed, for mercury. Very large relative standard deviations were obtained for the analysis of low level concentrations of lead, and arsenic at low concentrations also gave problems. Dr. Berman stated that a preliminary written report on the results would be ready in April and that the final report would be presented at the 1984 Statutory Meeting.
- 6.1.2.2 The Working Group agreed that this had been an interesting exercise, with generally good results. Concerning the poor results for determination of arsenic, it was noted that a large range of digestion techniques had been used. There is a need to examine these techniques carefully to evaluate which give the most accurate results.
- 6.1.2.3 Concerning the second phase of 7/TM/BT, which will be carried out in association with the 1985 Baseline Study of Contaminants in Fish and Shellfish, Dr. Berman reported that the preparation of uncompromised intercalibration materials was progressing and that materials were being provided by Drs. Jensen, Law and Topping. It was decided that the discussion of the

details of this second phase of the intercalibration should be carried out in the Sub-Group on Trace Metals (see Section 6B.4.3, below).

6.1.3 Intercalibration 1/TM/MS

6.1.3.1 It was agreed that the plans for the First Intercalibration on Analysis of Trace Metals in Marine Sediments (1/TM/MS) should be discussed at the joint meeting with the WGMS. (See report in C.M.1984/E:3.)

6.1.4 Review of Trace Metal in Sea water Intercalibrations

6.1.4.1 In addition to the discussion of this subject under item 6.1.1, above, this topic was discussed by the Sub-Group on Trace Metals in connection with proposals for a baseline study on trace metals in coastal waters.

6.2 Organics

6.2.1 Intercalibration 5/OC/BT

6.2.1.1 In the absence of Dr. J. Uthe, Coordinator of the Fifth Intercomparison Exercise on the Determination of Organochlorine Residues in Fish Oil (5/OC/BT), Dr. Kerkhoff summarized the results of this exercise, as reported in Doc. C.M.1983/E:38. The samples sent out were: (1) an unspiked fish oil, (2) the same fish oil spiked with amounts of four different chlorobiphenyls (CBs), and (3) small amounts of each of the added CBs. Thirty laboratories had participated in the exercise. Somewhat over one-half of the participants attempted to identify fully the four CBs. Although large interlaboratory coefficients of variation were found, a number of individual CBs were measured with an interlaboratory coefficient of variation equivalent to that associated with the measurement of PCBs using Arochlor 1254 as a standard. Dr. Kerkhoff stated that correct identification of individual CBs remains a problem, particularly for certain specific CBs. There are also some problems in the full recovery of each added CB. Based on his analysis of the results of this exercise, Dr. Uthe has concluded that systematic error is the major error contributing to the overall variance in results.

6.2.1.2 Dr. Kerkhoff then informed the Working Group about relevant work in the European Economic Community's Bureau of Community References (BCR). This work consists of the synthesis of individual CBs and the intercalibration of analysis of CBs. She stated that ten CBs have been synthesized thus far and will now be certified as standards. In terms of intercalibration, a step-by-step procedure will be carried out, beginning with the injection procedure into the gas chromatography system with electron capture detection. Temperature criteria for gas chromatography are also being considered. Dr. Kerkhoff agreed to keep the Working Group informed about developments in this work.

6.2.1.3 The Working Group agreed that further consideration of this topic should take place in the Organics Sub-Group.

6.2.2 Intercalibration 2/HC/BT, and

6.2.3 Intercalibration 3/HC/BT

6.2.3.1 An interim report on both the Second Intercomparison Study on the Determination of Petroleum Hydrocarbons in Biological Tissues (2/HC/BT) and the In-

tercomparison Study on the Determination of Polycyclic Aromatic Hydrocarbons (PAH) in Biological Tissues (3/HC/BT) was considered. In the absence of the Coordinators of these exercises, Dr. J.W. Farrington and Dr. A. Knap for 2/HC/BT and Dr. J. Uthe for 3/HC/BT, Dr. Calder summarized the status of these two exercises. Mussel homogenate samples for 2/HC/BT had been sent to 88 laboratories in ICES member countries as well as in IOC countries in other parts of the world, as this had been a joint ICES/IOC inter-comparison exercise. By the time of the meeting, about 48 data sets had been returned. Results would be accepted until the end of March 1984. Dr. Farrington would prepare a paper on the results of 2/HC/BT for presentation at the 1984 Statutory Meeting. Results had been reported using three different methods: (1) UV fluorescence, (2) gas chromatography, and (3) gas chromatography/mass spectrometry; data would be analysed on the basis of each group. Dr. Calder reported that a problem has arisen in that not all the internal standard could apparently be recovered, indicating that freeze-dried mussel may irreversibly absorb some of the added internal standard. This has resulted in problems in obtaining good quantitation.

- 6.2.3.2 For 3/HC/BT, samples of an oil and a dry residue had been distributed to 25 laboratories in ICES member countries only. Participants were requested to determine ten specified PAH compounds, and any other PAHs as desired. In the absence of Dr. Uthe, no further information was available on the progress in this exercise.
- 6.2.3.3 The Working Group agreed that further consideration of the analysis of petroleum hydrocarbons should be given during the meeting of the Organic Sub-Group.
- 6.2.4 Intercalibration 2/HC/MS
- 6.2.4.1 It was agreed that the discussion of a possible intercomparison exercise on analysis of hydrocarbons in marine sediments should be held during the joint meeting with WGMS (see report in C.M.1984/E:3).
- 6.2.5 Information on IOC/GIPME/GEMSI Hydrocarbon Workshop
- 6.2.5.1 This item was not considered because no information on the topic was available at the meeting.
- 6.3 Other Intercalibration and Quality Control Activities including the Availability and Preparation of Reference Materials and Standards
- 6.3.1 This topic was addressed by each of the three sub-groups which were established to consider in detail the analytical issues relating to trace metals, organics and nutrients. The discussion of this topic took place in the Trace Metals Sub-Group, see Section 6B, below.
- 6.4 Philosophy and Approach to Future ICES Quality Control Activities for all Classes of Analytes in Tissue, Water and Marine Sediments
- 6.4.1 This topic was addressed by the three sub-groups. See Section 6B, in particular, but also Sections 6C and 6D, below.



6.5 Plans for Future Intercalibrations

6.5.1 This topic was addressed by the three sub-groups (see Section 6B, 6C, and 6D, below) as well as by the joint session between MCFG and WGMS (see C.M. 1984/E:3).

6.6 OECD Principles of Good Laboratory Practice

6.6.1 The Working Group felt that it was unable to consider this item due to the absence of the proponent (Dr. M.C. de Barros) and the lack of information on the topic. Dr. de Barros had originally proposed that ICES consider formulating a code of "good laboratory practice" similar to that published by the OECD, (Good Laboratory Practice in the Testing of Chemicals, OECD, Paris, 1982). Some members of the Trace Metals Sub-Group had considered this document and felt that the current ICES Quality Control Philosophy based upon intercalibration and the provision of reference materials was a much more satisfactory method of ensuring good laboratory performance in marine monitoring and baseline activities than that formulated by the OECD.

6.6.2 The Working Group agreed, however, to defer further discussion until a formal proposal had been submitted by Dr. de Barros.

6A. FORMATION OF SUB-GROUPS ON TRACE METALS, ORGANICS, AND NUTRIENTS

6A.1 The Chairman proposed that sub-groups be formed for each of the major subject areas to consider in greater detail aspects of analytical techniques, quality control of data, issues relevant to the baseline studies of contaminants, and requests from the Oslo and Paris Commissions. The Working Group agreed, and three Sub-Groups were formed, as follows: (1) Sub-Group on Trace Metals (Chairman: Dr. Topping), (2) Sub-Group on Organic Chemistry (Chairman: Dr. Ehrhardt), and (3) Sub-Group on Nutrients and Carbonate Species (Chairman: Dr. Nehring). The Sub-Groups were given the following terms of reference:

To examine relevant papers and results of on-going activities, particularly intercalibration exercises, and

- (1) devise objectives and a strategy for future ICES quality control activities;
- (2) assess the need for attention to new matrices (marine materials) and/or determinands in future quality control activities;
- (3) assess the need for, and utility of, both compromised and uncompromised reference materials;
- (4) devise an approach (plan) for dealing with the above;
- (5) assess the practicality of including measurements in baseline programs. If, for certain contaminants, this is not yet possible, state the reasons!
- (6) assess/answer relevant Oslo and Paris Commissions requests;
- (7) Determine where leaflets on techniques (sampling and analytical) could be usefully prepared.

It was agreed that each Sub-Group could adapt these terms of reference to its own needs.

- 6A.2 The three Sub-Groups met concurrently on 21 February and progress reports on their work were given at the joint meeting between MCWG and WGMS on the morning of 22 February. The Sub-Groups resumed their work, again in concurrent sessions, on the afternoon of 22 February. On the morning of 23 February, the full Working Group considered oral reports summarizing the conclusions reached by each Sub-Group and their plans for future work. The account of the Working Group's consideration of these oral reports is contained in Section 6E, below.
- 6A.3 Each Sub-Group Chairman or his Rapporteur prepared a written report on subjects discussed, the conclusions reached, and plans for future work. These Sub-Group reports are contained in their entirety in the next three sections as follows:
- 6B. Report of the Sub-Group on Trace Metals
  - 6C. Report of the Sub-Group on Organic Chemistry
  - 6D. Report of the Sub-Group on Nutrients and Carbonate Species.

6B. REPORT OF THE SUB-GROUP ON TRACE METALS

6B.1 Item 1 of the Terms of Reference

- 6B.1.1 In relation to the terms of reference formulated by the Chairman of the Marine Chemistry Working Group, the Sub-Group agreed the following three points as its principal objectives or strategy in relation to quality control activities:
- (1) The maintenance, and where appropriate the improvement, of the quality of analytical data in relation to existing monitoring programmes (baseline studies, and trend monitoring);
  - (2) The development and testing of analytical methods for new contaminants;
  - (3) To make recommendations on, and subsequently evaluate, those analytical methods which are required for the measurement of contaminants in relation to
    - (a) input measurements;
    - (b) understanding of the movement, partitioning and speciation of contaminants within the marine ecosystem;
    - (c) biological effects measurements, and
    - (d) mass balances and fluxes.

Bearing in mind the above strategy, the Sub-Group went on to address the remaining parts of the terms of reference provided by the MCWG Chairman.

6B.2 Item 2 of the Terms of Reference

- 6B.2.1 It seemed clear to the Sub-Group that for the purposes of both research and monitoring studies in inshore waters there is a need to pay attention to major partitioning of metallic contaminants, in particular the incidence of metals in both aqueous and suspended particulate phases. For operational purposes, discrimination between these phases is made by filtration through a suitable filter membrane. All material in the filtrate is regarded as operationally "dissolved" and the material retained on the filter is defined as "suspended particulate". While we have, in previous experiments, paid considerable attention to dissolved phase metals and the separation of dissolved and particulate material, we have, as yet, not examined procedures for the analysis of suspended particulate material.
- 6B.2.2 In estuarine and coastal waters, important proportions of some metals will be associated with particulate material and, since some marine organisms can extract contaminants from both dissolved and particulate materials, it is important to assess the particulate metal concentrations. It is, therefore, concluded that for the immediate future, in combination with the continued attention to the improvement of dissolved metal data quality, there is a need to devise approaches to the analysis of particulate material.
- 6B.2.3 One of the most important applications of particulate measurements is in the context of particulate phase input fluxes to the marine environment. Any procedures for particle analysis will have as much application to particles discharged from rivers as they will to the ambient levels of contaminants in the particulate phase in the coastal zone.
- 6B.2.4 The Sub-Group proposed that a small sub-group should be established inter-sessionally to address this problem. The Chairman of MCWG agreed to raise this matter in plenary. Subsequently, at an ad hoc meeting of two members of MCWG and two members of WGMS, a proposal for evaluating the comparability of measurements of trace metals in suspended matter was tentatively agreed. An outline of this proposal, including the proposed participants, is documented in the report of the joint meeting between MCWG and WGMS (C.M.1984/E:3). Further details of this proposal will be presented to the ICES Statutory Meeting in 1984.
- 6B.2.5 In addition to this paper, a further paper will be prepared for the MCWG and the WGMS addressing the following topics:

- (1) A review of current procedures used for the collection and analysis of suspended particulate matter;
- (2) An assessment of the accuracy, precision and interlaboratory comparability of these measurements.

The Chairmen of WGMS and MCWG agreed to approach individuals on their respective Working Groups to write this paper, which would cover both inorganic and organic compounds.

6B.3 Item 3 of the Terms of Reference

- 6B.3.1 Dr. Berman introduced this topic by defining commonly used terms and discussing the availability and use of samples for quality control work.

### 6B.3.2 Reference materials

- a standard material in which the values have been certified and are accepted as good estimates of the true concentrations;
- are used in the validation of laboratory procedures and the development of new methods;
- are often used as calibration standards and as check samples (wasteful?).

Examples of these materials are given below:

#### Trace Metals in Sea Water

NASS-1      Open Ocean Water (NRCC)

#### Trace Metals in Biological Materials\*

NBS            Oyster tissue  
NRCC           TORT-1 (lobster hepatopancreas)  
NIES           Mussel (?)

Other NBS, NIES, and BCR biological materials (e.g., orchard leaves, bovine liver, citrus leaves) - all but bovine liver are plant materials.

6B.3.3 The ideal reference material will have a matrix very similar to that of the sample as well as equivalent metal concentrations. In effect, one should have a reference material for each type of sample. This, of course, is not feasible, but the need for a good number of fish and shellfish samples as well as a nearshore water sample and a riverine water sample is obvious.

### 6B.3.4 Research materials

6B.3.4.1 These standard samples are not certified but have consensus values for the metal concentrations through intercomparisons and individual laboratory data accumulated over the years. They are very useful but rather rare in the marine field. The majority are excess materials from intercalibration exercises.

6B.3.4.2 If available, they can be used somewhat in the same manner as reference materials, with the proviso that the confidence in the concentration values is not as high.

6B.3.4.3 Both of these types of materials are for subjective use. Because the values are known, they cannot be used as "unknowns" to assess a laboratory's performance. They are "compromised".

6B.3.4.4 "Uncompromised" samples (containing known, but undisclosed concentrations of contaminants) are very rare. They are as difficult to prepare and analyze as reference or research materials and, generally, very limited quantities are prepared, usually in order to assess laboratory capabilities for a particular project. Their use and need are obvious. The mechanism for their preparation and sources of appropriate financial support are not readily apparent.

\* Key to abbreviations: NBS = National Bureau of Standards (USA), NRCC = National Research Council of Canada, NIES = National Institute for Environmental Studies (Japan), BCR = Bureau of the Community on Reference Materials (European Community).

6B.3.5 The Sub-Group generally agreed that certified reference materials should be used principally for the testing of new analytical procedures since their cost and availability prohibit their use for routine quality control work. The use of research materials, particularly the ones used in and remaining from previous ICES intercalibration exercises was encouraged for "in-house" quality control measurements.

6B.3.6 In relation to ICES baseline and monitoring studies, the interlaboratory comparability of data should be checked periodically (2-3 year period) through an ICES intercomparison exercise. These exercises would use research materials which would be specially prepared by one or more ICES laboratories from fish and/or shellfish tissue. As in the past, this coordinating work would have to be done on a voluntary basis in the absence of an alternative scheme.

6B.4 Item 4 of the Terms of Reference

6B.4.1 The Sub-Group discussed and drafted proposals in relation to the proposed baseline study of trace metals in sea water (see Section 6B.5, below) and the second part of the Seventh ICES Intercalibration Exercise for Trace Metals in Biological Tissues (7/TM/BT).

6B.4.2 Baseline study of trace metals in sea water

6B.4.2.1 It was generally agreed that the capability for accurate and precise measurements of trace metals in sea water was now present in several laboratories in ICES member countries, following the successful conclusion of the intercomparison exercises and the workshop carried out in 5/TM/SW (Nantes, September 1982). It was therefore agreed that it would be useful if baseline measurements of trace metals in sea water could be included with measurements of contaminants in fish and shellfish tissue in the 1985 ICES Baseline Survey. Nevertheless, it is essential that other measurements in addition to analysis of trace metals be made so that an adequate basis for assessing the trace metal survey results will be available. These additional measurements should include salinity, temperature, silicate, nitrate, and phosphate. It was decided that an examination should be made of how wide an area of the coastal zone might be surveyed and how quality control might be maintained, realizing that there was insufficient time to conduct further intercalibration experiments for trace metals in sea water.

6B.4.2.2 Capability in sampling, sample storage and analytical methods has been established on the basis of the results of recent ICES intercalibrations for trace metals in sea water, particularly 4/TM/SW and 5/TM/SW. Competent laboratories include the following:

Institute for Marine Research, Kiel	(Dr. K. Kremling)
Institute for Marine Research, Rostock-Warnemünde	(Dr. L. Brüggmann)
Chalmers Institute, University of Göteborg	(Dr. S. Westerlund)
German Hydrographic Institute, Hamburg	(Dr. D. Schmidt)
Bedford Institute of Oceanography, Nova Scotia	(Dr. P. Yeats)
Skidaway Institute of Oceanography, Georgia	(Dr. H. Windom)
Institute for Marine Research, Reykjavik	(Mr. J. Olafsson)

Additional laboratories clearly have adequate analytical capability, as revealed by the ICES intercalibration 5/TM/SW. These laboratories include:

University of Liège	(Dr. G. Gillain)
Marine Pollution Laboratory, Denmark	(Dr. A. Jensen)
Greenland Geological Survey	(Dr. G. Asmund)
Laboratoire de Physique et Chimie marines, Villefranche-sur-mer	(Dr. P. Courau)
Laboratoire de Chimie Analytique, Université de Bretagne Occidentale	(Dr. J. Courtot, Dr. F. Quentel)
Institut Scientifique et Technique de Pêches Maritimes, Nantes	(Dr. E.M. Boutier)
Swedish Environment Protection Board, Laboratory for Coastal Research, Uppsala	(Dr. I. Gustavsson)
DAFS Marine Laboratory, Aberdeen	(Dr. P. Balls)

6B.4.2.3 However, the reliability of the sampling, sample pretreatment and sample storage procedures of these latter laboratories has not been assessed. Therefore, in considering their potential participation in baseline surveys, it was necessary to devise a procedure for quality control purposes, if these laboratories are to conduct baseline measurements. It was decided that several reference stations would need to be established. These reference stations would be occupied by participants in the baseline survey to permit an assessment of their overall capability for trace metal determinations in sea water. This requires that the reference stations be in areas of well-known and relatively invariant hydrographic characteristics, at least in the deeper waters of these stations. Furthermore, it would be preferable if the vertical profiles of these stations exhibited suitable gradients in nutrients and certain trace metals so as to provide additional information on performance than merely metal concentrations.

6B.4.2.4 It was suggested that the following areas/stations might be suitable for this purpose, subject to confirmation of their hydrographic stability and temporal invariance by the Shelf Seas and Oceanic Hydrography Working Groups.

Central North Sea  
Bay of Biscaye beyond the shelf  
North west of Scotland beyond the shelf  
Station "S" near Bermuda  
Southern Norwegian Sea (North of Iceland/Faroe Ridge).

At least one of these stations would need to be occupied by a participant in the baseline programme and a vertical profile for S, T, nutrients, and trace metals should be reported.

6B.4.2.5 A paper describing this approach to the inclusion of trace metals in sea water within the 1985 Baseline Programme will be submitted to the 1984 ICES Statutory Meeting for discussion (and amendment, if necessary) and approval by the Hydrography Committee and the Marine Environmental Quality Committee.

6B.4.3 Second part of the 7th ICES Intercomparison Exercise for trace metals in tissue (7/TM/BT)

6B.4.3.1 The Sub-Group agreed the following:

- 7/TM/BT will be carried out simultaneously with the 1985 Baseline Study of Contaminants in Fish and Shellfish by all participating laboratories;

- 5 samples will be distributed consisting of:

  - dogfish muscle
  - dogfish liver
  - Mytilus edulis (clean)
  - cod liver (defatted)
  - Mytilus edulis (contaminated);

- samples should be sent to participants by the beginning of 1985;

- results should be received by the coordinator by 31 March 1986;

- sufficient material should be sent so that the analyses will be carried out twice, once at the beginning of the laboratories' analytical processing of the baseline materials and again near the end;

- results will be required for the same six metals as in Part A (Cu, Zn, As, Cd, Hg, and Pb), plus any other results the laboratory may wish to submit;

- six replicate analyses will be done on each of the four samples for each of the metals;

- results will be quoted on a "dry weight" basis;

- the results of the intercalibration will be assessed by a special meeting of the trace metal sub-group of the MCWG prior to the MCWG meeting in 1987;

- it is suggested that the results of the 1985 Baseline Study be examined by the MCWG prior to their assessment by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic;

- the ICES Secretariat should send a list of all laboratories intending to participate in the 1985 Baseline Study on Contaminants in Fish and Shellfish to the Coordinator of 7/TM/BT as soon as possible;

- the Coordinator will enter into correspondence with the participating laboratories, especially with those who apparently had problems in the first part of ICES 7/TM/BT, in order to recommend methods of upgrading laboratory capabilities.

Drs. Berman and Topping agreed to prepare a paper for the Statutory Meeting describing the content of, and timetable for, the second part of 7/TM/BT.

The intercalibration exercise will be open to any other participants identified by the ICES MCWG Coordinator of the exercise, the ICES Secretariat, Delegates to ICES, etc.

6B.5 Item 5 of the Terms of Reference

6B.5.1 The Sub-Group discussed whether trace element analyses could be carried out as a part of the (proposed) baseline studies. It was agreed that for Cd, Cu, Ni, Zn, Hg, and possibly lead, analyses of water and biological tissues can be adequately made by a number of ICES laboratories at the present time. It was, however, pointed out that Cu and Ni may not be of significant interest in the baseline studies since they are not a widespread problem. Nonetheless, results of intercalibration studies have shown that they can be accurately analyzed.

6B.5.2 In the case of the Baseline Study of contaminants in the tissues of marine organisms, analyses of the above-mentioned trace elements should be included. Analyses of sea water, however, would require relevant ancillary data, such as salinity, temperature, and nutrients (see Doc. MCWG 1984/11).

6B.5.3 Prior to the inclusion of trace element analysis in a baseline study for sea water, the laboratories involved should have demonstrated their competence through past intercalibrations and should conduct a further intercalibration to demonstrate their ability to obtain comparable data. In this respect it was proposed that "calibration or reference stations" should be established in the study area, and each participating laboratory should obtain sea water samples from these stations to evaluate the comparability of the overall measurement procedures. (See Section 6B.4, above, for details of these proposals.)

6B.6 Item 6 of the Terms of Reference

6B.6.1 The Sub-Group was informed by Dr. Berman that a report on the 5th ICES Intercalibration on Trace Metals in Sea Water (conducted in Nantes, September 1982) has been completed and, together with the results of the recent intercalibration exercise on mercury (conducted by Drs. D. Cossa and P. Courau) and the results of the comparison of filtration procedures, will be recommended for publication as a joint report in the Cooperative Research Report series.

6B.6.2 The Sub-Group was informed by Dr. Windom that the review on atmospheric inputs to the sea, which he and Dr. A. Knap had promised for discussion at the meeting, had unfortunately not been prepared. Bearing in mind the need for this review by the JMG, the Sub-Group proposed that Drs. Windom and Topping should prepare this paper intersessionally for submission to MCWG at its meeting in 1985.

6B.6.3 The Sub-Group recognized the importance JMG attached to the estimation of net input from rivers to the sea, but felt that this matter was indeed a complex problem and one that was unlikely to be resolved for some time. They noted that a GESAMP sub-group had been set up to address this matter and that this topic would form part of the discussions and deliberations of the Nantes Workshop on Contaminant Fluxes in the Coastal Zone in May 1984. They agreed to await the outcome of these discussions before considering the preparation of a paper for transmission to JMG.



6B.6.4 The Sub-Group was informed by the Environment Officer of the current state of the data reporting forms for trace metals in marine samples. After a short discussion, it was agreed that members of MCWG should send their comments on the Preliminary Draft Interim Reporting Format on Contaminants in Sea Water to the Environment Officer by 31 May 1984 so that the revised version can be available for interested parties as soon as possible.

6B.7 Item 7 of the Terms of Reference

6B.7.1 After some discussion, the Sub-Group agreed that the preparation of ICES leaflets on Techniques in Marine Chemistry (covering sampling and analytical procedures) was the most useful method of quickly disseminating information to laboratories within the ICES community.

6B.7.2 In this context, the Sub-Group proposed the following topics for inclusion in this series, in addition to those already held by the ICES Environment Officer:

- (1) Guidelines on the sampling, pretreatment and storage of sea water for trace metal analysis.
- (2) Some examples of good analytical methods for trace metals in sea water used by competent laboratories at present. These would be identified by the coordinators of the relevant ICES intercalibration exercises for trace metals in sea water and an approach made to the potential author(s) to prepare the necessary leaflet.
- (3) Analytical methods for the measurement of trace metals in biological tissue drawn from laboratories which had proven capability in these analyses.
- (4) Guidelines for laboratories in the approach to "in-house" quality control, including such matters as estimating the limit of detection, precision and accuracy of analytical methods, etc.

6B.7.3 As before, the preparation of leaflets would remain the responsibility of individual authors who would submit their proposed draft to the ICES Environment Officer for distribution to the appropriate editorial sub-group of MCWG for consideration and approval, prior to publication.

6C. REPORT BY THE SUB-GROUP FOR ORGANIC CHEMISTRY

6C.1 The terms of reference were adopted as given by the Chairman of the Marine Chemistry Working Group.

6C.2 Polynuclear Aromatic Hydrocarbons

6C.2.1 Referring to items 1 and 2 of the terms of reference, the Sub-Group discussed the analysis of polynuclear aromatic hydrocarbons (PAH) in sea water. It was recognized that total PAHs, as determined by ultra-violet fluorescence (UVF), are being determined on a routine basis in the Baltic Sea and the North Sea. However, for the North Atlantic, the data base is insufficient. These measurements were successfully intercalibrated in the Kiel Workshop of 1981; additional intercalibrations are not required

for the immediate future. The Sub-Group agreed that there is a need to know the composition of the fluorescent material to assess properly the pollution status of the area, and with a view toward determining sources. Detailed investigations of the composition of the fluorescent material have been carried out in several laboratories. Background concentrations of this material are generally composed of only a few unsubstituted PAHs, such as anthracene, phenanthrene, pyrene, fluoranthene, and chrysene, strongly suggesting that the material is generated in combustion processes. It is only in the case of elevated UVF readings, indicating contamination by fossil fuels, that other PAHs are detected in the water. The Sub-Group concluded that UVF is a good screening method for inclusion in the Baseline Study Programme; however, it should be checked occasionally when UVF readings are low ( $< 1 \mu\text{g}/\ell$ ) for individual PAHs and more frequently as the UVF readings increase.

- 6C.2.2 For determination of individual PAH compounds, two methods were discussed, i.e., gas chromatography (GC) combined with either a mass spectrometer (MS) or specific ion detector (SID), or high pressure liquid chromatography (HPLC). The Sub-Group agreed that both approaches were acceptable, but recognized that GC-MS or GC-SID were applicable to a broader range of organic contaminants (e.g., chlorinated hydrocarbons). The Sub-Group emphasized that the overall expenses of conducting a monitoring programme (ship time, etc.) are so large that the maximum amount of information should be obtained from the samples collected. The higher cost of GC-MS or other sophisticated equipment is not excessive in comparison to these total costs.
- 6C.2.3 The UVF screening procedure can also be applied to sediments and this measurement is a likely candidate for inclusion in the Baseline Study Programme. Because the variability in composition and concentration of PAHs in sediments is likely to be much higher than in water, the correlation between UVF readings and individual compound analysis would have to be checked more frequently before a final recommendation can be made.
- 6C.2.4 In one study, a good correlation between UVF readings and the concentrations of individual PAH compounds in sediments was found. The National Research Council of Canada is planning to prepare three sediment reference materials for PAHs. These will be available later this year.
- 6C.2.5 The current intercalibration exercise for PAHs in tissues (3/HC/ET) is expected to provide sufficient information to decide whether a recommendation should be made for the inclusion of analyses of PAHs in tissues in the Baseline Study Programme.
- 6C.2.6 At present, only a small number of laboratories have demonstrated the ability to do individual PAH analysis, but the techniques for this procedure are described in the scientific literature and could be adopted by most laboratories.
- 6C.2.7 The Sub-Group discussed methods for the collection of suspended particulate matter (SPM) and settling particulate matter for trace organic analysis. Several collection methods (filtration, continuous-flow centrifugation, sediment traps) are well-documented in the literature. It was recognized that each of these methods collects a different fraction of the particulate material. The results of many analyses of trace metals

in particulate material have appeared in the literature, but few results have been published for trace organic analysis. The concentration of organic contaminants would be influenced strongly by the biogenic component of the particulate matter, which will vary greatly with season, geography and depth of sampling. At least 10<sup>2</sup> l of water would be required for trace organic analyses of suspended particulate matter. Members of the Sub-Group are requested to submit papers from the literature concerning collection and analysis of particulate matter prior to next year's meeting, at which the subject of trace organic analysis of particulate material will be discussed again and recommendations made.

6C.3 Chlorinated Hydrocarbons

- 6C.3.1 The analysis of individual chlorinated hydrocarbons in sea water is not recommended for the Baseline Study Programme because too few laboratories are capable of doing the analyses. For the same reason, an intercomparison exercise is not feasible at this time.
- 6C.3.2 The situation for particulate matter is the same as for sea water.
- 6C.3.3 No intercalibration for chlorinated hydrocarbons in sediments has been conducted. The National Research Council of Canada has available two sediment reference materials for polychlorinated biphenyls (PCBs). Analysis of these materials by a number of laboratories would provide a first assessment of comparability and would determine the need for future intercalibration exercises.
- 6C.3.4 Several intercalibrations for determination of PCBs in tissues have been conducted. Although improvement has been noted, laboratory comparability is still poor. There is evidence that systematic errors exist in current methods. These errors must be identified and eliminated before another intercalibration should be conducted. The EEC laboratories are studying such errors and a report is expected in April 1984. Dr. Kerkhoff has agreed to make this report available to the ICES Secretariat. ICES is conducting an interim study of chlorobiphenyl analysis in which solutions of individual congeners were distributed to several laboratories. However, many analysts did not deliver their results to the coordinator, Dr. Reutergerdh, by the deadline of January 1984. In view of the cost and time spent by the coordinator in synthesizing standards and preparing solutions, and the efforts of the other participants in conducting analyses, the Sub-Group strongly urged laboratories that have not delivered their results to do so, or to return the materials to the coordinator. Further intercalibration for PCBs is unwarranted until the above activities are completed.
- 6C.3.5 The Sub-Group strongly recommended the use of capillary columns for analysis of chlorinated hydrocarbons, and laboratories are encouraged to develop this capability. In the interim, packed columns may still be used, but when capillary columns become available, correlation of results obtained by the old and new methods will be required.
- 6C.3.6 The use of capillary columns will require the availability of pure congeners of PCBs for calibration and quantitation. ICES should either supply these materials or seek funds for their preparation. Dr. Kerkhoff has agreed to supply a list of the most useful congeners.

- 6C.3.7 Because of the limited number of laboratories capable of doing chlorinated hydrocarbon analysis with sufficient reliability, the Sub-Group suggested that for the 1985 Baseline Study, samples from a wide area be sent to these laboratories for analysis to determine levels and large-scale distribution of chlorinated hydrocarbons, especially PCBs. Other laboratories who wish to conduct analyses of PCBs and other chlorinated hydrocarbons should not be discouraged from doing so, but should be encouraged to analyse samples from as wide a geographical area as possible to permit an overlap of areas sampled by other laboratories.
- 6C.3.8 Other chlorinated hydrocarbons, including hexachlorobenzene, lindane isomers, dieldrin and DDT and its breakdown products, were also considered. The analytical situation for them is similar to that for PCBs; thus, any decision to include these compounds in future monitoring activities should be made only after decisions have been made regarding PCB analysis.
- 6C.3.9 The Sub-Group reviewed and discussed two papers on analysis of chlorinated hydrocarbons. The first was "Quantitative Determination of Polychlorinated Biphenyls (PCB) in Commercial Silica Gel by Capillary Gas Chromatography" by Å.Bergman, L. Reutergårdh and M. Åhlman (Doc. MCWG 1984/7.1). This paper forcefully demonstrated one of the many possible problems in the analysis of chlorinated hydrocarbons, namely, the contamination of silica gel by PCBs, which apparently is widespread. The observed pattern of contamination suggests that it occurs after the production of the silica gel, perhaps by adsorption of PCBs from the air. The second paper, entitled "The Evaluation of an Analytical Method for Polychlorinated Terpenes (PCC) in Biological Samples using an Internal Standard" by U. Wideqvist, B. Jansson, L. Reutergårdh, and G. Sundström, described a procedure for the analysis of polychlorinated terpenes (PCCs). This analysis is not yet a routine procedure, but the Sub-Group encouraged laboratories that have mastered PCB analysis to try the analysis of PCCs. Discussion of both papers emphasized the need to optimize operating conditions for each gas chromatograph and not merely rely on published conditions used by other laboratories.
- 6C.4 Additional Candidate Compounds
- 6C.4.1 The Sub-Group identified the following as additional candidate compounds:
- chlorinated dibenzodioxins
  - chlorinated dibenzofurans
  - phenols and chlorinated phenols
  - plasticizers
  - biocides.
- 6C.4.2 For each of these, analytical capabilities are insufficient at present for use in monitoring programmes, and the Sub-Group recommended that ICES not consider these compounds for monitoring in the near future. The Sub-Group was aware that methods are being developed and suggested that analysis of these compounds could be reconsidered in the future. Dr. Ehrhardt will provide an information paper on the analysis and occurrence of phenols in the marine environment, and Dr. Law will provide an information paper on the analysis and occurrence of phthalate plasticizers. Both papers will be available at the next meeting of the Working Group.

6C.5 Leaflets on Techniques in Marine Chemistry

6C.5.1 The Sub-Group agreed that information which does not meet the standards of international scientific journals should not be published by ICES. Methodological details which would not ordinarily be included in such journals may be suitable topics for ICES leaflets.

6C.6 Continued Activities of the Trace Organics Sub-Group

6C.6.1 The Sub-Group proposed that an ad hoc Group be formed to meet in 1985 in advance of the Marine Chemistry Working Group. This ad hoc Group should be charged with consideration of problems, such as those stated above, and should attempt to provide solutions and recommendations to the Marine Chemistry Working Group. (This proposal was subsequently endorsed by the full Working Group, see paragraph 17.3, below.)

6D. REPORT FROM THE SUB-GROUP ON NUTRIENTS AND CARBONATE SPECIES

6D.1 Definitions

6D.1.1 Phosphorus, nitrogen, and silicate compounds (inorganic and organic) are essential nutrients limiting primary production. Other nutrients are, for example, the carbonate species. Some of these parameters are often used as tracers in oceanography for identifying water masses.

6D.2 Comparability of Data

6D.2.1 Large-scale interlaboratory comparisons of methods in nutrient analysis have been performed (cf. Doc. ICES, C.M.1983/C:1). Nutrient data from these exercises were comparable.

6D.2.2 Intercalibrations under field conditions yield less satisfactory results (cf. Report of the Second Biological Workshop held in Rønne, Bornholm, Denmark 1982, published in Baltic Sea Environment Proceedings No. 9 (Helsinki 1983) and Doc. MCWG 1984/13.1). Reasons are inhomogeneities of the nutrient distribution in the water mass (patchiness) and/or sampling. Therefore, the Sub-Group strongly recommended that ad hoc intercomparisons between ships be conducted under field conditions at every opportunity.

6D.2.3 Furthermore, the Joint Panel on Oceanographic Tables and Standards (SCOR WG 10) is asked to examine the possibility of preparing recommended standards for alkalinity and calcium as well as buffers for pH-determination in order to get more comparable data for the estimation of the global carbon budget. Until the standards become available, the Sub-Group recommends that an intercalibration trial be conducted on these parameters. This intercalibration should be organized jointly by the ICES MCWG and SCOR WG 75 (Oceanic CO<sub>2</sub> Monitoring).

6D.3 Other Nutrient Compounds

6D.3.1 The Sub-Group could not identify any other nutrients of high priority. However, more attention should be paid to organic nutrient compounds (e.g., urea, amino acids, proteins, carbohydrates) and nitrogen gas in connection with the biological cycle in the sea.

6D.4 Leaflets on Techniques in Marine Chemistry

6D.4.1 There exist a lot of laboratory manuals and monographs on common nutrient analysis. Therefore, generally the preparation of leaflets is not necessary. If new nutrients of high priority are identified, the Sub-Group recommends that the description of appropriate methods of determination should be made available to the ICES community as soon as possible.

6D.5 Baseline Studies

6D.5.1 Nutrient analysis is included in oceanographic monitoring and other standard programmes. Large sets of data have been available for about three decades. Therefore, no extended baseline programmes are necessary on the nutrient distribution in 1985.

6D.6 Problems of High Priority in Nutrient Research

6D.6.1 The Sub-Group identified the following problems of high priority in nutrient research:

- Small-scale inhomogeneities in nutrient distribution in space and time (patchiness).
- Exchange of nutrients between the sea water and the atmosphere, the sediments, and the organisms, as well as inputs from rivers and other land-based sources.
- Long-term variations and mass-balances of nutrients in connection with possible eutrophication.
- Transfer of nutrients between the different links of the food web.

6D.7 Problems Related to Carbonate Species

6D.7.1 The Sub-Group recommends more intensive studies of the CO<sub>2</sub>/carbonate system in the deep water formation areas, especially during the winter season. Laboratories with an easy access to these regions (Labrador Sea, Norwegian Sea, etc.) should focus their work on time variations in the air/sea CO<sub>2</sub> gradient and the state of the CO<sub>2</sub>/carbonate system in surface waters.

6D.8 Oslo/Paris Commissions Requests

6D.8.1. In response to the request of the Oslo/Paris Commissions, item XIII, the Sub-Group refers to the Special Meeting on "Problems of unusual phytoplankton blooms", which will be arranged by ICES in Copenhagen in October 1984.

6D.9 Alkalinity/Carbonate Intercalibration

6D.9.1 It was noted that Dr. F. Culkin (U.K.) had agreed to prepare standardized sea water samples (S = 35 o/oo, 38.4 o/oo and ca. 30 o/oo) for the conduct of an alkalinity/carbonate system intercalibration. The experiment would be coordinated by Dr. Poisson, who would also assess the homogeneity of the samples prior to distribution.

Participants would be charged for the samples and shipment costs. The Sub-Group requested ICES to provide moral support for this activity and hoped to be kept informed of progress so that ICES laboratories could participate.

6E. CONSIDERATION OF SUB-GROUP REPORTS BY MCWG

- 6E.1 Each of the Sub-Groups was requested to submit a report of the results of further discussions since the presentation of their reports on the previous day.
- 6E.2 Dr. Topping described the results of further discussions within the Sub-Group on Trace Metals. The Sub-Group had provided more details in regard to plans for the 1985 Baseline Study, in particular, concerning the manner in which quality control may be achieved in the Baseline Survey on trace metals in sea water. It had been decided that, since there would not be adequate time for the conduct of additional intercalibrations, reference stations would be established with the assistance of the Oceanic Hydrography and Shelf Seas Hydrography Working Groups.
- 6E.3 The logistics of the supply and analysis of biological tissue reference materials (7/TM/BT, part 2) for the Baseline Study of Contaminants in Fish and Shellfish had been devised as well as a provisional timetable for the receipt of results and their analysis. This is described in the Report of the Sub-Group on Trace Metals (Section 6E.4.3). Finally, it had been proposed that a position paper on the analyses of suspended particulate matter be sought for the 1985 MCWG meeting. The Chairmen of MCWG and WGMS agreed to approach jointly several individual scientists to carry out this task. Initial approaches by the Chairmen of these two Working Groups will be made to Dr. A. Saliot (France) and Dr. S. Westerlund (Sweden) to find out whether they would be willing to prepare papers on the determination of organic and inorganic constituents, respectively, in suspended particulate matter.
- 6E.4 During the discussion on this presentation, Dr. Weichart asked if the decision by the Sub-Group to proceed with the baseline study for trace metals in sea water was in contradiction to the conclusions of the ad hoc Hydrography Committee/Marine Environmental Quality Committee group that met in connection with the 1983 Statutory Meeting (Paper WGMPNA 1984/8.3). Dr. Topping replied that the conclusions of the Sub-Group were entirely consistent with the content of the second paragraph of the ad hoc Group Report, in which it was stated that baseline surveys of trace metal concentrations in sea water, if accompanied by additional measurements of physical oceanographic variables, would be very useful. The Chairman added that he saw no inconsistency between the reports because the first paragraph of the ad hoc Group report was merely intended to discourage major reassignment of resources to baseline surveys at the expense of geochemical and hydrographical process studies.
- 6E.5 Having concluded the discussion of the report of the Sub-Group on Trace Metals, the Working Group approved the report.
- 6E.6 The report of the Sub-Group on Organic Chemistry was presented by Dr. Calder. In further discussions, the Sub-Group had decided to seek the provision of information on the collection and analysis of suspended

particulate matter for organic constituents. This conclusion was similar to that proposed by the Sub-Group on Trace Metals and would be covered by the approach to Dr. Saliot and the request to all members of MCWG to supply information on this topic for the 1985 MCWG meeting. The Sub-Group had further agreed that overviews on the analysis and occurrence of phenols and phthalates would be sought and individual members, namely Drs. Ehrhardt and Law, respectively, had agreed to prepare these overviews.

6E.7 In addition, the Sub-Group considered it essential to provide greater time for Sub-Group discussions on problems related to trace organic analyses, particularly in respect to organochlorine compounds. A proposal for a two-day Sub-Group meeting prior to the next MCWG meeting had been made, and this item was deferred until the considerations of MCWG meeting recommendations (see Section 17, below).

6E.8 There was little discussion of the report, and it was accepted by the Working Group.

6E.9 Additional discussions within the Nutrient and Carbonate Sub-Group were summarized by the MCWG Chairman in the absence of Dr. Nehring. Further details concerning the carbonate/alkalinity measurements needed in deep water formation areas were provided and the need was stressed for attention to be paid to nutrient fluxes from sediments, in atmospheric deposition and in river discharges. The Sub-Group had requested ICES to provide moral support for planned alkalinity/major ion intercalibrations planned by IOS (Dr. Culkun) in connection with IAPSO and GESAMP Working Group activities. The Chairman had agreed to explore ways in which ICES could support these activities and to try to ensure the involvement of ICES laboratories in any intercalibration activities. The Sub-Group report was accepted by the Working Group without modification.

6E.10 The Chairman expressed his appreciation to all members of the Sub-Groups and in particular their Chairmen (Drs. Topping, Ehrhardt, and Nehring) for their valuable work.

## 7. STANDARD ANALYTICAL PROCEDURE FOR ORGANOCHLORINE DETERMINATIONS

7.1 Most of the discussion of this topic had already taken place during the meeting of the Sub-Group on Organic Chemistry, as reported in Section 6C, above.

7.2 Dr. Reutergårdh presented two papers on analytical methods for organic constituents, Docs. MCWG 1984/7.1 and MCWG 1984/7.2, both of which had been considered earlier by the Sub-Group on Organic Chemistry (see paragraph 6C.3.9, above). The Working Group agreed to attach these two papers as annexes to its report. (See Annexes 3 and 4.) It was noted that versions of these papers will eventually be published in the open literature.

## 8. OSLO AND PARIS COMMISSION REQUESTS

8.1 The Working Group had discussed this item in general under Agenda Item 4.4, above, and specific consideration of each request relevant to MCWG was thereafter given under the most relevant item of the agenda and, particularly, in the work of the three Sub-Groups. (See, among others, Sections 6E.6 and 6D.8, above, and Section 9.1, below.)



9. OVERVIEWS ON FLUXES AND TRANSPORT OF CONTAMINANTS IN THE MARINE ENVIRONMENT

9.1 Atmospheric Deposition of Trace Metals

9.1.1 This subject was discussed by the Sub-Group on Trace Metals in which it was decided that work on the review of the atmospheric deposition of trace metals to the North Atlantic would be continued by Drs. Windom and Topping, and possibly also Dr. A. Knap. The report will be presented at the 1985 MCWG meeting. (See paragraph 6B.6.2.)

9.2 Furans and Dioxins

9.2.1 A revised version of the review paper on "Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans" by Dr. Mairin O'Sullivan was reviewed (Doc. MCWG 1984/9.2). This paper had been presented at the 1983 meeting of MCWG and the revised version had taken account of suggestions made by Working Group members as well as additional data, provided by Dr. L. Reuter-gårdh, on the concentrations of these contaminants in several species of organisms from the Baltic Sea. Dr. Reuter-gårdh stated that the report represented an overview of all available information on furans and dioxins in the marine environment.

9.2.2 The overview provided information on the structure of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs), their sources, methods of analysis, occurrence in the environment, and toxicity. It was noted that there was very little information on the concentrations and distribution of these substances in the marine environment.

9.2.3 Given this paucity of environmental data on these substances, the Working Group recommended that additional efforts be made to obtain data on the concentrations and distribution of PCDDs and PCDFs in the marine environment.

9.2.4 The Working Group agreed that the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA) should review this paper and thereafter it should be forwarded to the Advisory Committee on Marine Pollution (ACMP). The MCWG expressed its appreciation to the author of the paper, Dr. Mairin O'Sullivan, and also to Dr. Reuter-gårdh for his assistance.

9.3 Polycyclic Aromatic Hydrocarbons

9.3.1 A paper on this subject had been reviewed at the 1983 MCWG meeting and certain amendments had been requested. However, the lead on this topic had been taken over by Dr. A. Moinet of WGMPNA and no further version of the paper was presently available.

9.4 Photo-degradation Products of Petroleum Hydrocarbons

9.4.1 Dr. Palmork presented document MCWG 1984/9.4 "An Overview of Auto/Photo-oxidation of Petroleum in the Marine Environment", which he and Dr. K. Tjessem had prepared. An earlier version of the paper had been reviewed at the previous MCWG meeting and Dr. Palmork stated that all the comments and suggested amendments had been taken into account during the revision of the paper.

- 9.4.2 The paper contained an overview of the occurrence of auto- and photo-oxidation, methods for the analysis of the compounds produced by these processes, information on possible pathways for photochemical oxidation, and an indication of the importance of these processes in terms of experiments on the toxicity of petroleum hydrocarbons.
- 9.4.3 In the discussion, Dr. Ehrhardt reported on the results of studies conducted by his Institute on reactions with singlet oxygen. It was reported that the mussel sample used in the Second Intercomparison Exercise on Petroleum Hydrocarbons in Biological Tissues (2/HC/BT) contained photodegradation products at higher concentrations than those of PAHs and other aromatic hydrocarbons. It appeared that photochemical degradation has been underestimated in many of the previous studies on the degradation of petroleum hydrocarbons. Furthermore, in studies of the effects of oil on biota, care must be taken that effects observed are due to the oil itself and not to photo-degradation products, which may be very toxic.
- 9.4.4 The Working Group agreed that the paper was very valuable in providing a warning regarding the photodegradation of petroleum hydrocarbons and decided that the paper should be passed on to ACMP, for its consideration. The Working Group thanked the authors, Drs. Palmork and Tjessem, for preparing the paper.
- 9.5 Carbon Dioxide
- 9.5.1 Dr. Poisson gave an oral presentation of the paper which he and Dr. A. Papaud had prepared, entitled "Le cycle du carbone et sa perturbation par les activités humaines: un aperçu du probleme." He provided a general overview of the carbon cycle and of the amounts of carbon contained in the various reservoirs - atmosphere, oceans, biosphere and lithosphere. While an equilibrium had existed between CO<sub>2</sub> concentrations in pre-industrial times, during the post-industrial period the equilibrium has been disturbed owing to an increase in CO<sub>2</sub> from the burning of fossil fuels and the decreased absorption of CO<sub>2</sub> due to deforestation. There has been a clear increase in pCO<sub>2</sub> in the atmosphere since the beginning of the industrial revolution. The estimated future increase in pCO<sub>2</sub> has been calculated using a model and various potential scenarios of the combustion of fossil fuels; all scenarios indicate a doubling of pCO<sub>2</sub> during the next century. This will result in an increase in the temperature of the lower layer of the atmosphere, which will be greatest at the poles of the earth. Other substances can also affect the temperature of the lower layer of the atmosphere and they must also be taken into account. Dr. Poisson pointed out that the atmospheric increase in CO<sub>2</sub> is a factor in a much wider problem and cannot be separated from the broader context; much work must be carried out to be able to understand the trends in CO<sub>2</sub> and its effects.
- 9.5.2 In the discussion of this paper, it was noted that even the additional amounts of nitrates and phosphates entering the oceans from anthropogenic sources will have little to no effect on the deposition of organic carbon from the extra CO<sub>2</sub>. The additional CO<sub>2</sub> can eventually decrease the pH of the ocean by up to 0.5 pH units, which is enough to seriously affect sensitive marine fauna. The effect of acid rain on the carbon cycle was not known.

- 9.5.3 As the full written report was not available at the meeting, it was agreed that the Environment Officer would circulate the report to all members as soon as possible for review and comment. Members should send their comments directly to Dr. Poisson. Although the Working Group consideration of the report was not finished, it was felt that the ACMP may wish to see the report already at this stage. On behalf of the meeting, the Chairman thanked Dr. Poisson for the excellent presentation of this interesting and topical subject.
- 9.5.4 In terms of further work related to the CO<sub>2</sub> cycle in the oceans, the Sub-Group on Nutrients was requested to provide additional relevant data, particularly temporal data. These data must be of known good quality. The MCWG also felt it could be useful to ask the members of the former Working Group on Primary Production Methodology whether they saw a need for standards to be prepared for alkalinity, total CO<sub>2</sub>, etc.
- 9.5.5 The MCWG reiterated its support, given in Section 6D.9, above, for the development of standardized sea water samples by Dr. F. Culkin, IOS, and the intercalibration exercise on alkalinity and carbonate determinations, coordinated by Dr. Poisson. The Working Group expressed a desire to take part in this, and any other, intercalibration exercise and also to be kept informed of the relevant work carried out by other groups, e.g., the Joint Panel on Oceanographic Tables and Standards.
- 9.6 Zinc
- 9.6.1 The Working Group noted that the paper it had reviewed the previous year, "Zinc in the Marine Environment - An Overview" by Dr. P.A. Yeats, had been forwarded to the WGMFNA for review. Dr. Thurberg of the WGMFNA had been requested to add toxicological information on zinc, and it was anticipated that the final paper would be submitted to ACMP at its next meeting.
- 9.7 Organosilicons
- 9.7.1 Dr. Kerkhoff reported that work on this overview was continuing and a paper may be ready on the subject for next year's meeting.
- 9.8 Alkyl-tin Compounds
- 9.8.1 Dr. Thibaud presented the paper "Les composés alkylétains" (Doc. MCWG 1984/9.8), which he and Mr. Cl. Alzieu had written. The paper contained information on the production and use of alkyl-tin compounds in general, their physico-chemical properties, and their toxicity to marine fauna. The most toxic alkyl-tin compounds in terms of marine fauna are the derivatives of the tri-alkyl series, particularly tri-butyl tin (TBT) as the oxide or fluoride. The effects are especially acute on the larval stages of molluscs, for which development is inhibited at concentrations of TBT at or below 1 µg/l. The report then provided information on methods to analyse for alkyl-tins and, given the difficulty of these analyses, cited only a few figures on the concentrations of various types of alkyl-tin compounds in the marine environment. Dr. Thibaud reported that owing to the serious effects of alkyl-tin compounds, especially TBT, on the growth of molluscs, the use of anti-fouling paints containing these compounds has been banned for pleasure boats in France. A similar ban has been issued in Sweden, while the United Kingdom is presently considering issuing such a ban.

- 9.8.2 In the discussion of this paper, it was felt that it could be useful to add a section on the degradation of alkyl-tin compounds in the marine environment. The question was also raised as to whether the tin added to the marine environment after the degradation of alkyl-tin compounds could be detected in the sediments. This was considered to be unlikely.
- 9.8.3 The Working Group thanked Dr. Thibaud and Mr. Alzieu for preparing this paper and agreed that it should be forwarded first to the WGMFNA and thereafter to ACMP.
- 9.9 Polychlorinated Terphenyls
- 9.9.1 The Working Group considered paper MCWG 1984/9.9 "Polychlorinated Terphenyls: A Review" by Mr. A.A. Jensen and Mr. K.F. Jørgensen. This paper was based on Jensen, A.A. and Jørgensen, K.F.: "Polychlorinated Terphenyls (PCTs): Use, Levels and Biological Effects," which was published in The Science of The Total Environment 27:231-250. A very short version had been presented at the previous year's meeting; the present version was an expanded review based on the guidelines for overviews.
- 9.9.2 The report described the production of PCTs in various countries and noted that most countries have ceased production of these compounds. Some figures were given on the concentrations of PCTs reported in various marine organisms and available information was summarized on the effects of PCTs on experimental animals. The paper concluded that there is a need to monitor the concentrations of PCTs in the marine environment.
- 9.9.3 In the discussion, Dr. Kerkhoff mentioned that the concentrations reported for PCTs in marine organisms seemed very high, as she has been unable to detect PCTs in samples of fish and shellfish from Dutch waters. It was reported, however, that PCTs were detected in eels from the Baltic Sea in a recent study. The Working Group therefore noted that, while the paper represented a faithful review of the literature cited, much of this literature was rather old. Given that the methodology for measuring PCTs has developed considerably in recent years, values from the older literature may not be valid today. With this comment attached, the Working Group agreed that the paper should be forwarded to WGMFNA and thereafter to ACMP. The Working Group expressed its appreciation to the authors for providing the paper.
- 9.10 Other Overviews
- 9.10.1 No other overviews were available for the Working Group to review and no plans were made for the preparation of additional overviews.
10. BASELINE SURVEYS
- 10.1 This topic was discussed by the three Sub-Groups. The main consideration took place in the Sub-Group on Trace Metals and is reported in Section 6B.4.2, above, on the Baseline Study of Trace Metals in Sea Water. The discussion in the Sub-Group on Organic Chemistry is found in paragraph 6C.3.7, above, and on the Sub-Group on Nutrients and Carbonate Species in Section 6D.5, above.

11. REFERRED STATUTORY MEETING PAPERS

- 11.1 The first papers for consideration were the reports of the Belgian study "Distribution, transport and fate of Bi, Cd, Cu, Hg, Pb, Sb, and Zn in the Belgian coastal marine environment" (Docs. ICES C.M.1982/E:34 - E:39) and "Boundary Conditions for heavy metals at the air-sea interface" (Doc. ICES C.M.1982/E:33). Dr. Vandamme informed the Working Group that the results of these studies would be the subject of a paper that would be presented at the ICES/IOC/NOAA Symposium on Contaminant Fluxes Through the Coastal Zone (Nantes, 14-16 May 1984) and thus would be discussed at that meeting. The Working Group therefore agreed that discussion of these papers in MCWG was inappropriate and looked forward to seeing the results of the Nantes Symposium and Workshop, at which the Belgian studies would be considered.
- 11.2 The referred paper C.M.1983/E:14, "Biochemical approach for estimation of maximum tolerable burden of some metals in the Baltic ecosystem," had been read by few members of the Working Group, largely because the ICES Statutory Meeting papers had not yet been distributed within their countries. The Chairman stated that he had referred this paper to the Working Group because it contained aspects of interest in the context of biological turnover, assimilative capacity and trace metal budgets. He had, however, some reservations regarding the numerical values in the paper but thought it warranted discussion.
- 11.3 It was decided to delay consideration of this paper for a further year, and the Chairman agreed to ensure that the paper was distributed to all members by the Environment Officer so that a full discussion could be held at the 1985 MCWG Meeting.

12. NEW CONTAMINANTS

- 12.1 The main discussion of this item took place in the Sub-Group on Organic Chemistry (see paragraph 6C.4.1, above), where it was decided that attention should be given to the following groups of compounds:

chlorinated dibenzodioxins  
chlorinated dibenzofurans  
phenols and chlorinated phenols  
plasticizers  
biocides.

13. NUTRIENT STUDIES

- 13.1 Most of the discussion of this subject took place in the Sub-Group on Nutrients and Carbonate Species, as reported in Section 6D, above.
- 13.2 Dr. Koroleff reported on the results of a nutrient intercalibration that had been carried out as part of the Second Biological Intercalibration Workshop held in Rønne, Bornholm (Denmark) on 17-20 August 1982, under the auspices of the Helsinki Commission. Analysts from all seven countries around the Baltic Sea took part, with six research vessels operating.

- 13.3 In the first part of the nutrient intercalibration, mixed samples were distributed to all participants for analysis according to the routine procedures for each laboratory. The nutrients analysed were:  $\text{PO}_4\text{-P}$ , Total-P,  $\text{NO}_3\text{-N}$ ,  $\text{NO}_2\text{-N}$ ,  $\text{NH}_3\text{-N}$  and  $\text{SiO}_4\text{-Si}$ . The concentrations of most nutrients were very low, close to the detection limit. The coefficients of variation obtained, however, were better in most cases than those obtained at the Kiel Intercalibration Workshop in 1977.
- 13.4 For the second part of the nutrient intercalibration, the research vessels met at a station and sampled water from 0-60 m depth. The ships were around 0.7 nm from each other, and the results showed a greater variability in nutrient concentrations than had been obtained with the mixed sample, probably owing to patchiness in the water body.
- 13.5 Based on the results of this intercalibration, the Workshop had recommended that no changes be made to the methods of determining nutrients in the Baltic Monitoring Programme and that no additional nutrient species should be added to the programme. As the results from the field experiment had been strongly influenced by patchiness, it was recommended that any further intercalibration exercises on nutrients should be carried out on the same sample of sea water. Finally, the Workshop cautioned that the introduction of automated procedures for analysis should be accompanied by careful checking against the basic manual procedures.
14. TRACER STUDIES
- 14.1 The Chairman opened the consideration of this item by querying as to the possible interest in the Working Group on the use of Freon-11, tritium, etc. as tracers in the ocean, and also as to the possible use of nutrients as tracers in physical oceanographic studies.
- 14.2 In the discussion, it was pointed out that nutrients can be used as tracers in the Baltic Sea because nutrient concentrations are highly correlated with density layers rather than with depth. However, in areas outside the Baltic Sea, there are only a few instances where nutrients could be used as tracers, using nitrogen in combination with oxygen (N/O) or phosphorus in combination with oxygen (P/O). For example, N/O and P/O have been used as tools in studies in the Arctic Sea. It was generally agreed that for studies in the open ocean, freon would be a good tracer.
- 14.3 Mr. Olafsson reported that a Nordic Symposium on Tracers in Physical and Chemical Oceanography in the North Atlantic will be held in Reykjavik in August 1984. Experts from both Nordic and non-Nordic countries will be invited to attend.
- 14.4 The Working Group felt that a short review should be made on tracer studies. As this subject should be one of interest to the Working Group on Oceanic Hydrography, the Chairman proposed that he write to the Chairman of that Working Group to discuss the most useful way of carrying out any further work on this topic.
15. LEAFLETS ON TECHNIQUES IN MARINE CHEMISTRY
- 15.1 The Chairman reminded the Working Group that at its previous meeting it had been decided that leaflets on methods of sampling, sample preparation

and analysis should not be prepared. In taking note of this decision, the Advisory Committee on Marine Pollution had requested the MCWG to reconsider this decision and make sure that it is final.

- 15.2 Several members felt that methods change so quickly that they should not be published as they are obsolete by the time the publication is issued. Other members felt that it would be useful to have methods published, particularly when they represent the successful methods from an intercalibration exercise. It was noted as an example that the successful methods from 7/TM/BP could be described quite easily, either as an addendum to the report of the exercise or as a separate leaflet.
- 15.3 The Working Group generally agreed that the dissemination of descriptions of successful methods would be a good culmination of an intercalibration exercise. It was agreed, however, that the three Sub-Groups should discuss the applicability of leaflet descriptions of methods in each particular area.
- 15.4 The Sub-Group on Trace Metals agreed that the preparation of ICES leaflets on Techniques in Marine Chemistry was the most useful method of quickly distributing information to laboratories in the ICES community. Accordingly, this Sub-Group requested its members to submit draft leaflets for publication by ICES. See Section 6B.7, above, for the full report. The Sub-Group on Organic Chemistry felt that methods should generally be published in international scientific journals, but that any methodological details not ordinarily published in such journals may be available for ICES leaflets (see Section 6C.5). The Sub-Group on Nutrients and Carbonate Species felt that there are already a number of laboratory manuals on methods to analyse for the common nutrients, but if new nutrients of high priority become identified, methods for their determination should be published in the ICES series (Section 6D.4).
16. ANY OTHER BUSINESS
- 16.1 Dr. Koroleff informed the Group that some trace metal standards which had been prepared by his Institute in 1947-1949 had been recently found. Analysis of the present concentrations of these standards had shown only very small changes in concentrations over these years.
17. RECOMMENDATIONS
- 17.1 In beginning the discussion of the next meeting of the Working Group, a brief discussion was held concerning the structure of the various Working Groups in ICES concerned with marine pollution. The majority of MCWG were interested in reviewing the work on marine pollution with a view to restructuring the Working Groups concerned with this subject. One possibility mentioned was that there should be a large parent Working Group, with a number of Sub-Groups on the various specialized subjects.
- 17.2 In terms of the relationship of the meetings of MCWG with those of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA), the MCWG agreed that it was important that meetings of MCWG and WGMPNA take place on a back-to-back basis over two weeks at the

same location. The MCWG meeting should take place during the first week, followed by the WGMPNA meeting. For 1985, the MCWG recommended that it meet in Copenhagen for 4 days at a time convenient to ICES to consider the following:

- (a) the report of the results of the first phase of 7/TM/BT and progress in the second phase;
- (b) reports on the results of 2/HC/BT and 3/HC/BT;
- (c) the overview paper on the atmospheric deposition of contaminants to the North Atlantic Ocean; and
- (d) plans for and progress in the Baseline Studies.

17.3 In addition, it was recognized that the expressed desire of regulatory agencies and environmental managers for the inclusion of chlorinated hydrocarbon analysis in the baseline studies and monitoring programmes cannot be satisfied until the many methodological problems are solved. To date, too little time has been available in plenary sessions of the MCWG for discussion of analytical problems for trace organic chemicals, especially the chlorinated hydrocarbons. Longer and more in-depth discussions would allow these problems to be solved in a much shorter time than otherwise. Therefore, the MCWG recommended that an ad hoc sub-group of specialists meet for two days immediately prior to the next meeting of the MCWG. This sub-group should emphasize the analysis of PCBs because substantial new information will become available during 1984.

Specific tasks for the sub-group will be:

1. to distribute, in advance of the meeting, papers describing advances in analytical methodology for PCBs and other chlorinated hydrocarbons;
2. to review and evaluate the results of the intercalibration for PCB congeners being coordinated by Dr. L. Reutergårdh;
3. to review and evaluate results of methodological studies for chlorinated hydrocarbon analysis, in particular the study being conducted within the European Community;
4. to recommend specific actions to improve the analysis of PCBs in environmental samples.

Individuals who have participated in the activities described in items 2 and 3 above are specifically requested to attend. Dr. Reutergårdh was requested to serve as convener of the ad hoc sub-group.

17.4 The full recommendation for the next meeting of the MCWG and of the ad hoc Sub-Group on Trace Organic Chemicals appears as Recommendation 3 in Annex 6.

17.5 The Working Group then reviewed and reaffirmed its recommendation that the reports on the results of the Fifth Round Intercalibration on Trace Metals in Sea Water should be published as a volume of the Cooperative Research Report series, and approved in principle that the report on the results of



the Fifth Intercalibration on Organochlorines in Biological Tissues should be published in this same volume, subject to review of the final report. (See Recommendation 1, Annex 6.)

- 17.6 Concerning the Baseline Study on Trace Metals in Sea Water, the Working Group noted that the Council had given approval in principle in 1982 (C.Res. 1982/4:8) to the conduct of this exercise. However, in the event that further endorsement should be necessary, the Working Group approved a new recommendation on the conduct of this Baseline Study (Recommendation 2, Annex 6).
- 17.7 The Working Group reviewed in general the list of intersessional activities to be carried out before the next meeting. This Action List is attached as Annex 5.
- 17.8 As there was no further business, the Chairman thanked all the participants for their work, and especially the Chairmen and rapporteurs of the various Sub-Groups: Drs. Topping, Ehrhardt, Nehring, Calder, Law and Reutergårdh. The Chairman also thanked the Rapporteur, Dr. Pawlak.
- 17.9 On behalf of all participants, the Chairman expressed the special thanks of the Working Group to the host Institute, the Institut für Meereskunde, to the Director of the Institute, Professor K. Voigt, to the ICES Delegate, Dr. H.J. Brosin, and to Dr. Brüggmann who had handled the practical arrangements of the meeting, as well as to the staff of the Institute.
- 17.10 The Working Group thanked the Chairman for his excellent guidance of the meeting and the Chairman closed the meeting at 14.00 hrs on 23 February 1984.

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NOTE: A Joint Meeting between the Marine Chemistry Working Group and the Working Group on Marine Sediments in Relation to Pollution was held on 22 February. The report of this Joint Meeting is found in Document C.M.1984/E:3.

ANNEX 1

MARINE CHEMISTRY WORKING GROUP  
Rostock-Warnemünde, 20-23 February 1984

A G E N D A  
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1. Opening of Meeting
2. Adoption of Agenda
3. Report of the 71st Statutory Meeting
4. Reports of Other Related Activities
  - 4.1 Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic
  - 4.2 Working Group on Marine Sediments in Relation to Pollution
  - 4.3 ICES/SCOR Working Group on the Study of the Pollution of the Baltic
  - 4.4 Joint Monitoring Group of the Oslo and Paris Commissions
  - 4.5 IOC/GIPME/GEMSI
  - 4.6 Integrated Global Ocean Monitoring (IGOM) Meeting
  - 4.7 Other relevant activities of multilateral and international agencies
5. Reports on Projects and Activities in ICES Countries
6. Intercalibration and other Quality Control Activities
  - 6.1 Trace Metals
    - 6.1.1 Intercalibration 5/TM/SW
    - 6.1.2 Intercalibration 7/TM/BT
    - 6.1.3 Intercalibration 1/TM/MS
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    - 6.2.1 Intercalibration 5/OC/BT
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  - 6.3 Other Intercalibration and Quality Control Activities including the availability and preparation of reference materials and standards
  - 6.4 Philosophy and approach to future ICES quality control activities for all classes of analytes in tissue, water and marine sediments
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7. Standard Analytical Procedure for Organochlorine Determinations
8. Oslo and Paris Commissions Requests
9. Overview on Fluxes and Transport of Contaminants in the Marine Environment
  - 9.1 Atmospheric Deposition of Trace Metals
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14. Tracer Studies
15. Leaflets on Techniques in Marine Chemistry
16. Any Other Business
17. Recommendations

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ANNEX 2

MARINE CHEMISTRY WORKING GROUP

Rostock, 20 - 23 February 1984

LIST OF PARTICIPANTS

E Andrulewicz  
Institute of Meteorology and  
Water Management  
Dept. of Mar. Phys. and Chemistry  
Waszyngtona 42  
81-342 Gdynia  
Poland

G Asmund  
Grønlands Geologiske Undersøgelser  
Østervoldgade 10  
1350 Copenhagen K  
Denmark

S Berman  
National Research Council of Canada  
Division of Chemistry  
Ottawa, Ontario K1A 0R9  
Canada

J M Bewers (Chairman)  
Bedford Institute of Oceanography  
P.O. Box 1996  
Dartmouth, Nova Scotia  
B2Y 2M6  
Canada

L Brüggmann  
Institut für Meereskunde  
Akademie der Wissenschaften der DDR  
Seestraße 15  
2530 Rostock-Warnemünde  
German Democratic Republic

J Calder  
National Oceanic and Atmospheric  
Administration  
N/OMS 32  
Rockville, Maryland 20852  
U.S.A.

W P Cofino  
Government Institute for Sewage  
and Waste Water Treatment  
P.O. Box 17  
8200 AA, Lelystad  
The Netherlands

M Ehrhardt  
Institut für Meereskunde  
Abteilung Meereschemie  
Düsternbrooker Weg 20  
2300 Kiel  
Federal Republic of Germany

L Falkowski  
Institute of Oceanology  
Polish Academy of Sciences  
P.O. Box 68, Sopot  
Poland

S H Fonselius  
Institute of Hydrographic Research  
Box 2566  
403 17 Göteborg  
Sweden

Helga Gegusch  
National Board of Nuclear Safety  
and Radiation Protection of the GDR  
Waldow Allee 117  
1157 Berlin  
German Democratic Republic

R Gellermann  
Bergakademie Freiberg  
Sektion Physik  
Cottastraße 4  
9200 Freiberg  
German Democratic Republic

I Gustavsson  
Swedish Environment Protection Board  
The Laboratory for Coastal Research  
170 11 Drottningholm  
Sweden

U Harms  
Bundesforschungsanstalt für Fischerei  
Labor für Radioökologie der Gewässer  
Wüstland 2  
2000 Hamburg 55  
Federal Republic of Germany

ANNEX 2 (cont'd)

P Hartmann  
Bezirks-Hygiene Inspektion und Institut  
Gertrudenstrasse 9  
2500 Rostock-Warnemünde  
German Democratic Republic

A Jensen  
Marine Pollution Laboratory  
Jegersborg Allé 1B  
2920 Charlottenlund  
Denmark

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

F Koroleff  
Institute of Marine Research  
P.O. Box 33  
00931 Helsinki 93  
Finland

R Law  
Ministry of Agriculture,  
Fisheries and Food  
Fisheries Research Laboratory  
Burnham-on-Crouch  
Essex CMO 8HA  
England

G Manthey  
Bezirks-Hygiene-Institut  
Abt. Anorgan. Fettstoffe  
Gertrudenstrasse 9  
2500 Rostock-Warnemünde  
German Democratic Republic

M Marchand  
Centre Océanologique  
de Bretagne (CNEXO)  
B.P. 337  
29273 Brest Cédex  
France

M Mohnke  
Institute for Chemical Toxicology  
Pfermoserstrasse 15  
7050 Leipzig  
German Democratic Republic

D Nehring  
Institut für Meereskunde  
Akademie der Wissenschaften der DDR  
Seestrasse 15  
2530 Rostock-Warnemünde  
German Democratic Republic

J Olafsson  
Marine Research Institute  
Skúlagata 4  
Reykjavik 101  
Iceland

O Vagn Olsen  
Danish Institute of Fisheries and  
Marine Research  
Charlottenlund Castle  
2920 Charlottenlund  
Denmark

C Osterroht  
Institut für Meereskunde  
Abteilung Meereschemie  
Düsternbrooker Weg 20  
2300 Kiel  
Federal Republic of Germany

Michael O'Sullivan  
Department of Fisheries and Forestry  
Fisheries Research Centre  
Abbotstown  
Dublin 15  
Ireland

K H Palmork  
Institute of Marine Research  
P.O. Box 1870  
5011 Bergen-Nordnes  
Norway

Janet Pawlak (Rapporteur)  
Environment Officer  
ICES  
Palægade 2-4  
1261 Copenhagen K  
Denmark

J Pemkowiak  
Institute of Oceanology, PAN  
P.O. Box 68, Sopot  
Poland

M Perttilä  
Institute of Marine Research  
P.O. Box 33  
00931 Helsinki 93  
Finland

ANNEX 2 (cont'd)

A Poisson  
Université Pierre & Marie Curie  
Lab. de Physique et Chimie Marine  
Tour 24  
4, Place Jussieu  
75230 Paris Cédex 05  
France

L Reutergårdh  
National Swedish Environment  
Protection Board  
Special Analytical Laboratory  
Box 1302  
171 20 Solna  
Sweden

K-H Rohde  
Institut für Meereskunde  
Akademie der Wissenschaften der DDR  
Seestraße 15  
2530 Rostock-Warnemünde  
German Democratic Republic

G Schlungbaum  
Universität Rostock  
Sektion Biologie  
Freiligrathstrasse 7-8  
2500 Rostock-Warnemünde  
German Democratic Republic

Y Thibaud  
ISTPM  
B.P. 1049, rue de l'Ile d'Yeu  
44037 Nantes Cédex  
France

G Topping  
Marine Laboratory  
P.O. Box 101  
Victoria Road  
Aberdeen AB9 8DB  
Scotland

Anna Trzosińska  
Institute of Meteorology and  
Water Management  
Dept. of Mar. Phys. and Chemistry  
Waszyngtona 42  
81-342 Gdynia  
Poland

K Vandamme  
Rijksstation voor Zeevisserij  
Ankerstraat 1  
8400 Oostende  
Belgium

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

G Wiese  
Universität Rostock  
Sektion Biologie  
Freiligrathstrasse 7-8  
2500 Rostock-Warnemünde  
German Democratic Republic

H Windom  
Skidaway Institute of Oceanography  
P.O. Box 13687  
Savannah, GA. 31416  
U.S.A.

ANNEX 3

QUANTITATIVE DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCB)  
IN COMMERCIAL SILICA GEL BY CAPILLARY GAS CHROMATOGRAPHY

by

Åke Bergman, Lars Reutergårdh\* and Maria Åhlman

Section of Organic Chemistry  
Wallenberg Laboratory  
University of Stockholm  
S-106 91 STOCKHOLM  
S w e d e n

\*National Swedish Environment Protection Board  
Special Analytical Laboratory  
Wallenberg Laboratory  
University of Stockholm  
S-106 91 STOCKHOLM  
S w e d e n

PCB is an environmental pollutant of global significance that has been determined in air, water, sediments and biota (1-3). The use of PCB in open systems was strongly restricted during the 1970s in many countries after PCB was found to be accumulated in a number of species and also to be biomagnified. PCB is still manufactured, but at least in western countries it is mainly used in closed systems, such as in transformers and capacitors (4). However, contamination of the environment from these sources does occur, e.g., via a slow continuous leakage or by accidents such as transformer fires. Another source for the environmental contamination by PCB might be the thermal degradation of chlorinated paraffins (5).

In order to identify the constituents of the complex mixtures from various environmental sources, more or less complicated clean up procedures must be followed. The isolation of PCB in such samples might involve separations on silica gel, in columns or on thin layer chromatography (TLC) plates. Several batches of silica gel were found to be contaminated by PCB during methodological development of the analysis of PCB (6,7). Furthermore, silica gel coated TLC-plates were reported to contain up to 40 ppm contaminants, including several polychlorinated aromatic compounds (8). The present report concerns the qualitative and quantitative determination of PCB as a contaminant of commercial silica gel for liquid chromatography.

EXPERIMENTAL

Four silica gel products from Merck: Kieselgel 60, particle size < 0.063 mm (batch No. 9034314), 0.040-0.063 mm (batch No.: 2665636), 0.063-0.100 mm (batch No.: 2739041) and Kieselgel 60 reinst 0.063-0.200 mm (batch No.: 2632096) were investigated. In an additional study, a silica gel product

from Woelm Pharma: Silica Woelm 63-200, particle size 0.063-0.200 mm (batch No.: 2230) was analyzed. The silica gel was obtained from the supplier in Sweden and the containers were opened directly before analysis. The silica gel (30.0 g) was wet packed (<0.063 mm) or dry packed (0.040-0.063 mm, 0.063-0.100 mm, 0.063-0.200 mm) in a glass column. Each silica gel was analyzed in triplicate. The silica gel was treated with methylene chloride (p.a. Merck) and the first 100 ml eluting from the column was collected. 2,2',5,6'-Tetrachlorobiphenyl (IUPAC No.: 53), used as the internal standard, was added to give a final concentration of 20 pg/ $\mu$ l. The methylene chloride was evaporated (Rotavapor) and the residue was redissolved in n-hexane (5 ml, all glass distilled). The hexane solutions were treated with concentrated sulphuric acid (Merck, dens. 1.84), in order to determine persistent contaminants (9). The hexane was subsequently dried on a sodium sulphate (Merck) column and the solvent was evaporated. The samples were dissolved in iso-octane (3.0 ml) prior to the gas chromatographic (GC) analysis. All solvents and chemicals were tested for impurities in a blank procedure.

The analyses were carried out on a Hewlett-Packard 5880 gas chromatograph fitted with a  $^{63}\text{Ni}$  electron capture detector and a automatic liquid sampler. A BP-1 (SGE) fused silica capillary column (25 m x 0.22 mm ID) was used. The helium carrier gas flow was 0.3 ml/min. The column temperature was programmed 90°C (7 min), 30°C/min to 180°C (2 min.), 2°C/min to 260°C (2 min.), the detector temperature was 320°C and the injector temperature was 270°C. Argon:methane (90:10) was used as the detector make up gas (30 ml/min.). The quantitative analyses were carried out in the splitless mode (valve opened after 6 min.) with a reference mixture of 12 polychlorinated biphenyls and by comparison to the technical PCB-product that best resembled the sample, as described elsewhere (9,10).

Gas chromatography - mass spectrometry (GC-MS) was performed by negative chemical ionization on a Finnigan 4000 mass spectrometer with a Finnigan IncoS 2400 data system. The gas chromatograph was equipped with a BP-1 (SGE) fused silica capillary column (25 m x 0.22 mm ID). The flow rate of the helium carrier gas was 0.5 ml/min. The column was programmed 70°C (2 min.), 20°C/min., 300°C (20 min.). The ion source temperature was 200°C, the reactant gas was methane and the ionization energy was 70 eV.

## RESULTS AND DISCUSSION

Gas chromatograms of the persistent contaminants obtained from the silica gel < 0.063 mm and 0.063-0.100 mm are shown in Figure 1, in addition to a chromatogram of a highly chlorinated commercial PCB mixture, Aroclor 1260. Even though differences can be seen between the chromatograms of the silica gel samples and of Aroclor 1260, the general patterns are quite similar. The eluates from silica gel 0.040-0.063 mm and 0.063-0.200 mm gave chromatograms that were similar in all important details to those shown in Figure 1. In order to further characterize the contaminants, GC-MS was performed and mass chromatograms corresponding to PCB containing 5-9 chlorine atoms were determined as shown in Figure 2. No PCB was detected in the blank samples.

Evidently, PCB is present in the silica gel batches tested. The contents of PCB in the different silica gel products from Merck are given in Table 1. The results were determined by the use of two different reference mixtures



as described under experimental. The major constituents of the silica gel PCB contaminants were tentatively identified (cf. IUPAC numbers in Figure 1) and also found to correspond to the major homologues and isomers of the technical PCBs, Aroclor 1254 and 1260. The silica gel from Woelm Pharma (0.063-0.200 mm) was not included in the initial study but was later verified to contain PCB at a level of 10-20 ng/g silica gel. For comparison, the PCB level in silica from Mallinckrodt (Silicar) was reported to be 31 ng/g (lot TEE) and 163 ng/g (lot PXR) (6).

Silica gel is commonly obtained by the addition of mineral acid to sodium silicate and the product formed is thereafter ground, washed, dried and activated (11). If PCB is present in the starting material for this process, the levels of PCB in the different silica gel preparations should be at approximately the same level. Since this is not the case and the higher concentrations of PCB in the present study are determined in gels with smaller particle sizes (Table 1), it is reasonable to assume that the contamination takes place either during the latter part of the process or by the adsorption of ambient PCB. Silica gel columns have been used to sample airborne organochlorines (12,13). Furthermore, indoor air PCB levels are known to be at least 10 times higher than outdoor levels (14).

The present results stress the fact that PCB might be a contaminant of commercial silica gel in general, and as a precautionary measure, the gels should be purified before use in trace analysis, e.g., by methylene chloride as described above. The amount of silica gel used for separations by liquid chromatography is at least ten times that of the sample weight. This means that the addition of contaminants from the gel must be considered but should not play a serious role if proper analytical techniques are used. However, since clean silica gel is especially important for trace analysis it would also be important to determine at what stage the PCB contamination occurs during manufacture.

#### ACKNOWLEDGEMENT

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Table 1. Average concentrations and standard deviations (SD) of PCB in silica gel (Merck) for liquid chromatography analyzed in triplicate. The quantitative analyses were performed with A: a standard of twelve polychlorinated biphenyls <sup>1)</sup> and B: Aroclor 1254 or 1260 as a standard.

Silica gel particle size (mm)	Concentrations (ng/g)			
	A	±SD	B	±SD
0.063 <sup>2)</sup>	37	6.2	40	1.3
0.040-0.063 <sup>3)</sup>	17	1.1	18	0.6
0.063-0.100 <sup>3)</sup>	16	2.2	18	1.2
0.063-0.200 <sup>3)</sup>	9	2.3	13	3.7

<sup>1)</sup> PCB numbers according to IUPAC (15): 44, 52, 95, 101, 110, 118, 128, 138, 153, 170, 180 and 194.

<sup>2)</sup> Aroclor 1260 used as a standard in method B

<sup>3)</sup> Aroclor 1254 used as a standard in method B.

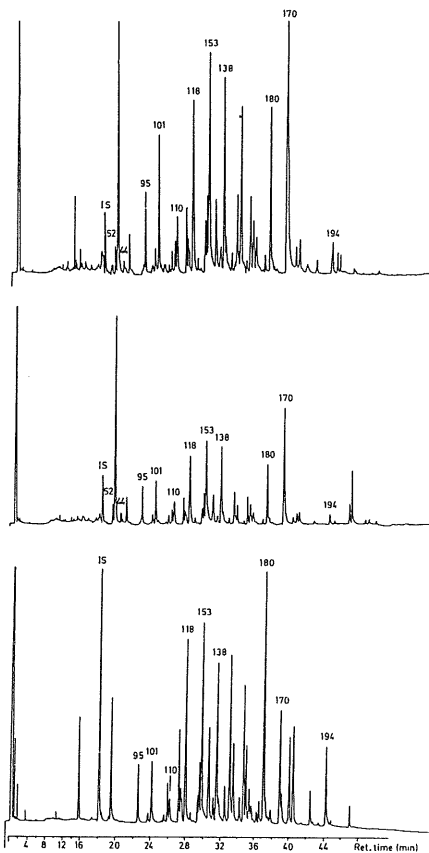


Figure 1. Gas chromatograms of the persistent contaminants obtained from silica gel (Kieselgel 60)  $< 0.063\text{ mm}$  (upper),  $0.063\text{--}0.100\text{ mm}$  (middle) and of Aroclor 1260 (bottom). PCB numbers according to IUPAC (15) are superimposed on the chromatograms. The internal standard (IS) was 2,2',5,6'-tetrachlorobiphenyl.

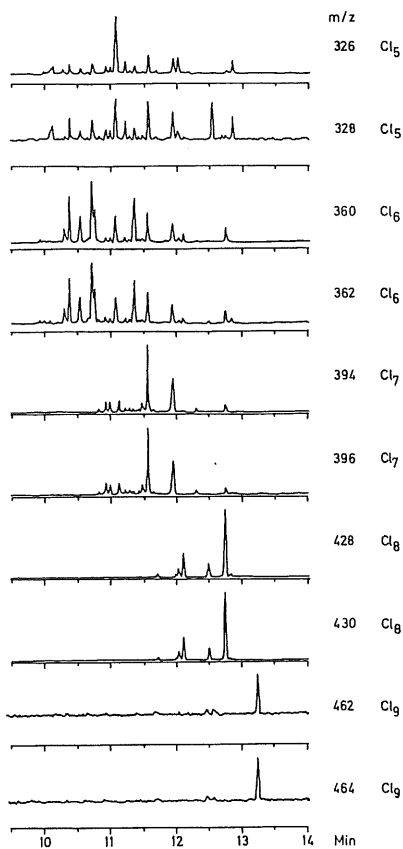


Figure 2. Mass chromatogram with  $M^+$  and  $(M+2)^+$  of the persistent contaminants obtained from silica gel (Kieselgel 60) < 0.063 mm. The number of chlorine atoms substituted on the biphenyl is indicated.

ANNEX 4

THE EVALUATION OF AN ANALYTICAL METHOD FOR POLYCHLORINATED TERPENES (PCC)  
IN BIOLOGICAL SAMPLES USING AN INTERNAL STANDARD

by

Ulla Wideqvist, Bo Jansson, Lars Reutergårdh and Göran Sundström

National Swedish Environment Protection Board  
Special Analytical Laboratory  
Wallenberg Laboratory  
S-106 91 STOCKHOLM, Sweden

ABSTRACT

The quantitative analysis of PCC (Toxaphene) residues in biological samples using gas chromatography with electron capture detection has been evaluated. Dieldrin 603, a chloroalicyclic compound is used as internal standard and modifications of the injection system for proper evaporation of this high-boiling compound is described. In the clean-up procedure PCB (and 1-3% of the PCC) are removed by adsorption chromatography. Chlordane components and DDT compounds remaining in the PCC fraction constitute 5-10% and 13-16%, respectively, of the peak area in the chromatograms of the samples investigated. The quantitative results are influenced by the number of PCC-peaks chosen for the calculations and have to be specified together with the PCC-levels reported. The recoveries of PCC from spiked samples (20 µg PCC per gram crude fat above "natural" level) are 61-98%, the lower figures obtained with samples containing low levels of PCC-residues. The practical limit of detection is about 10 ng PCC per g extracted fat.

INTRODUCTION

The polychlorinated terpenes (polychlorinated camphenes, PCC or camphechlor) are known under several trade names such as Toxaphene, Strobane, Melipax and Phenacide. They are used as pesticides and seem to have replaced DDT in many countries. The total world consumption of PCC products today is unknown but according to FAO statistics (1) about 13 000 tonnes were used in 1980 in the USA alone. Other large consumers are Egypt, Mexico, Korea, Pakistan, Czechoslovakia, Hungary, and Poland.

Several reviews and literature compilations on the chemistry and biological effects of PCC have been published (2-8). Due to known or suspected risks to the environment and humans, the use of PCC is presently under discussion and the indications that the PCC are carcinogens have thereby attracted special attention (9). In the USA, the use of PCC has therefore recently been restricted (10).

The presence of PCC in the environment in, or close to, the application areas has been studied for a long time (see for example citations in reference 3).

Bidleman and Olney (11) detected PCC in the air over the Atlantic Ocean after the application season in the USA. Aerial transport mechanisms might thus be responsible for the widespread occurrence of PCC. In Sweden PCC residues have been found in marine, as well as in freshwater fish although this type of pesticide has not been used in amounts large enough to account for their presence at the levels found (12). Analyses of atmospheric fall-out have later shown that aerial transport most likely is responsible for the presence of PCC in the Swedish environment (13). PCC have also been identified in organisms from areas such as the Antarctic Ocean, Alpien lakes and the Peruvian coast (14,15) and the Canadian east coast (16).

The need for accurate analytical methods for monitoring studies of the environmental distribution of PCC is thus acute. A review of the methods described has recently been made by Ribick and co-workers (17). One of the major problems in the analytical procedures is the separation of PCC from other globally occurring halogenated substances, such as polychlorinated biphenyls (PCB) present in the samples. This is normally performed by liquid chromatography using an adsorbent. Both PCB and PCC are complex compound mixtures and the separation of these mixtures is difficult. Thus, the activity of adsorbents used is critical as has been shown by Tai and co-workers (18). Another difficulty is the evaluation of the gas chromatograms used in the final quantitative calculations. The choice of chromatographic peaks to be included in the calculations depends upon the resolution, the presence of interfering substances and the degree of automation of the procedure.

In the present paper we describe an evaluation of the method used today in our laboratory for the analysis of PCC residues in biological samples using capillary gas chromatography with electron capture detection (ECD). An internal standard has been included in the procedure in order to control the many individual steps involved - extraction, fractionation, chemical treatment and quantification.

## EXPERIMENTAL

### Material

The organic solvents used were acetone, *n*-hexane and diethyl ether, all tested by gas chromatography (ECD) for interferences and re-distilled when necessary. The concentrated sulphuric acid (89%, BDH Chemicals Ltd.) and potassium dichromate (E. Merck) used in the clean-up procedure were of analytical quality.

Toxaphene (EPA standard, code 6740, 67-69% chlorine) and Chlordane (technical, Fluka AG) were used as analytical standards, and Dechlorane 603 (Hooker Chemical Corp., for structure see Figure 1) as internal standard (30 pg/μl hexane).

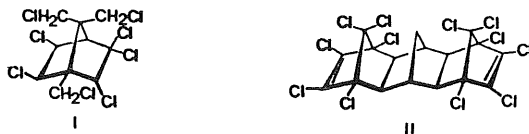


Figure 1. Chemical structure of a major Toxaphene component (I) and Dechlorane 603 (II, schematically) used as internal standard in the analysis of polychlorinated terpene residues.

For column chromatography deactivated silica gel (3% water on Kieselgel 60, 0.040 - 0.063 mm, E. Merck) was used.

#### Clean up

All tissue samples were extracted according to Jensen *et al.* (19). An aliquot of the extracted fat was dissolved in the internal standard solution (100 mg fat/ml solution), and further treated by the procedure described by Jansson *et al.* (12). Blank procedures were continuously run to ensure the purity of all materials used.

#### Gas chromatography

All gas chromatographic analyses were performed on a Hewlett-Packard HP 5840 instrument equipped with a 7671A autosampler and an electron capture detector ( $^{63}\text{Ni}$ -ECD). The column used was a 25 m fused silica column with SP 2100 as stationary phase (Hewlett-Packard). All injections were made in splitless mode at 50°C. For conditions see Figure 2.

### RESULTS AND DISCUSSION

#### Internal standard

To ensure the accuracy of the analyses of the complex PCC mixtures an internal standard should be used. Our internal standard was selected from the following

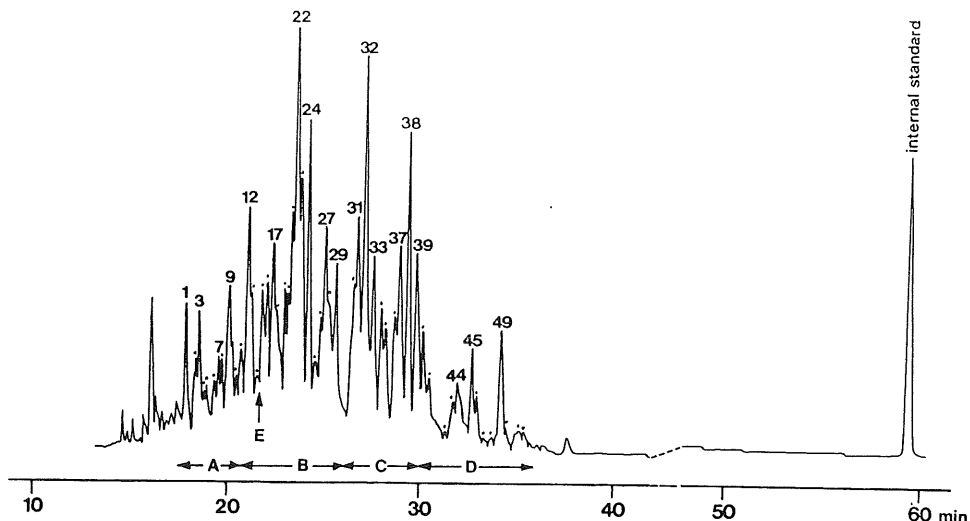


Figure 2. Capillary gas chromatogram of Toxaphene standard (6 ng) with added internal standard (200 pg).  
Column: fused silica with SP 2100 stationary phase (Hewlett-Packard). Carrier gas: 0.3 ml 10% methane in argon/min.  
Column temperature: 50°C (5 min.), 30°C/min. to 190°C, 1°C/min. to 220°C, 10°C/min. to 260°C (20 min.).

criteria:

- the compound should not interfere with the PCC components in the gas chromatograms;
- it should elute in the PCC fraction in the chromatographic clean up procedure;
- it should resist sulphuric acid treatment and oxidation with the dichromate-sulphuric acid reagent;
- it should be detectable by ECD;
- the compound should preferably not have use patterns that makes it probable to be present in the environment.

Dechlorane 603, Figure 1, (20) fulfilled the criteria given above with the possible exception of the last one. Two disadvantages of Dechlorane are due to its high boiling point: the low reproducibility of the splitless injection, which is discussed below, and the prolonged time of analysis. Still, this compound was considered for further testing and proven useful for the purposes intended.

#### Quantification

The quantifications were based on the numbered peaks in the regions A-D indicated in the gas chromatogram of the Toxaphene standard given in Figure 2. In the quantification of PCC in biological samples the components co-eluting with chlordane- and DDT-related compounds (peaks 6, 9, 10, 11 and 14, 23, 24, 32 respectively, Figure 2) were excluded. The sum of the corresponding peak areas in standard and samples were calculated and correlated to the area of the internal standard peak.

From the peak pattern of Toxaphene it was obvious that the characteristics of the capillary column used changed during its lifetime. A new column showed, during a couple of months, a gradual change in relative peak areas when comparing an early cluster of peaks (A, Figure 2) with a late one (D). As the column was ageing, the relative area of the early peaks decreased, from 25% to 11% and the latter increased, from 3% to 12% of the total area with the largest changes occurring during the first two weeks. A new column thus seems to contain active sites which decompose late eluting components of Toxaphene.

A new 25 m fused silica column resolves about 60 PCC peaks in the regions A-D in the gas chromatogram (Figure 2). To maintain a good resolution, experiments showed that the column should be replaced after 300-400 runs of PCC-containing samples.

The fractionation of samples on silica gel columns does not separate the chlordane and the DDT compounds from the PCC. To investigate to what extent these compounds interfere in the PCC determination a mixture of them and PCC was chromatographed. The ratio between PCC-levels and the levels of the interfering substances injected were based on their levels in Baltic herring. The Toxaphene peak area covered by the interferences was calculated and is summarized in Table 1.



Table 1. *Interference from chlordane- and DDT-components in the analysis of chloroterpenes (Toxaphene)*

Compound	Amount injected (ng)	Per cent covered of total area of Toxaphene (6 ng injected)
Chlordane (techn.)	1	5* - 10
p,p'-DDE	1	13** - 16
p,p'-DDD	2	
p,p'-DDT	0.5	

\* lowest value obtained on old columns

\*\* lowest value obtained on new columns

As can be seen from the table reasonably accurate quantifications of the Toxaphene standard can be achieved in the presence of chlordane and DDT-components at the levels found, if the gas chromatographic resolution is sufficient. Thus, it seems to be possible to quantify the PCC residues in environmental samples without removal of chlordane and DDT compounds from the sample.

To study how the selection of peaks influence the quantitative result, the PCC levels were calculated on the basis of different clusters of peaks in one sample of herring (*Clupea harengus*) and one of guillemot (*Uria aalge*). The clusters chosen and the resulting analytical data are presented in Figures 2-4 and Table 2.

Table 2. *Calculated PCC levels in biological samples. Comparisons of results obtained by using different clusters in the chromatograms for quantification.*

Region of the chromatogram used*	PCC-level, µg/g fat	
	herring (oil)	guillemot (egg homogenate)
A + B	9.0	17
C + D	6.7	31
B + C	8.8	20
A + B + C + D	8.3	21
Eleven peaks from all regions	10	25

\*see Figure 2

It can be concluded that it is important to include as many peaks as possible in the calculations to avoid misinterpretations due to differences in individual peak areas and to allow comparison between different biological samples.

#### Reproducibility of the splitless injection

The high boiling point of the internal standard Dechlorane initially caused problems due to the construction of the injection port. During splitless injection in the silanized empty glass liner, it was discovered that Dechlorane was not quantitatively recovered. It was assumed that the internal standard did not entirely vaporise and therefore was not transferred into the column.

The conditions were improved when an inert material was inserted into the liner, thereby giving a more effective vaporization. Three materials were tested: acid-treated and silanized glass-wool (one commercial brand and one treated in the laboratory), untreated quartz-wool and acid-treated silanized glass beads (0.4 mm diam.). To test the materials, a solution of hexachlorobenzene (HCB) and Dechlorane was injected splitless using the autosampler. HCB was used as internal standard under the assumption that its (relatively) low boiling point would result in a complete vaporization before reaching the column even in an empty liner. The ratio of the peak areas of Dechlorane to HCB was calculated under the assumption that an increased ratio implies a better vaporization of Dechlorane. The two types of glass-wool and the quartz-wool gave similar results while Dechlorane was discriminated in the empty liner and in the one filled with glass beads. In the subsequent work the liner filled with the commercial glass-wool was used.

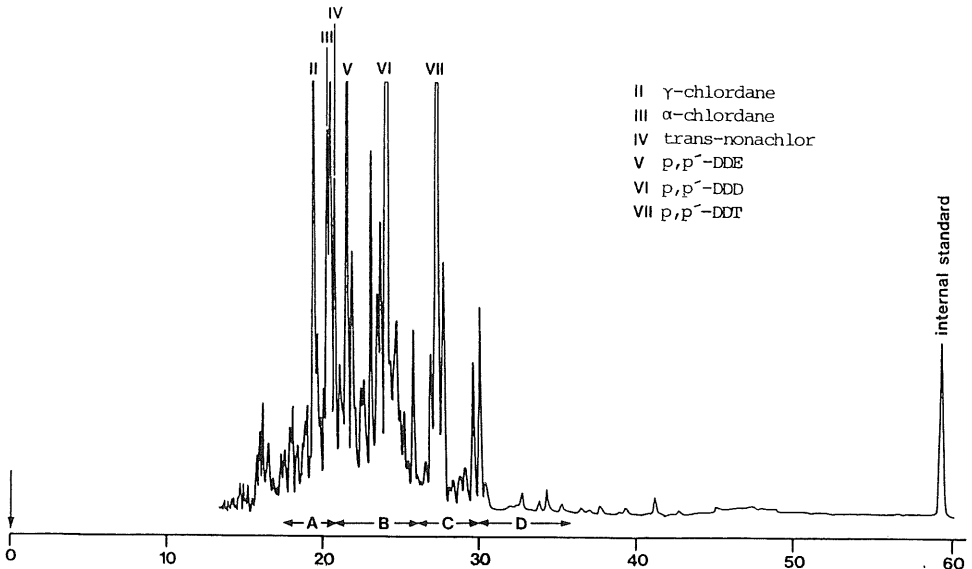


Figure 3. Capillary gas chromatogram of silica gel fraction 2 from Baltic herring oil (0.5 g). 3  $\mu$ l injected of a final volume of 2 ml containing 100 ng internal standard.

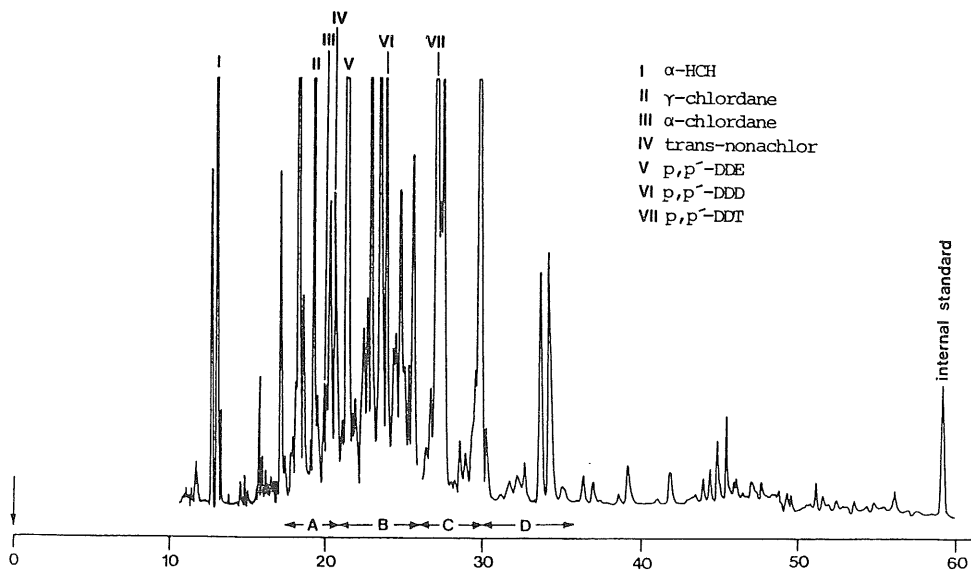


Figure 4. Capillary gas chromatogram of silica gel fraction 2 of fat extracted from guillemot eggs (0.5 g). 3  $\mu$ l injected of a final hexane volume of 2 ml containing 130 ng internal standard.

The difference between an empty glass liner and one filled with glass-wool was also demonstrated by analyzing twelve samples of herring oil prepared in accordance with the method described. The samples were injected once in each type of liner. The amount of PCC was calculated and correlated to the area of the internal standard. The mean value and standard deviation for the twelve samples were  $8.9 \pm 2$  mg/kg fat when injected in the empty liner and  $7.7 \pm 0.5$  mg/kg when injected in the glass-wool filled liner, with a coefficient of variation of 21% and 7%, respectively.

To further investigate the reproducibility of the injection technique, 15 consecutive injections were made of a solution containing 2 ng of Toxaphene and 100 pg of Dechlorane per  $\mu$ l. The test was repeated two days later. Variations in the absolute areas were calculated for the sum of Toxaphene peaks and the Dechlorane peak and also the variation of the relative peak areas of these compounds, Table 3.

Table 3. *Reproducibility of splitless injections of Toxaphene and Dechlorane 603*

Day No.	Injection No.	Coefficients of variation (%) of absolute and relative areas		
		Toxaphene	Dechlorane	Toxaphene/Dechlorane
1	1 - 15	4.6	2.0	4.1
3	16 - 30	4.3	4.5	1.7
	1 - 30	11	7.8	4.5

Thus, the reproducibility is quite acceptable although the variation of the absolute areas increases when injections are made with time intervals longer than one day. This shows the importance of always running standard solutions together with samples.

Linearity and detection limits

Linear dynamic range and minimum detectable quantity of toxaphene and the internal standard Dechlorane 603 were determined for the electron capture detector used. Five different concentrations (0.1 - 5 ng/μl) of a Toxaphene solution were injected (splitless) as duplicates at two occasions. Dechlorane (100 pg/μl) was used as an internal standard and each concentration quantified against the intermediate Toxaphene concentration of 1 ng/μl. Both peak area and manual peak height measurements were made of the peaks in regions A - D of the chromatograms (Figure 2 and Table 4).

Table 4. *Linearity of Toxaphene detection in an electron-capture detector*

Real conc. (ng/μl)	Calculated concentration (ng/μl)	
	peak area	peak height
0.10	—*	0.069
0.51	0.62	0.49
1.0	1.0	1.0 ("standard")
2.0	2.9	2.3
5.1	8.3	6.2

\*improper integration (see text)

Calculating the mean and distribution for the ratio between calculated and real concentration as a function of real concentration gave coefficients of variation of 24% for peak area and 14% for peak height. Considering the limited concentration range, the difference between real and calculated concentrations is not satisfactory. For quantitative work it is therefore necessary to run standards of approximately the same concentration as expected in the samples analyzed.

When low PCC levels ( $< 1.5 \text{ ng}/\mu\text{l}$ ) were analyzed, a negative peak occurred in the gas chromatograms at position E, see Figure 2. No explanation was found for this phenomenon, but as a consequence components eluting in the vicinity of E and thereafter were miscalculated due to improper baseline setting in integration. In later studies with another gas chromatograph (HP 5880) no such negative peak appeared and the detection limit was considerably lowered to about 5 pg of Toxaphene in a standard solution (21).

The linearity of Dechlorane 603 was examined in the same manner using HCB ( $10 \text{ pg}/\mu\text{l}$ ) as internal standard (Table 5). In this case the coefficient of variation was 14% for peak area and 10% for peak height calculations.

Table 5. *Linearity of Dechlorane 603 detection in an electron-capture detector*

Real conc. ( $\text{pg}/\mu\text{l}$ )	Calculated concentration ( $\text{pg}/\mu\text{l}$ )	
	peak area	peak height
5.3	—*	4.6
11	—*	9.8
26	21	24
53	53	53 ("standard")
106	120	114
213	237	237

\*improper integration

#### Recovery of PCC in the clean up procedure

The recovery of PCC after acid treatment and fractionation on silica gel was studied on fat extracts from herring, guillemot and elk. Since the elk contains no detectable amount of PCC it was used as a "reference" fat. Samples of fat (0.5 g) from the three species were spiked with 10  $\mu\text{g}$  Toxaphene and 300 ng Dechlorane or 20  $\mu\text{g}$  Toxaphene and 600 ng Dechlorane, respectively. Duplicates of spiked and unspiked samples were analyzed together with standard solutions with the same amounts of Toxaphene and Dechlorane and two blanks containing 150 ng of Dechlorane.

Samples and standards were cleaned up as described - oxidation excluded - and analyzed. All calculations were based on an untreated Toxaphene standard. The results, given in Table 6, show a recovery of more than 70% for most of the samples with the highest value for the guillemot. The recoveries of Dechlorane in fraction 2 from the blank runs were 97% and 94%, based on the injected volume.

To investigate the effect of oxidation on the recovery, three Toxaphene standard solutions were analyzed after different treatments. One was untreated, the second oxidized and the third was fractionated on silica gel and fraction 2 oxidized and analyzed. The last two samples were quantified against the first untreated one. The recoveries were 83% for the oxidized standard and 89% for the fractionated and oxidized standard.

Alterations in the chromatographic pattern as a result of fractionation and oxidation were also investigated. The chromatograms of the three standard solutions and of one fractionated unoxidized standard were compared. The areas of the peak clusters A - D (Figure 2) in the chromatograms were calculated and related to the area of the sum of all peaks. The four chromatograms exhibited only small differences in relative peak area with a maximum of 4% for cluster B comparing an untreated standard and an oxidized one. Overall, Toxaphene components seem to remain unchanged after both fractionation and oxidation.

Table 6. Recovery of Toxaphene from spiked fat samples processed through the complete analytical procedure except extraction

Sample type	Background level µg/g fat	Per cent recovery after spiking of 0.5 g samples with Toxaphene	
		10 µg	20 µg
Standard		85 2 <sup>a</sup>	111 2 <sup>a</sup>
		81 1 <sup>a</sup>	81 3 <sup>a</sup>
Elk (suet) ( <i>Alces alces</i> )	0.2	67	78
		76	67
Herring (oil) ( <i>Clupea harengus</i> )	8.2	61	80
		87	90
Guillemot (egg homogenate) ( <i>Uria aalge</i> )	21	98	89
		95	88

<sup>a</sup>Per cent Toxaphene in fraction 1, calculation based on injection volumes

Fraction 2 of five of the twelve herring oils mentioned above were also oxidized and then analyzed for PCC. The mean value and standard deviation were calculated to  $7.7 \pm 0.8$  µg/g fat. If the peaks covered by DDE, DDD and DDT in the chromatogram of unoxidized samples are included in the calculation the result is  $8.4 \pm 0.9$  mg/kg fat. This should be compared with the calculated amount for the same five samples before oxidation which is  $7.2 \pm 0.3$  mg/kg fat. The quantification thus seems to be more affected by the number of peaks included in the calculation than by the oxidation process.

#### CONCLUSIONS

The analyses of xenobiotica in environmental samples demand methods with good sensitivity and selectivity. Polychlorinated hydrocarbons can be detected with good sensitivity by ECD as described in this work, but for multicomponent chemicals, such as PCC, gas chromatography with ECD has a limited selectivity. This can be overcome by special clean-up methods, as demonstrated in this work, or by the use of a more specific detection. Chemical ionization mass spectrometry with multiple ion detection techniques have been used for this purpose

using either positive (22) or negative ions (23). The mass spectrometer is, however, expensive, and the ECD method has to be used at least for monitoring purposes.

The method described here has from an intralaboratory perspective (and partly also interlaboratory) proven to be satisfactory and is presently being used for a survey of the presence of PCC in the Baltic environment (24). The aim so far has been to obtain values of the total concentration of PCC in a sample. In the future we will probably try to use more of the information available in the gas chromatograms. High resolution columns and, as recently demonstrated (25), pattern recognition techniques will most likely make this possible.

#### ACKNOWLEDGEMENT

This work has been performed in close cooperation with Östen Andersson, Gun Blomkvist and Karl-Erik Linder, Swedish National Food Administration, whose contributions are gratefully acknowledged. The biological samples were generously provided by Mats Olsson, Swedish Museum of Natural History. We are indebted to Hooker Chemicals and Plastics Corp through their Research Center, for a generous gift of Dechlorane 603, and the US EPA, Health Effects Research Program for a number of other reference compounds.

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ANNEX 5

ACTION LIST  
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The following intersessional activities have been agreed by the Working Group:

1. The Chairman of MCWG should provide a clear summary of the present status of PCB analysis to the June 1984 meeting of ACMP, as well as summaries concerning any other relevant items of advice on the ICES work programme from the Oslo and Paris Commissions or advice to other groups, as necessary. (Paragraph 4.4.2)
2. The Environment Officer should send information on relevant sea water reference standards available from the Canadian National Research Council to the Secretariat of the Oslo and Paris Commissions for transmission to JMP laboratories. (Paragraph 6.1.1.3)
3. Dr. H. Windom and Dr. G. Topping should prepare a review paper on the atmospheric deposition of contaminants to the North Atlantic Ocean and appropriate methods for measuring atmospheric deposition to the sea, for presentation at the 1985 MCWG meeting. (Paragraph 6B.6.2)
4. All members should review the Preliminary Draft Interim Reporting Format For Contaminants in Sea Water and send their comments to the ICES Environment Officer by 31 May 1984. (Paragraph 6B.6.4)
5. Members of the Sub-Group on Organic Chemistry are requested to circulate papers from the literature on the collection and analysis of particulate matter for trace organic compounds prior to next year's meeting so that an informed discussion of this subject can take place at that meeting. (Paragraph 6C.2.7)
5. Dr. Kerkhoff should keep members of the Sub-Group on Organic Chemistry and the ICES Secretariat informed concerning developments in the work on PCB analysis in the EEC ECR. (Paragraph 6C.3.4)
7. Members who have received samples of CBs from Dr. Reutergårdh for participation in an interim study are requested to analyse these samples or return them to Dr. Reutergårdh as soon as possible, so that this study may be completed. (Paragraph 6C.3.4)
8. Dr. Kerkhoff has agreed to supply a list of the most useful congeners for analysis of PCBs. (Paragraph 6C.3.6)
9. Dr. Ehrhardt has agreed to prepare an information paper on the analysis and occurrence of phenols in the marine environment for the 1985 MCWG meeting. (Paragraph 6C.4.2)
10. Dr. Law has agreed to prepare an information paper on the analysis and occurrence of phthalate plasticizers in the marine environment for the 1985 MCWG meeting. (Paragraph 6C.4.2)

ANNEX 5 (cont'd)

11. The Chairman of MCWG and the Chairman of WGMS (Dr. H. Windom) have agreed to approach several scientists to prepare papers on the determination of organic and inorganic constituents in suspended particulate matter, for consideration at the 1985 MCWG meeting. (Paragraph 6E.3) In addition, all members are requested to provide information on this topic for the next MCWG meeting. (Paragraph 6E.6)
  12. The Chairman has agreed to explore ways in which ICES could support the alkalinity/major ion intercalibrations planned by IOS in connection with IAPSO and GESAMP activities and to try to ensure the involvement of ICES laboratories in these intercalibration activities. (Paragraph 6E.9)
  13. The Chairman has offered to write to the Chairman of the Oceanic Hydrography Working Group to discuss the most fruitful way of carrying out a review of the use of tracers in oceanographic studies. (Paragraph 14.4)
  14. All members who wish to report on the results of relevant research activities in their laboratories or countries should prepare a short written statement, giving references and contact persons and send this to the ICES Environment Officer for distribution prior to the next MCWG meeting. (Paragraph 5.1)
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ANNEX 6

RECOMMENDATIONS

Recommendation 1

The Marine Chemistry Working Group recommends that the reports on the results of the Fifth Round Intercalibration on Trace Metals in Sea Water, comprising the administrative report (C.M.1983/E:28), the report on Section 1: Comparison of filtration procedures (C.M.1983/E:18), the report on Section 3: intercalibration of analysis of various trace metals (C.M.1983/E:24), and the report on the results of Section 4: intercalibration of analyses of mercury, should be published in a volume of the Cooperative Research Report series; the report on the results of the Fifth Intercalibration on Organochlorines in Biological Tissues should be published in the same volume.

Recommendation 2:

The Marine Chemistry Working Group recommends that, recalling the approval in principle given in C.Res. 1982/4:8, a baseline survey of trace metals in coastal waters of the North Atlantic should be conducted in 1985/1986/1987 in association with the 1985 Baseline Study of Contaminants in Fish and Shellfish. Details of the plans are given in the 1984 MCWG report and in a paper to be presented to C.M.1984.

Recommendation 3:

- (a) The Marine Chemistry Working Group recommends that the next meeting of the Working Group be held for four days at ICES headquarters in February 1985 to consider
  - (i) the report of the results of the first phase of the Seventh Intercalibration Exercise on Trace Metals in Biota and progress in the second phase;
  - (ii) reports on the results of the Second Intercomparison on Analysis of Hydrocarbons in Biological Tissue and the Third Intercomparison on Analysis of Hydrocarbons in Biological Tissue;
  - (iii) the overview paper on the atmospheric deposition of contaminants to the North Atlantic Ocean; and
  - (iv) plans for and progress in the Baseline Studies.
- (b) In order to resolve the serious difficulties involved in analysis of trace organic compounds, especially PCBs, an ad hoc Sub-Group on Trace Organic Compounds (Convener: Dr. L. Reutergårdh) consisting of specialists in this field, should meet for 2 days at ICES headquarters, immediately prior to the MCWG meeting in 1985, with the following terms of reference:

ANNEX 6 (cont'd)

- (i) to distribute, in advance of the meeting, papers describing advances in analytical methodology for PCBs and other chlorinated hydrocarbons;
- (ii) to review and evaluate the results of the intercalibration for PCB congeners being coordinated by Dr. L. Reutergårdh;
- (iii) to review and evaluate results of methodological studies for chlorinated hydrocarbon analysis, in particular the study being conducted within the European Community;
- (iv) to recommend specific actions to improve the analysis of PCBs in environmental samples.

