

**REPORT OF THE
MARINE CHEMISTRY WORKING GROUP**

Reykjavik, Iceland

3-7 April 1995

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International Council for the Exploration of the Sea
Conseil International pour l'Exploration de la Mer

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1 OPENING OF THE MEETING

The Chairman, W. Cofino, opened the meeting of the Marine Chemistry Working Group (MCWG) at 09.45 hrs on 3 April 1995. Mr J. Jakobsson, Director of the Marine Research Institute and former President of ICES, welcomed the participants.

Working Group members introduced themselves and briefly described their main area of research interests and responsibilities in the field of marine chemistry.

The list of participants is given in Annex 1 of this report.

2 ADOPTION OF THE AGENDA

At the meeting, ICES provided additional agenda points arising from requests from the Helsinki Commission to ICES for 1995. These additional agenda points included:

- 1) to provide advice on analytical methods and choice of matrices for the measurement of the presence of organotin compounds in the marine environment;
- 2) to provide information concerning the transfer of halogenated organic compounds through the food chains;
- 3) to provide, to the extent possible, information on the concentrations that are not harmful to man or nature of the contaminants specified in the HELCOM list of priority heavy metals and persistent organic pollutants on the basis of existing scientific knowledge.

Points 1 and 3 were included in the agenda of the Trace Metal Subgroup, points 2 and 3 in the agenda of the Organic Subgroup. With these modifications, the MCWG adopted the agenda distributed by the Chairman. The agenda is provided in Annex 2.

Plenary presentations were scheduled for Wednesday, 5 April (J. Boon, J. Biscaya and J. Klungsøyr).

The work was done in three subgroups. The members and guests were grouped as follows:

Chemical Oceanography (Chairman: S. Carlberg): A. Aminot, D. Kirkwood, M. Krysell, K. Mäkelä, O. Vagn Olsen, S. Ólafsdóttir;

Trace Metals (Chairman: B. Pedersen): G. Audunsson, S. Berman, J.F. Chiffolleau, W. Cofino, G. Ducastel, J. Olafsson, J.R. Larsen;

Organic Subgroup (Chairman: D. Wells): A. Abarnou, T. Alsberg, J. de Boer, J.P. Boon, J. Biscaya, S. Einarsson, M. Cleemann, M. Haarich, J. Klungsøyr, R.J. Law,

M. Lebeuf, E. Nixon, T. Nunes, P. Roose, W. de Waal, E. Yngvadóttir.

3 REPORT OF THE 82ND ICES STATUTORY MEETING

The Chairman informed the participants that all of the tasks requested for consideration by the MCWG at the 1994 Statutory Meeting were incorporated in the draft agenda.

4 REPORTS ON RELATED ACTIVITIES

4.1 OSPARCOM

ICES has been requested by OSPARCOM to "review the Report on Background Concentrations of Natural Compounds and to supplement it with additional information, if available. This review also needed to consider comments made on this report in OSPAR working groups and in the NSTF". This item was put on the agenda of all three subgroups.

4.2 Intergovernmental Oceanographic Commission (IOC)

Owing to a mistake of the Chairman, no attempts had been made to have an IOC observer present at the meeting. It was agreed that the Chairman should take contact with the IOC in order to discuss their participation at next year's meeting.

4.3 ICES

4.3.1 Participation of scientists from developing countries in ICES working groups

The Council decided at the 1994 Annual Science Conference to allow participants from developing countries to attend ICES meetings (excluding those of Advisory Committees) in order to improve the contribution of ICES towards the training and education of developing country scientists. The accepted procedure is that access may be granted on a person-by-person basis for specified meetings, and that developing country scientists may be "introduced" under the auspices of ICES Delegates (i.e., Member Country delegations), or through accepted international organizations (e.g., FAO) requesting the Council to grant, via the General Secretary working in consultation with the President, access to individual developing country scientists. In line with current practice, staff of international organizations will not normally be able to participate in Study and Working Group meetings.

The MCWG noted these new guidelines with interest. The MCWG emphasized, however, that a single visit to a meeting is not very efficient and recommends that

structural, long-term relationships are built up to the extent possible.

4.3.2 Overviews on marine contaminants

OSPARCOM has dropped its formal request for overviews on marine contaminants, but is still very interested in receiving anything that ICES produces. HELCOM has retained its formal request for overviews. ACME has decided not to publish entire overviews, but would like them to be published elsewhere or, at a minimum, provided as paper to the Annual Science Conference. The OSPARCOM Environmental Assessment and Monitoring Committee was not very satisfied with this arrangement. The ICES Environment Secretary, Janet Pawlak, suggested as a compromise that the MCWG report contains an extended summary of the overview along the lines of those in the 1994 ACME report, including additional key information and several of the most important references. Only material that the MCWG as a whole agrees to should be contained in this extended summary.

4.3.3 ACME primary and secondary shadow members for MCWG

Stig Carlberg and Jon Ólaffson are also in 1995 the primary and secondary shadow members of ACME for the MCWG.

4.3.4 Chairmanship of ICES Working Groups under ACME

The ACME has agreed on the following rules governing the chairmanship of working and study groups reporting to ACME:

“the chairmanship of each ACME working or study group should be reviewed every three meetings and a decision should be made on the basis of situation at that time; the maximum period of chairmanship is two terms, i.e. six years; the ACME will accept nominations for new chairman from the working group, but will not be bound by them.”

The present Chairman was appointed in 1990, the first meeting being chaired in 1991. This implies that next year the maximum of two terms will be completed. In 1996 the nomination of a new MCWG chairman will be on the agenda.

4.4 EU-S, M&T QA pilot project "QUASIMEME"

The three strands of the QUASIMEME programme, viz, a) management; b) operation; and c) communication have continued to develop during 1994–1995. The QUASIMEME Steering Group met in Copenhagen in May 1994 to agree the future programme for the remaining two years of the present phase of the project.

Laboratory Testing and Learning Programme

Two further rounds of the scheme have been completed during January–May 1994 (Round 2) and June–November 1994 (Round 3).

Round 2 included:

- Nutrients in sea water (nitrite, nitrate, ammonia, phosphorus);
- Metals in sediment and biota (all for sediments, Cd, Cu, Hg, Pb, Zn, As, Ni and Cr);
- Chlorobiphenyls (CBs) and Organochlorine Pesticides (OCPs) in fish oil and sediments.

In addition sediment digests were prepared as part of the stepwise learning programme to improve the measurement of metals in sediment.

Round 3 repeated most of the exercises of Round 2 with different samples. Some samples were blind duplicates from Round 2. Total-N and total-P were added to the nutrients; As, Ni and Cr were requested as part of the whole suite of metals. Full tissue homogenates were used for the biota samples in place of the fish oil previously used.

The analysis for PAH was introduced into the scheme with two sets of standard solutions. Full assessment reports from both Rounds 2 and 3 are currently available from the QUASIMEME Project Office.

In general there would appear to be a gradual improvement in the analysis although many of the data sets are spoilt by mis-reporting. Transcription errors, errors in reporting the wrong units and factors of 2, 5, 10 and 1,000 were common amongst these data.

In the future rounds, the project will consolidate these schemes and continue the stepwise improvement programme for each of these matrix-determinand combinations, but especially for OCPs, PAH and lipid determinations. Additional determinands in the future will most likely include: non-*ortho* CBs, metal species e.g., TBT, methyl Hg and matrices e.g., metals and HCHs in sea water.

QUASIMEME Database

In response to the requests from participants, a database and data collector have been developed to enable laboratories to transfer the results of each exercise electronically. After the usual difficulties of developing and using a product at the same time it is now fully operational. It is faster and considerably less prone to errors in data transfer at least at the Project Office. The initial period of two-to-three man-months of data logging and checking has been transferred into two to three days of work.

Workshops

Two workshops were held during 1994–1995. A "Lipids Workshop" in Dublin in October 1994 discussed in detail the results of the initial intercomparison study and the recommendation regarding lipid measurement as a cofactor for organic trace analysis of biota. In overview it was restated that a total method (e.g., Bligh and Dyer) was preferred and that laboratories should improve and validate their total methods. Future exercises would be included in the next laboratory testing scheme.

A report of the Lipids Workshop is available from the QUASIMEME Project Office.

The second workshop was held in Hamburg in March 1995 to cover the problems relating to the determination of metals in sediment and biota. This was a three day workshop with hands-on studies organized by Dr Uwe Harms and Dr Britta Pedersen.

Details of the workshop will be available in May 1995 from the QUASIMEME Project Office.

Video

A second video has been produced as an initial step towards a series of training videos. This video covers the principles and practise of "Sample Handling of Biota" and gives advice on the problems which can arise from sampling to the laboratory analysis.

Copies are available for distribution from the QUASIMEME Project Office.

QUASIMEME Links

Links between QUASIMEME and the Baltic State laboratories have been taken a stage further by providing materials for the laboratory testing schemes. These links have been coordinated by Dr Uwe Harms. An assessment can be made on the data provided by these laboratories and all QUASIMEME reports and information have been made available.

Further links have also been established between QUASIMEME and the new emerging QA programme for the NAFTA countries (Mexico, USA and Canada). QUASIMEME was represented at the project development meeting in Queretero, Mexico in November 1994.

4.5 Quality Assurance in the Baltic Sea

In March 1995 the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the

Baltic Sea met in Tallinn. Draft guidelines were prepared for QA for trace metals and organic contaminants in biological tissues and nutrients in sea water. A list of persons responsible for QA/QC in the different Baltic laboratories participating in the Baltic Monitoring Programme and the Coastal Monitoring Programme has been compiled. These people will review the guidelines and finalization will be done by correspondence. A large meeting involving all reporting laboratories is envisaged within about two years.

S. Carlberg reported that HELCOM has adopted a quality assurance policy very similar to the one adopted by OSPAR a few years ago.

4.6 Other Activities

S. Berman discussed the developments regarding quality assurance in North America. The national laboratories of Mexico, the United States and Canada started about two years ago to cooperate intensively in the field of quality assurance. The programme expanded from physical measurements to chemical measurements. QA of environmental monitoring has been given a high priority, although no funds have been set aside for this topic. In November 1994, a workshop was organized to discuss the design of the QA programme. D. Wells was also invited to this workshop as the representative of the QUASIMEME project.

The MCWG noted with great interest the developments in North America. The MCWG emphasized the need to maintain and preferably expand the participation of North Americans in the group. MCWG can play an important role as a platform where developments in North America and Europe (North Sea, Atlantic, Baltic Sea) come together.

5 REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES

No reports were submitted under this heading.

6 REQUESTS FROM ACME AND REGULATORY AGENCIES

Requests from ACME were included in the agenda.

7 PLENARY PRESENTATIONS

Plenary presentations were given by J. Biscaya, J. Boon and J. Klungsøyr. These presentations were highly valued by all participants.

8 SUBGROUP ACTIVITIES AND DISCUSSIONS

8.1 Trace Metal Subgroup

8.1.1 Investigate the possibilities of organizing an ICES baseline study on contaminants in the near future

Existing and earlier international and national programmes were reviewed as background information for further discussion in the group.

Several international baseline studies in Europe have already been initiated and organized by the Oslo and Paris Commissions, and the Helsinki Commission in cooperation with ICES.

There has been a baseline study for trace metals in:

- biota in 1985 (both convention areas);
- a supplementary study for biota in 1990 (OSPARCOM area);
- sea water (1986–1987, OSPARCOM area);
- sediment (1990–1991, OSPARCOM area);
- sediment (1993, Helsinki Convention area, in progress).

Many difficulties have been encountered during the assessments of the different baseline studies (e.g., poor comparability of the results due to different or lacking QA procedures; different fish species were used; lack of a suitable common procedure for normalization of sediment data of different qualities from different areas).

In principle, the baseline studies should have been repeated every fifth year for the different matrices according to the earliest guidelines of OSPARCOM. These guidelines have successively been changed resulting in aperiodic baseline studies with time. For the Helsinki Convention area, each baseline study has been decided upon separately.

Various national baseline studies also exist, especially for biota. They are more like time trend studies, as they are repeated annually. This is the case for the large mussel watch programme in the U.S.A, where mussels from some 150 stations have been analysed annually for the last 9 years with only relatively few laboratories contracted to do the analyses. In Iceland, mussels from 8 stations are analysed annually. Also, France has a very large mussel watch programme.

The new monitoring programme of the OSPARCOM will presumably focus on time-trend studies for the trace metals as the most efficient strategy for following and understanding changes in the marine environment. The time-trend monitoring programme is and will be to a great extent based on the national programmes. These

time-trend programmes (or the annual baseline studies) have been coordinated to a large extent through the use of the same guidelines, participation in ICES intercomparisons and, now, the QUASIMEME programme.

Even though the group realizes that there is still a lack of information for some metals of interest including organometallics (e.g., the distribution of various organotin compounds, Ag (especially around point-sources)), the members felt that it would not be possible at present to organize an ICES baseline study outside the existing international monitoring programmes (OSPARCOM and HELCOM) especially considering the present economic restrictions at several potential participating institutes and laboratories. They also felt that the different national programmes are now somewhat coordinated through the participation of their countries in the international programmes although the choice of fish/shellfish species which are monitored in the different countries is not harmonized.

The group also stressed the importance of harmonizing as much as possible any new or revised national programme with international guidelines especially concerning the areas to be monitored, the choice of species, matrices and QA procedures. This would make the results from different countries more comparable in the future.

8.1.2 Review and report on the progress with respect to a project on estuarine behaviour of metals

A workshop on estuarine behaviour (or at least the distribution) of trace metals in estuaries was to have been held in Reykjavik the week before this meeting. Unfortunately, S. Westerlund who was in charge of the organization of the workshop has very recently changed his job and country of residence and was not able to convene the workshop.

The scientists concerned with this project are still interested including, we believe, those who were not able to be present at this meeting. It was decided to prepare once more for such a workshop intersessionally, to be coordinated by J.F. Chiffolleau. This study will be planned with a few colleagues using their own national data sets and also, if possible, the ICES estuarine data sets. The strategy will be to try testing the data sets with common programs, e.g., a commercially available program like the ECoS program from the Plymouth Marine Laboratory.

It is anticipated that the group will consist of J.F. Chiffolleau, a Dutch representative, P. Yeats and P. Balls. The workshop will be held in conjunction with the 1996 MCWG meeting.

8.1.3 Need for developing methods for the determination of speciated metals in sea water

There was no report presented to the group. It would appear, however, that there are growing pressures upon regulatory agencies to regulate effluents according to the "toxic species" (e.g., the free metal ion, Cu^{++} , Ag^{+}) rather than total metal concentrations. Also, it is very obvious that speciation measurements are required for metal transport and biological effect studies.

In the marine environment metal ion concentrations are usually only a small proportion of total metal concentrations. The group noted that there are still many problems in many laboratories regarding the analysis of sea water for total metal concentrations and that it would be premature to focus now on metal speciation other than for well-defined and environmentally important species such as organotins and organomercury.

8.1.4 Interlaboratory study on analyses of sea water for trace metals

Forty-eight laboratories replied to the questionnaire regarding this proposed interlaboratory study. Forty laboratories indicated a desire to participate. This was considered a sufficient degree of interest to warrant the planning of an exercise.

The question arose as to whether the exercise should be coordinated by ICES or by QUASIMEME. The major advantage of the latter would be the greater possibility of periodic studies rather than the irregular pattern of past MCWG studies. This would be a necessary condition for many laboratories to maintain their accreditation for this type of analysis. The group prefers the QUASIMEME alternative but is doubtful that this study can be inserted into the QUASIMEME agenda in the near future and is concerned about its continuation in general. A disadvantage of an ongoing periodic ICES exercise is the growing uncertainty regarding the ability of expert laboratories to volunteer personnel time and laboratory resources to this type of activity.

After some discussion it was determined that there were experienced ICES laboratories available and willing to cooperate in carrying out an initial exercise if operational funding could be obtained through participant subscription or funding from ICES. A possible scenario for the collection and processing of samples in 1996 for this exercise was discussed as well as a tentative timetable which could result in a report presented at the MCWG meeting in 1997. The decision was made to submit a proposal to the ICES Council calling for ICES sponsorship of this exercise.

However, it was felt that it would be preferable to be able to transfer responsibility for the future studies in this ongoing programme to QUASIMEME, if possible.

The exercise will be coordinated by Dr B. Pedersen (Denmark) with the cooperation of Dr J. Olafsson (Iceland), Dr J.F. Chiffolleau (France) and Dr S. Berman (Canada).

Dr Wells offered the use of the QUASIMEME facilities to support the exercise.

8.1.5 A comparison of the general performance of the NOAA and QUASIMEME interlaboratory studies for trace metals

A report was presented by Shier Berman which attempted to compare the proficiency of European laboratories participating in the QUASIMEME programme and North American laboratories in the NOAA quality assurance programme regarding the analyses of sediments and biological tissues for trace metals. This was done for each of the two sediments and biological tissues used in the second round of QUASIMEME compared with two sediments and biological tissues used in recent NOAA exercises.

NOAA and QUASIMEME use different methods of data evaluation. In order to compare results, the QUASIMEME data were recalculated in the same manner as NOAA data. The results for Cd, Hg, Zn, As, Cu, Pb, Cr and Ni were compared for the tissues and the same analytes plus Al for the sediments. This is the QUASIMEME list of analytes. The NOAA list is rather longer with 13 and 18 metals for the tissues and sediments, respectively. The annual NOAA exercises are now entering their ninth year.

The main problem in the comparison lies with the differences in the analyte concentrations of the samples used in the two studies.

The conclusion, based on these limited number of samples, is that there is no significant difference between the abilities of the two sets of laboratories to analyze the above list of analytes in sediments. The "NOAA laboratories" may be somewhat more proficient regarding the analysis of biological tissues for trace metals.

It was suggested that it would be interesting to arrange for the two studies to use identical samples for one of their exercises in the near future.

The report is attached as Annex 4.

8.1.6 Review the "Report on Background Concentrations of Natural Compounds" and supplement it with additional information, if available

The report on this topic has been incorporated in a report of the entire MCWG given in Section 9, below.

8.1.7 Relationship between trace metal concentrations and lipid contents in biological tissues

Jan Rene Larsen presented information on progress made within the Working Group on Statistical Aspects of Environmental Monitoring (WGSAM) which had met in March. WGSAM had focused its attention on metals in cod liver and examined data from Sweden and Norway. The liver was viewed as composed of three primary components: fat, water and lean tissue. The data demonstrated that the greatest variability was associated with changes in fat content and that water and lean tissue were usually in nearly constant proportions. With respect to copper, their data showed no clear association between this metal and any of the primary components. However, time trend data on Cd in cod from the Kattegat conform better to a proposed model when either expressed on a lean/dry weight basis or when adjusted for fat content and expressed on a dry or wet weight basis.

The second item discussed was the presentation by Gudjon Atli Audunsson: "The relationship between trace metal concentrations and lipid contents in cod liver". These Icelandic data from one laboratory demonstrated: i) a strong linear relationship between fat weight and dry weight, and ii) a good linear log-log relationship between liver size and the amount of liver fat. When expressed on a wet weight basis, fairly strong log-log relationships were apparent between Cd and Zn concentrations and the liver fat contents, but no such relationship could be seen for copper.

In the discussion which followed, it was apparent that the relationship between metals and lipids is not resolved. Issues mentioned included the metal burden of the whole fish and relations between metal concentrations in the muscle tissue and in the liver. It was recognized that the choice of liver as a matrix for monitoring metals had to some extent been based on an historic ease of measurement since higher concentrations in livers made the analyses more feasible for many laboratories a decade ago. It was also suggested that fish species showing smaller variations in liver fat content might be more suitable for monitoring purposes. The pros and cons of using fish livers for monitoring metals were discussed, but without conclusions other than noting that analysis of individual livers is still recommended and that the use of pooling based on liver size should be explored. It was agreed that in any revision of the monitoring guidelines, account should be taken of knowledge gathered over recent years.

There is a need for a better understanding of the chemical associations between various metals and liver lipid types and also of the chemical associations between metals and the lean tissue components. There appears to be a possibility for Nordic support of a Danish-

Norwegian-Icelandic study group which would address these associations.

8.1.8 Review the overviews on organotin and organomercury compounds

No review of organomercury was presented.

The subgroup therefore only reviewed an overview on butyltin compounds (Evers *et al.*, March 1995). The paper was provided by W. de Waal and was based on a summary of the Rijkswaterstaat report (RIKZ - 95.007 (ISBN90-369-0473-0)). The group found that the overview covered the most important aspects of the environmental chemistry and toxicity of tributyltin including a reference list with key references. The group has therefore only very few comments which are given below.

It was suggested that a paragraph should be added to the section "Occurrence in aquatic systems" that there are indications for the occurrence of tributyltin in the shipping lanes of the North Sea. This is important as it shows that it is also necessary to monitor butyltin compounds outside the usual point sources.

The overview should include a small paragraph concerning the analysis of butyltin compounds (methodology, detection limits, analytical problems).

In the section "Conclusions and recommendations", a recommendation should be made that future monitoring programmes should include, in addition to the analysis of tributyltin, also the analysis of the degradation products (dibutyltin and monobutyltin) and other organotin compounds such as triphenyltin.

8.1.9 Review "new" contaminants and determine where overviews would be warranted

Triphenyltin (TPT) was raised as a "new" contaminant by the subgroup. Through J.F. Chiffolleau, Pierre Michel of IFREMER, Nantes agreed to prepare a review on TPT for the next MCWG meeting.

The possibility of a review for organo-Hg, covering the most recent developments, will be investigated by Dr G. Ducastel, Belgium.

8.1.10 Any other business raised by the subgroup

The subgroup discussed the possibility for plenary presentations covering the "metal" area at the next MCWG meeting. Subjects suggested were;

- Results of the baseline survey of metals in Atlantic waters, a project supported by IOC/UNESCO;
- Behaviour of metals in estuarine areas.

It was decided that the subgroup chairman and Dr J.F. Chiffolleau should work on the subject intersessionally.

Dr Britta Pedersen, Denmark, was appointed as chairman to deal intersessionally with matters which may arise.

8.1.11 Advice to HELCOM concerning the request to ICES in 1995

In addition to the original agenda, the subgroup also dealt with two requests from HELCOM to ICES for 1995 for advice:

To provide advice on analytical methods and choice of matrices for the measurements of the presence of organotin compounds in the marine environment.

The subgroup recommended the following:

A preliminary survey of the existing concentrations of organotin compounds should be made before a new monitoring programme is started. For this purpose, sediment samples should be analysed. The highest concentrations in the marine environment are expected to be found in the sediments, as the organotin compounds are accumulated here and only very slowly degraded. Sediment samples from coastal areas including areas close to and in different types of marinas and also from an important shipping lane (e.g., a major shipping lane between Sweden and Finland) should be analysed. Also, existing samples from the 1993 sediment baseline study should be analysed, if possible; mussel tissue samples from the same areas could form a supplement to the sediment samples.

From the geographical survey, suitable sites for further trend monitoring should be chosen. It is recommended that a biological tissue sample (*Macoma balthica*) should be chosen as a matrix, as models have shown that the concentrations in mussel tissues reflect a recent exposure which will make it possible to follow a change in the load by measuring the concentrations in a biological tissue. The sediment concentration represents an integrated exposure.

It is important to find a good biological indicator for less saline areas for effect monitoring. Here more research is needed.

Only a few specialized laboratories should be used for the analysis of all samples, due to the rather difficult analysis.

To provide, to extend possible, information on the concentrations that are not harmful to man or nature of the contaminants specified in the HELCOM list of priority heavy metals and persistent organic pollutants on the basis of existing scientific knowledge.

The subgroup concluded that it was not really possible to provide or to extend this information within a short time frame. The subgroup could therefore only recommend a way to proceed to get the wanted information.

It was the opinion of the group that there already exists good compilations of scientific data on harmful effects of metals on the marine environment. These are, e.g.,

- a list compiled by the U.S. Environmental Protection Agency (U.S. EPA) (official name to be provided by Dr S. Berman);
- the report of the OSPARCOM Workshop on Assessment Criteria for Chemical Data of the Joint Monitoring Programme (JMP);
- a national report of the Netherlands called "Zeewaardig" ("Seaworthy").

Data from these reports (and others) are suggested to be further assessed and compiled by the ICES Working Group on Biological Effects of Contaminants for HELCOM.

8.2 Organic Subgroup

8.2.1 Organic parameters which can be monitored on a routine basis (OSPAR 1.1.)

A preliminary list of organic contaminants which can be monitored in biota and sediments on a routine basis was prepared during the MCWG meeting of 1994 (MCWG, Brest, 1994). This list has been updated, using the most recent information from several intercomparison exercises. The MCWG will update this list annually. Where information was available from intercomparison exercises, standard deviations and reproducibilities are given under the heading "laboratory capability" in Table 1. Only a few specialist laboratories are able to produce reliable data for a number of compounds at present. In addition to the compounds mentioned, polychlorinated naphthalenes, chlorinated paraffins, polybrominated diphenylethers, polybrominated biphenyls, polychlorinated terphenyls, tris(4-chlorophenyl)methanol, chlorophenols, tris(4-chlorophenyl)methane and volatile short-chain (C₁-C₃) alkanes can also be determined by some specialist laboratories. However, for these compounds there are neither intercomparison exercise data, nor are CRMs or certified standards available. Laboratories should be encouraged to measure such compounds since there is a lack of information on them, and also considering their relatively high production figures and bioaccumulative properties. The production of CRMs for such compounds is also recommended. The subgroup stressed that ACME and the Commissions should be aware that the production of CRMs, establishing acceptable QA/QC and conducting intercomparison

∞ Table 1. Organic contaminants that can be monitored in biota and sediments on a routine basis.

| Organic contaminant | Recent I/C data available ¹⁾ | QC material available | Laboratory capability ⁸ |
|--|--|-------------------------------------|--|
| 1. Chlorobiphenyls, CBs 101, 118, 138, 153, 180 | Yes (sediment, lean and fatty fish tissue, seal oil) ²⁾ | CRMs (SRMs) and certified standards | sediment: CBs 118, 138, 153 s _R ³⁾ 15%, R 50% seal oil: CBs 138, 153, 180 s _R 15%, R 50% fish oil: CBs 101, 118, 138, 153, 180 s _R 15%, R 50% lean fish: CBs 118, 138, 153, 180 s _R 50–70% R 200%–330% |
| 2. Non-ortho CBs 77, 126, 169 | Yes (fish oil) ⁴⁾ | No | Some specialist laboratories; s _R 20–50%, R 65–200% (fish oil) |
| 3. Organochlorine pesticides HCHs, DDT, DDD, DDE, HCB, dieldrin, trans-nonachlor | Yes (sediment, fish oil) ⁵⁾ | CRMs and certified standards | fish oil: s _R 15–30%, R 50–100% sediment: s _R 35–100%, R 130–800% |
| 4. PAHs | No | CRMs and certified standards | Unknown |
| 5. Chlorinated dioxins and furans | No | CRMs and certified standards | Some specialist laboratories |
| 6. CHBs (toxaphene) | Yes ⁶⁾ | No | Some specialist laboratories; s _R ca. 50%, R 200% (fish oil) |
| 7. Organotin (TBT, TPT) | No | CRM (TBT) | Some specialist laboratories |
| 8. Methyl mercury | No ⁷⁾ | No | Some specialist laboratories |

- 1) This column refers to work carried out with regard to marine environmental analyses
- 2) Refs: ICES Cooperative Research Reports on ICES/IOC/OSPARCOM CB intercomparison exercise; QUASIMEME reports on CB intercomparison exercises (1993–1995)
- 3) s_R standard error; R; reproducibility
- 4) Refs: Voogt, P. de et al. (1994). Anal. Chem 66, 1012–1016; Wells, D.E. Report on ICES intercomparison exercise on non-ortho CBs, MCWG 1994.
- 5) Ref: QUASIMEME reports on CB and OCP intercomparison exercises (1994–1995)
- 6) Ref: Andrews, P.A. (1994). Interlaboratory study on the analysis of toxaphene. Proc. 24th Intern. Symp. Environ. and Chem., May 16–19, Ottawa, Canada; a second study is under way.
- 7) Recently information from an intercomparison exercise in sediment came available in the EU (S,M&T). A CRM (sediment) is in preparation.
- 8) Where the between laboratory coefficient of variation exceeds 50% it is reasonable to conclude that there is insufficient agreement for the group of laboratories, as a whole, to undertake these measurements. A selection of more experienced laboratories would be recommended.

exercises for these compounds can take at least three years. Apart from the CBs mentioned in the list, several laboratories are able to analyze a number of different CBs, for which in some cases CRMs are also available. There is, however, no information on the comparability of data on these additional CBs from the different laboratories.

8.2.2 Review an assessment of methodology for the determination of lipids in biological tissues and consider the need for an intercomparison exercise for measurements of lipids in marine samples

First of all, the group was informed of the work concerning the determination of lipids that has been undertaken within the QUASIMEME project. The project includes an ongoing lipid intercomparison exercise which has already included a workshop. This resulted in a report which contains the results of the first step of the lipid intercomparison exercise, the outcome of the various discussions, copies of the posters presented and a summary of a questionnaire that was circulated to the participants beforehand. This report is available on request from the QUASIMEME Project Office. The results obtained in the intercomparison exercise compared well, especially for those laboratories using the Bligh and Dyer total lipid extraction method, considering that most laboratories were applying this method for the first time. This method was, as a result, recommended for the determination of total lipids and participants were asked, during the next step of the intercomparison exercise, to determine total lipids according to Bligh and Dyer alongside the determination of extractable lipids using their routine laboratory method. This intercomparison exercise will continue for the duration of the project, and should provide both an indication of the overall laboratory performance, and an assessment of the Bligh and Dyer method and the extractable lipid methods. However, the fact that the Bligh and Dyer method is considered to be the best available creates an additional problem, as it involves the use of chloroform, production of which could cease in the near future under the Montreal Protocol. A number of laboratories are therefore working on alternative methods that do not require the use of chlorinated solvents. It was suggested that this work should be co-ordinated, so that effort is not duplicated. Another suggestion was that the group should reconsider the applicability of lipid proportion as a normalizing factor for organic contaminant data. The lipid content of an organism is, for instance, dependent on its physiological state and may therefore influence the validity of lipids as a cofactor, for instance during fish spawning.

To conclude, three different topics can be defined, namely: the intercomparison of lipid determinations, the search for alternatives to the Bligh and Dyer method, and the importance of lipids as a co-factor. An intercomparison exercise is currently running under the

QUASIMEME project. The outcome of this exercise will be made available so there is no need to duplicate this effort.

Reconsidering the need of lipids as a co-factor, different topics may be discussed:

- Why use a normalizing factor? What is the function of lipids as a normalizing factor?
- Advantages and disadvantages of using lipids as a normalizing factor.
- Alternatives or additional co-factors to lipids as a normalizing factor.
- Advantages or disadvantages of using a selected class of lipids as a normalizing factor.

Four laboratories represented at this MCWG meeting¹ are currently working on alternatives for the Bligh and Dyer method:

- 1) Netherlands Institute for Sea Research, NIOZ, NL
- 2) National Institute for Coastal and Marine Management, RIKZ, NL
- 3) Fisheries Research Station, Belgium
- 4) Institute of Applied Environmental Research, Stockholm University, Sweden.

Representatives of these laboratories agreed that arrangements should be made by Wilfried de Waal to facilitate the transfer of information between the labs with a view to preventing unnecessary duplication of experiments. It was agreed that the individual labs will forward a short overview of their lipid research programme to the coordinator before the end of April 1995. The combined overview will be distributed thereafter and the participating labs will keep each other informed through the coordinator on a regular basis. An update on the progress of this work will be presented on behalf of the group of labs by the coordinator for the MCWG meeting in 1996.

Another team will consider the importance of lipids as a co-factor. Alain Abarnou, Eugene Nixon, Michael Haarich, Thomas Alsberg and Patrick Roose will consider this topic intersessionally and prepare a report for the next meeting. Patrick Roose will act as co-ordinator.

¹ Additional labs working in this area will be identified by QUASIMEME by including a reference to this MCWG action in their next meeting.

8.2.3 Overviews of Contaminants in the Marine Environment

8.2.3.1 Chlorinated Alkanes in the Marine Environment

This document was an updated version of the paper submitted at MCWG1994, with additional data included. Dr Boon asked whether these compounds were mutagenic in their action, or carcinogens as a result of influencing gene expression. This information will be sought and added if possible. This group agreed that this document was now ready for submission to ACME and, accordingly, decided to attach it as an annex to this MCWG report (Annex 5).

8.2.3.2 Benzene and its C₁-C₂ Alkyl derivatives in the Marine Environment

This document was an updated version of the paper submitted at MCWG1994, with additional data included. Some minor changes were recommended. The group approved this overview for transmission to ACME and appended it to the MCWG report (Annex 6). Dr P. Roose was thanked by the group for his hard work in preparing these two documents.

8.2.3.3 Evaluation of review notes: modern pesticides

The subgroup agreed that the review document on "modern" pesticides presented to the last MCWG meeting should be updated with more background information from a recent Dutch publication by W. de Waal and presented at next year's meeting.

8.2.3.4 Overview on butyltin compounds

The paper presented by W. de Waal was based on the summary of a Dutch Rijkswaterstaat report (RIKZ-95-007). This is a report of a series of overviews that each summarize the information on different classes of contaminants.

It was the general opinion of the group that the report contains a lot of very thorough scientific information on environmental chemical and toxicological processes, but at present the policy paragraph is restricted to the situation in the Netherlands. The Organic Subgroup made the **recommendation** that the national situation should be investigated for each ICES Member Country before this report is to be forwarded to ACME. The information for the different countries will be collected by the following persons:

| | |
|---------|------------|
| Belgium | P. Roose |
| Canada | M. Lebeuf |
| Denmark | M. Cleeman |
| France | A. Abarnou |
| Germany | M. Haarich |

| | |
|----------|--|
| Ireland | E. Nixon |
| Norway | J. Klungsøyr |
| Portugal | J. Biscaya |
| Spain | T. Nunes |
| Sweden | T. Alsberg |
| U.K. | R.J. Law (who already presented some information at the meeting) |
| U.S.A. | S. Berman |

Action: The information should be sent to W. de Waal before 1 September 1995.

Only a few remarks were made on the contents of the paper:

- R. Law had a question about the Ecological Quality Objective (EQO) stated for sediment in the paper. On p. 3 (last sentence) a quality objective of 1.5 mg/kg dry weight is mentioned. However, on p.2, item 5 it is mentioned that the river Rhine at Lobith contains relatively high levels mounting up to 122 mg TBT/g sediment. On p. 4 it is stated that the Dutch EQOs are exceeded on average by a factor of 400 for inland water sediment. In view of both statements, it would seem possible that the EQO on p. 3 should read 1.5 mg/g dry weight.
- J. Boon mentioned with respect to statements on p. 4 (3rd paragraph) and p. 6 (2nd paragraph from bottom), that the first dose-effect relationships have now been established also for the common whelk (*Buccinum undatum*). In this species, the juvenile stages seem to be most sensitive.

8.2.3.5 Sources of data on chemicals transported at sea

R. Law and J. Klungsøyr prepared a note on existing sources of information and systems of data management in relation to potential hazards in the transport at sea of chemicals, which can as a consequence be discharged into the marine environment.

This subject was presented in a response by members of the group to have the required information at hand in case of an emergency spillage at sea or along the coast. This paper can be used to identify the action necessary to deal with such an incident.

The document was presented by R. Law. A brief introduction lists the main types of transport and the categorization of noxious liquid substances. It is mentioned that action is currently underway to harmonize regulations within IMO, the regulatory body for this activity, under the Marine Pollution Convention (MARPOL 73/78).

The classification system of IMO was described. The hazard assessment of the chemicals transported is carried out by the EHS group of GESAMP. An entry from the

GESAMP/EHS Composite List of Hazard Profiles was given as an example. This composite list is available from IMO on paper (ca. 50 pages) and may also be available in software form, but it is recommended to use the hard-copy, as the software is not very user-friendly.

The information on ships' cargoes, according to the document, is held by the industrial companies which produce and ship the materials, and possibly by trade associations such as the European Chemical Industry Council. IMO has no responsibility for the compilation of such information.

In case of an incident, the first source of information is the ship's manifest, held by the shipper or agent at the port of departure. This is often of low quality for reading and is subject to mistakes, but the implementation of an EC Directive in September 1995 will improve the system to a great extent. The Directive aims at giving search and rescue organizations rapid access to information. Each EU Member State will have to appoint a national contact, from which information on any vessel within Community waters can be obtained.

Another useful source of information is the AQUIRE Database, available on-line at the U.S. EPA laboratory in Duluth, which contains (screened) information on toxicity, bioaccumulation and sublethal effects of chemical substances on aquatic organisms. The database covers literature published since 1970.

The document includes some literature references. For updating it in the future, the authors recommended to ask for information from the Chemical Industries Association.

The subgroup agreed that this is a very useful information document. It was suggested to complete it by including a list of the relevant national authorities that should be contacted in case of accident. Each member of the subgroup should obtain the information from his country and send it to R. Law before 20 April 1995.

The subgroup agreed that after these additions the document should be sent via the MCWG Chairman to ACME for information.

8.2.4 Investigate the possibilities of organizing an ICES baseline study on contaminants in the near future

The subgroup felt that prior to organizing such a baseline study it was essential to have clear objectives and a clear structure for such an exercise. Ad hoc integration of information was unlikely to produce a coherent overview.

In most cases the chemical measurements made in baseline studies are at or near the limits of detection for many laboratories and it would be important to have a

full QA programme to underpin any such activity. The last ICES baseline study in 1985 produced a large amount of data, but considerably less real information due to different laboratory expertise and lack of QA data. It was pointed out that the laboratories invited should be able to demonstrate that their performance was suitable for the task and that blind samples should be included in any such study.

Dr Jan Boon emphasized that data for toxicological studies should be included with any study on chemical measurements, i.e., a biological effects study should be carried out along with the chemical measurements.

8.2.5 Review of results of the Intercomparison Programme on the Analysis of CBs in Marine Media

A draft assessment report was presented by Jacob de Boer. The report showed that a measurable improvement had been obtained over the four steps of the study in the participants' ability to analyse chlorobiphenyls (CBs). Much better results were obtained in comparison with other interlaboratory studies on CBs occurring at similar concentrations. On the other hand, the demanding requirements of international monitoring programmes still necessitate further improvements if the whole group of laboratories is to be included. Standard errors of around 15% were obtained in seal oil and sediments for three CBs, corresponding to reproducibilities of around 50%. The determination of CBs in lean fish tissue resulted in standard errors of around 100%. The results obtained in the laboratories in the last three steps of the study (steps 2, 3b and 4) were assessed and the values for the Euclidean distance were plotted to demonstrate the improvement in the laboratory's performance. Laboratories with deviating results were identified for each matrix. This report should not serve as a selection mechanism for laboratories for possible future monitoring programmes or baseline studies since the performance of a laboratory may differ from time to time. Also there is additional information which should be considered in the reports on the individual steps, such as chromatographic conditions and information from principal component analyses. During baseline studies or monitoring programmes, blind samples should be distributed for analysis alongside the environmental samples, and laboratories should demonstrate their ability to measure CBs by delivering quality control (QC) charts.

The group thanked Jacob de Boer for his presentation and for the preparation of the report. The group also conveyed its appreciation to Jaap van der Meer. The information was considered to be very valuable. The group fully agreed with and stressed the need for quality assurance (QA) as an integral part of baseline studies and monitoring programmes. This observation was judged to be of particular importance to the ASMO and SIME groups. With regard to baseline studies and monitoring

programmes, it was stressed that prior to the organization of such programmes it was necessary to establish if there is any disparity between what should be measured (or what information is asked) and what can be measured by laboratories in terms of precision and accuracy. For example, even when only 6 or 7 selected laboratories with good performance are considered, their best performance would still give standard errors of around 10%, corresponding to reproducibilities of 25–30%.

It was recommended that this assessment report should be published in the *ICES Cooperative Research Report* series, if possible with the report on step 4 of the intercomparison programme. It was also recommended that the information should be prepared for publication in open literature.

8.2.6 Investigations on CB-patterns in mammals and fish

8.2.6.1 MCWG Research Project "The development of PCB patterns in different species of fish-eating mammals in relation to food and biotransformation capacity"

Participants: J.P. Boon and J. van der Meer (NIOZ, NL), R.J. Law and C.R. Allchin (MAFF, UK), J. Klungsøyr (IMR, Norway), P.E.G. Leonards (IES, NL), E. Storr-Hansen (NERI, DK), H. Spliid (Techn. Univ., DK), J. Utne-Skaare (Vet. Inst., Norway), D.E. Wells and C. McKenzie (SOAFD, UK).

This research project involves the interpretation of data on concentrations of PCBs in fish-eating mammals of a number of laboratories participating in the work of the MCWG. A large number of calculations had been carried out intersessionally and the team working on this project also met for a workshop from 18 to 20 February 1995 at NIOZ.

J.P. Boon gave a presentation on the results obtained intersessionally. The data made available to this project by the different laboratories together had involved a number of years of analytical effort. These results from the different laboratories were merged without any problems related to the chemical analysis. The intercalibration exercises carried out within the framework of the MCWG have been supportive in obtaining reliable data for the project. For logistic reasons this amount of data could not have been gathered by a single laboratory. Last, but not least, the team involved experienced a high level of mutual cooperation and stimulating discussion which has largely contributed to the success of the work and which has also directed new research within the individual laboratories.

The hypothesis of the project can be stated as: differences in CB patterns between marine mammals and fish can be explained in terms of availability in food and biotransformation by the cytochrome P450 system.

The great majority of samples used for the calculations were blubber samples of which the data on the concentrations of PCBs were already available at the different laboratories. Some previously published comparisons of PCB patterns in different tissues of marine mammals have shown that the PCB pattern in blubber is a good representation for the pattern in the majority of other tissues. For the discussion of the results of the calculations, all PCB congeners have been divided into different structural groups with regard to phase I metabolism by the cytochrome P450 system, as derived from previously published experimental and field studies on seals and cetaceans.

- I. Congeners without any vicinal hydrogen (H) atoms. (e.g., CB-153, CB-180, CB-183, CB-187, CB-194).
- II. Congeners with vicinal H atoms only in the *ortho*- and *meta*-positions in combination with ≥ 2 *ortho*-Cl substituents. (e.g., CB-99, CB-128, CB-138, CB-163, CB-158, CB-170).
- III. Congeners with vicinal H atoms in the *ortho*- and *meta*-positions in combination with ≤ 1 *ortho*-Cl (e.g., CB-28, CB-105, CB-118, CB-156, CB-157).
- IV. Congeners with vicinal H atoms in the *meta*- and *para*-positions in combination with ≤ 2 *ortho*-Cl (e.g., CB-44, CB-49, CB-52, CB-101).
- V. Congeners with vicinal H atoms in the *meta*- and *para*-positions in combination with ≥ 3 *ortho*-Cl (e.g., CB-149).
- VI. Congeners with vicinal H atoms **both** in the *ortho*- and *meta*-positions and *meta*- and *para*-positions in combination with ≤ 1 *ortho*-Cl (e.g., CB-31).

The calculations carried out were based on absolute concentrations (level 1; Principal Component Analysis (bi-plots)) and on PCB patterns which were made independent of absolute concentrations by normalizing the data to the concentration of CB-153, the CB congener present in the highest concentrations and belonging to structural group I, and thus highly resistant to enzymatic attack:

$$Ratio_{153} = \frac{[CB - X] \text{ (in } \mu\text{g. g}^{-1} \text{ lipid)}}{[CB - 153] \text{ (in } \mu\text{g. g}^{-1} \text{ lipid)}}$$

Subsequently, the CB-patterns in tissues of the fish-from eating mammals were compared with cod liver oil (CRM-349) as a general model for the CB-pattern in fish the North Sea by calculation of R_{rel} . R_{rel} is the relative ratio of a given congener (CB-X) in a tissue of a marine mammal in comparison to its diet, i.e., fish:

$$R_{rel} (CB - X) = \frac{Ratio_{153} (CB - X \text{ in mammals})}{Ratio_{153} (CB - X \text{ in CRM - 349})}$$

The results were presented in the form of a box-and-whisker plot (level 2 calculations).

For individual congeners, some plots combining data on absolute concentrations and pattern analysis were also made (level 3 calculations).

Although the project is still going on, the preliminary conclusions can be summarized as follows:

- 1) For the PCB congeners expected to be persistent, i.e., those belonging to the structural groups I and II, the cod liver oil CRM-349 provides a very reasonable source pattern from which the PCB pattern in predators can be derived.
- 2) The majority of the PCB patterns show a strong co-variance in co-variance bi-plots. Such congeners show mostly, but not always, R_{rel} values around unity.
- 3) Congeners with R_{rel} values < 1 often vary in a different manner than the persistent congeners, resulting in an increasing angle α in level 1 calculations.
- 4) The R_{rel} values of metabolizable congeners often relate in a concentration-dependent manner to the absolute concentration of CB-153 (level 3 calculations).
- 5) The metabolic capacity especially for congeners with m,p vicinal H-atoms increases in the order whale, delphinidae, *Phoca groenlandica* < harbour porpoise < grey seal, harbour seal < otter. Thus, the more strongly a species is associated with the terrestrial environment, the better its metabolic capacity for this type of congener seems to be. In rat, this type of congener is metabolized by the cytochrome P450B family, possible exception is *Phoca groenlandica*.
- 6) There is a considerable difference in pattern in the population of grey seals from Arctic waters and waters around Scotland.

- 7) The resistance to biotransformation of congeners belonging to the same structural group differs:
 - Group III ($o,m/\leq 1$): CB-28(3) < CB-118(5), CB-105(5) < CB-156(6). The latter sometimes behaves as a completely persistent compound.
 - Group IV ($m,p/\leq 2$): CB-44, CB-49(4) < CB-101(5) < CB-52(4).
 - Group V ($m,p/\geq 3$): CB-149(6) is persistent in cetaceans but appears to be degradable by grey seal, otter and cormorant.
 - Group VI ($o,m + m,p/\leq 1$): CB-31(3) is degradable in all species investigated.

In the discussion afterwards, Jacob de Boer mentioned that there are two or three different sources of CB-70 standards on the market but that they are in reality supplying different compounds and that analysts can therefore have no confidence in any of them. Jan Boon suggested that in view of this he might exclude the data for CB-70 from consideration altogether. The authors intend to submit a paper summarizing this work to the journal *Environmental Science and Technology*.

Following the finalization and publication of the joint data study prepared by Boon *et al.*, a second study will be undertaken to compare and contrast different multivariate methods such as PCA, Discriminant Analysis, and SIMCA on a common data set of a wide range of different species. This is a co-operative project among 6 MCWG institutes.

8.2.6.2 Distribution of PCB congeners in two fish species from Swedish waters

Tomas Alsberg presented a status report on a work carried out jointly at Stockholm University and the Swedish Museum of Natural History. The aim of the project was to produce a model for predicting the concentrations of planar CBs from the measured concentrations of the non-planar congeners. Herring of different ages (2 and 5 years, and 2 and 6 years) taken from two different locations, and pike from a single location but collected in different years (1971 and 1992) were used for the model calculations. They concluded that it might be possible to construct a model using data for CB-126 and/or CB-169, but that for CB-77 the data were more variable and modelling would probably be both more difficult and less successful. It was stressed that these were only preliminary results and that further work was needed.

8.2.6.3 Report of the investigation on CB patterns in marine mammals

David Wells presented the document "Chlorobiphenyls in Marine Mammals from Scottish Coastal Waters".

Organochlorine residues (including chlorobiphenyls (CBs)) have been determined in blubber samples taken from marine mammals stranded in Scotland since 1990, in order to assess their exposure to toxic contaminants. Data for a small number of individuals (ca. 3–25) from each of eleven species of seals and cetaceans are now available, and a multivariate statistical technique, discriminant analysis, has been applied to the data in order to investigate differences in the CB patterns. The raw data are first normalized to a single persistent compound (CB-153) to reduce the effects of co-factors, such as age, sex, condition and location. As output from the statistical analysis, the discriminant factors are plotted to display the species differences in relation to the uptake from food and metabolism of the CB congeners. Differences in the CB patterns in the different species result in spatial separation of, e.g., cephalopod and fish eaters, with sufficient resolution to distinguish, e.g., bottlenose dolphins from striped dolphins from harbour porpoises. Overlain vectors indicate the major CBs contributing to the spatial separation in each case, and can point to significant differences between the diet or metabolic capacity of different species.

8.2.7 Plans for an intercomparison exercise on non-ortho CBs in marine media

This item was based on a request from OSPARCOM to ICES to develop a QA programme for non-ortho and mono-ortho substituted CBs, including guidelines for sampling and analysis and to organize an intercomparison exercise for these Cbs.

Dr Wells introduced a summary report of work carried out by three laboratories under an EU-funded S, M&T programme and pointed out that an informal intercomparison exercise was requested at the 1994 MCMG meeting.

Summary report of the development of methods for the determination of non-ortho CBs in marine samples

Over the last 18 months the laboratories of the Institute for Environmental Studies, Amsterdam, RIVO-DLO, IJmuiden and SOAFD Marine Laboratory, Aberdeen, have been engaged in the development and validation of methods for the determination of mono-ortho and non-ortho CBs in environmental samples for the EU S, M&T programme.

The methods currently available have been critically evaluated (Hess *et al.*, 1995). As a result, the following general conclusions have been made:

- 1) Non-ortho and mono-ortho CBs occur at significantly lower concentrations ($\times 10^{-1,000}$) than the usual CBs that are monitored, *cf.* CB-153. Therefore, the intake mass required is proportionally higher.
- 2) The greater intake of mass also results in a greater amount of co-extracted materials, e.g., lipids, to be removed. This must be undertaken by well-established methods.

Great care must be made to remove all but the smaller traces of lipid a) to reduce subsequent interference on the GC, and b) to prevent a loss of LC column performance when separating the mono-ortho and non-ortho CBs.
- 3) Separation of CBs from other organochlorine groups e.g., OCPs is essential, e.g., silica gel separation.
- 4) The CB fraction should be separated into at least three fractions containing the di- and tri-ortho CBs, mono-ortho CBs (and some di-ortho CBs), and the non-ortho CBs. This is best effected by using either a porous graphitic carbon column or a pyrenyl-silica (PYE) column. In general, other methods such as active alumina and carbon columns are less robust, repeatable and are less superior in terms of resolution and durability.
- 5) Each fraction should be measured using high resolution capillary GC and either ECD or MS as a detector. Where MS is used i.e., either PICI or NICI it is advisable to use ^{13}C analogues as internal standards. This can reduce interference effects, and increase sensitivity and specificity. ECD may be used provided the sample has undergone sufficient clean-up. Detection limits are likely to be lower when using MS.

These notes are only a general summary of these studies. A full report is currently in preparation and will be available later during 1995.

From these studies the following conclusions can be reached:

- 1) The methodology to reliably measure mono-ortho and di-ortho CBs is currently available and has been published. Further specific details will be available later during 1995.
- 2) The determination of mono-ortho and non-ortho CBs should be developed as part of an overall strategy of CB measurement and not as a separate analysis. The value of obtaining data on as many CBs as possible, i.e., extending the monitoring congeners, is a preferred approach to focusing on

the non-*ortho* CBs in isolation. The methods of analysis should reflect this approach.

- 3) There should be a systematic, stepwise approach to developing these methods in as many marine laboratories as possible using the valuable information from previous exercises, e.g., the ICES I/C series and the QUASIMEME project.
- 4) The stepwise I/C should be developed into a continuous laboratory testing scheme to extend the existing CBs which are currently being determined, e.g., in QUASIMEME to include the non-*ortho* CBs.

Current:

di/tri-*ortho* CBs: CB-28, 52, 101, 138, 180
mono-*ortho* CBs: CB-118, 105, 156, (CB-157)
non-*ortho* CBs: CB-77, 126, 169

- 5) In view of the current interest in and requirements to provide a QA system for these additional compounds, the programme should include ca. 1–4 stages over a two-year period, i.e., six monthly development programme.

The required stepwise learning programme for mono-*ortho* substituted CBs is already being undertaken by QUASIMEME.

It was agreed by the subgroup that:

- Analysis of planar CBs should primarily be carried out in connection with measurements of biological effects of these contaminants.
- Analysis of planar CBs is also relevant in connection with risk assessment to human health.
- At this stage the analysis of planar CBs on a routine basis in spatial distribution and temporal trends studies is not recommended, due to the difficulties associated with the analysis of these compounds, by other than a few specialist laboratories.
- In spatial/temporal trend studies, the more dominant CBs, e.g., CB 153, can be used to represent the burden of CBs since these can be analysed much more easily.
- Clarification on what is meant by sampling is required, i.e., does this cover sample handling or a sampling programme.
- Following an initial assessment of laboratories, a stepwise improvement programme will be carried out which should lead into a continuous testing scheme.

It was noted that QUASIMEME will start a programme for the stepwise improvement of the analyses of non-*ortho* CBs in marine matrices in June 1995. All laboratories, including non-QUASIMEME laboratories, will be able to participate provided that they have the equipment and capability for analysis and that they agree to participate in all steps. This is similar to the arrangements for the previous ICES and QUASIMEME QA programmes. The outcome of this initial step and the continuation of the programme will be reviewed by MCWG in 1996.

8.2.8 Report on Background Concentration of Natural Compounds

See Section 9.1 of this report for a coverage of this topic.

8.2.9 Reviews on "new contaminants"

Jan Boon presented information on a review concerning contaminants which may have andro-oestrogenic activity which has been published in Environmental Health Perspectives. The full reference is given in the attached list.

Robin Law offered to prepare a note for MCWG 1996 about Irgarol 1051, a s-triazine herbicide used in antifouling paint which has been detected in marinas in France and the UK.

Jacob de Boer agreed to prepare a note on tris(4-chlorophenyl)methane and tris(4-chlorophenyl)methanol, their concentration levels in biota and their toxicity.

If possible, these notes should be circulated to subgroup members one month prior to MCWG 1996.

8.2.10 Limits of detection (HELCOM)

A limit of determination of 1 µg kg⁻¹ wet weight for single PAH compounds in biological tissues could be attained using both HPLC/UVF and GC/MS methodologies, whilst utilizing modest sample masses. No collaborative studies have been conducted to date which indicate the degree of interlaboratory comparability that can be achieved at this concentration, however; indeed earlier studies conducted within ICES (Farrington *et al.*, 1986; Uthe *et al.*, 1986) have shown poor comparability even at higher concentrations. Further studies involving the determination of PAHs are under way within QUASIMEME. In fish tissues PAH concentrations are likely to be low because of their high metabolic capacity towards these compounds, and analysis of fish muscle should generally be considered for assurance purposes only (Law and Biscaya, 1994). In shellfish the metabolic capacity is lower, and bioaccumulation can yield higher concentrations in their tissues. Shellfish are therefore considered more suitable for studies of the spatial distribution of PAHs in the environment, although care must still be taken in

choosing sampling locations as relatively small local sources can be important in determining PAH burdens.

Farrington J.W., David A.C., Livramento J.B., Clifford, C.H., Frew, N.M. and Knap, A. 1986. ICES/IOC intercomparison exercise on the determination of petroleum hydrocarbons in biological tissues (mussel homogenate) - ICES/2/HC/BT. ICES Coop. Res. Rep. No. 141, pp. 1-75.

Law, R.J. and Biscaya J. 1994. Polycyclic aromatic hydrocarbons (PAH) - Problems and progress in sampling, analysis and interpretation, Mar. Pollut. Bull, 29: 235-241.

Uthe, J.F., Musial, C.J. and Sirota, G.R. 1986. Report on the intercomparative study 03/HC/BT on the determination of polycyclic aromatic hydrocarbons in biological tissue. ICES Comp. Res. Rep. No. 141, pp.76-85.

8.2.11 Provide information concerning the transfer of halogenated organic compounds through the food chains (HELCOM)

In phytoplankton and zooplankton, adsorption/desorption processes probably control the transfer of halogenated compounds from water to the algae, although they may subsequently be absorbed. In some species of zooplankton, as well as in invertebrates and fish, the uptake of halogenated compounds can occur from water via the gills, as well as from food and particulate material. Within their bodies exchange equilibria between body lipids, blood and water control the concentrations. Due to the lipophilic nature of the contaminants, lipid physiology plays an important role, and leads to redistribution, for instance, during spawning. Also, in fish the equilibria established are dependent upon the size of the organism (the larger the fish, the greater the bioaccumulation that occurs). In the transfer from fish to birds and mammals, biomagnification occurs and the highest concentrations are found in these top predators; but in these animals there is often also a greater potential for enzymatic biotransformation to compounds that can be excreted, but which may also be either more or less harmful than the original compounds.

Some of the properties of chemicals which are important for bioaccumulation are:

- *Hydrophobicity* (or inversely the solubility)
Molecules having an octanol-water partition coefficient (K_{ow}) in the range 10^3 - 10^6 are bioaccumulated. These molecules should not have polar functional groups that increase their solubility, and also facilitate their degradation. Chloroaromatic (halogenated) and chloroaliphatic compounds satisfy these requirements.

- *Persistence*
The compounds should not be easily degraded, either chemically or photochemically, or biodegraded or biotransformed (can we define a half-life value in water, sediment, and biota?). A suitable cutoff value of the half-life value in water, sediment, and biota could be selected for this parameter.
- *the size of the molecule and the spatial configuration* should also be considered because of limitations upon the transport through gills and/or membranes that constitute the biological tissues.

Molecular mass around 200-500 Da and molecular size around (ca. 10 Angstroms) may represent the upper limit in this case.

The literature concerning food-chain transfer and bioaccumulation is extensive and to summarize all the information available would represent a considerable task. For specific aspects, however, more detailed information could be provided at a later date in response to a focused request.

8.2.12 Any other business

Dr Wells withdrew as chairman of the Organic Subgroup. The subgroup thanked Dr Wells for his inspiring chairmanship and for all his contributions. Dr Klungsøyr was elected as chairman for the intersessional period and for the meeting next year.

8.3 Chemical Oceanography Subgroup

8.3.1 Assess and report on the outcome of the ammonia questionnaire prepared in association with the Fifth Intercomparison Exercise on the Analysis of Nutrients in Sea Water

Of the 132 participants in NUTS 5, 106 submitted results for ammonia. When the first dozen or so sets of results were received, it was already apparent that the determination of ammonia was causing some problems.

Soon after the deadline for submission of results, a mailshot containing histogram representations of the results was sent out to participants, and those that had determined ammonia were asked to complete and return a questionnaire asking for details of their analytical methods, calibration procedures, etc., so that an evaluation of them could be undertaken.

A short interim report was prepared and circulated in 1993 pending a more detailed investigation of the responses to the questionnaire.

A draft of this was considered by the subgroup which recommended that it should be made available in two versions:

- a) the full report, modified and expanded as necessary, to be sent to those participants who returned the questionnaire;
- b) a less detailed version, revised as necessary to render it suitable for publication in the open literature, reprints to be made available to potential participants in NUTS 6.

Some specific points worth mentioning here are:

- Despite the fact that almost all of the participants claim to be using the indophenol blue method, there are enormous disparities between reagent concentrations, reagent combinations, and even the order of addition of reagents.
- Discrepancies in calibration procedures are the most likely sources of error.
- It is interesting to note that among the non-respondents (40%) there is a greater tendency towards poor quality results.

Aminot and Kirkwood will finalize this report.

8.3.2 Discuss plans for the Sixth Intercomparison Exercise for Nutrient in Sea Water

The subgroup agreed that there should be no information mailshot announcing NUTS 6 until the NUTS 5 report has been printed and distributed.

The provisional number of participants for NUTS 6 is approximately 150. According to the original timetable, samples should be distributed to the participants in late 1996. It is likely that the determination of nitrite will be excluded from NUTS 6 but silicate will be included. Alain Aminot is currently running stability tests on silicate samples, and will be able to provide more information at the next MCWG meeting in early 1996. The other determinands will be phosphate, nitrate and ammonia. Participants will be encouraged to determine total nitrogen and total phosphorus, but there will be no assigned values for these, nor for silicate.

The subgroup agreed that three concentration levels should be prepared, and that samples of low salinity should be included, if possible.

8.3.3 Review a note on organophosphorus compounds containing C-P bonds which are suitable to check recoveries

Since the work on this subject was reported in 1994, A. Aminot has undertaken further research resulting in a nine-page document which has been prepared with a view to publication in the open literature.

A large variety of phosphorus-containing compounds were tested and the most significant finding was that recoveries from sea water were generally very different from those in fresh water. Virtually 100% recovery is readily obtained from fresh water in all cases but not so for sea water.

Alkaline persulphate is preferable to acidic systems. Workers are advised to beware of making assumptions about the recovery achievable in their particular systems, and to check a variety of compounds for themselves.

Riboflavin phosphate is reckoned to be too labile for use in this context. Aminoethylphosphinic acid (having a C-P bond) was considered more realistic but it gave an anomalously high (108%) recovery in fresh water, with respect to high temperature combustion. Phytic acid and phosphorylcholine chloride are also suitable compounds for such tests.

When undertaking recovery checks, the purity and stability of phosphorus-containing compounds must be considered. For example, care must be taken in oven-drying, as partial decomposition will give rise to a higher than theoretical phosphorus content for the residue.

8.3.4 Review and report on the progress made in the determination of dissolved organic carbon (DOC)

The information presented by Alain Aminot at last year's MCWG meeting in Brest, indicating that wet oxidation methods for the determination of DOC in sea water gave comparable results to methods involving high temperature combustion (HTC), has now been confirmed by independent investigations.

An intercomparison within the Joint Global Oceanographic Flux Study (JGOFS) showed that there was no significant difference in results from several different methods, both HTC and wet oxidation (Marine Chemistry 48 (1995): 91-108).

In addition, Alain Aminot and Professor Mohamed Abdullah (personal communication) presented further evidence from their own laboratories that the wet oxidation/UV technique can give results that show excellent comparability with results obtained by HTC.

Concern was expressed by the subgroup over the way DOC data are gathered and treated. As the nature of DOC is not yet well established, and since the DOC composition undoubtedly varies both seasonally and geographically, there are potential dangers in treating a non-specific determinand like DOC as a single component with known behaviour. Many users tend to overestimate the usefulness of DOC in linking variations in the DOC content in sea water to the variations of other substances. Unless the DOC fraction is more specifically characterized, it is unlikely to supply useful information for monitoring. There is a need for more background work on how DOC should be used before it can be generally recommended for inclusion in monitoring programmes.

8.3.5 Review the "Report on Background Concentrations of Natural Compounds" and supplement it with additional information if available

This topic is covered in Section 9.1 below.

8.3.6 Chemical analysis of anoxic waters

8.3.6.1 Problems related to determinations of constituents in anoxic waters

The authors of this work, M. Krysell and K. Mäkelä, draw on their specific experiences in the Baltic Sea.

The effects of the presence of H₂S are described in relation to determinations of nutrients, halogenated organics, heavy metals, pH and alkalinity.

The subgroup discussed in detail the experimental work on phosphate contained in the paper. Phosphate recoveries were compared at various sulphide concentrations in a manual and an automated method, both based on the formation of molybdenum blue.

The manual method was seriously deficient at a sulphide concentration of 200 µmol/l. S. Carlberg described how he had circumvented this very problem several years ago, by adding the ascorbic acid to the sample before the acid/molybdate. A satisfactory explanation for why this is effective has not yet been found.

In addition to producing turbidity, H₂S is a potential interferent in the determination as described above in that it may react with the antimony-containing reagent. An antimony-free method using hydrogene as reductant was recommended to the authors.

The determination of ammonia by the indophenol blue method showed a systematic decrease in sensitivity with increasing sulphide concentration. The decrease reaches approximately 20% at a sulphide concentration of 70 µmol/l.

The intention is to broaden the scope of the investigation with a view to publication in the open literature.

8.3.7 Future work programme

The subgroup discussed several work items for the intersessional period. These items are listed in the Action List in Annex 3.

8.3.8 Quality Assurance Guidelines for the Baltic Monitoring Programme

Shortly before the end of the meeting, the subgroup received the draft report of the recent meeting of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea. The members of the subgroup agreed to review the document and comment by correspondence to S. Carlberg before 15 May 1995. More detailed comments are possible up to September 1995.

8.3.9 Election of Chairman

The subgroup unanimously re-elected Mr Stig Carlberg as chairman for the intersessional period.

9 PLENARY DISCUSSIONS OF SUBGROUP WORK

The MCWG adopted the points of view and the recommendations put forward by the respective subgroups.

9.1 Review the Report "Background Concentrations of Natural Compounds" and Supply it with Additional Information if Available

This report has been discussed in the three subgroups. This section collates the outcome of these discussions as agreed upon during the plenary session.

The report gives a very acceptable definition of background concentrations of natural compounds, but then fails to treat this concept in a consistent manner. The information presented in the report as background concentrations is a mixture of:

- 1) present-day concentrations from areas that can be used for reference purposes (reference concentrations);

- 2) "historical concentrations", that may be used for some kind of reference although they do not meet the requirements for background concentrations;
- 3) background concentrations.

This inconsistent use of the concept is disturbing, will inevitably cause confusion among readers, and may lead to incorrect use of the information in, e.g., assessment work.

The report states the fact that ministers from various countries have agreed to reduce the loads of some 36 natural and unnatural compounds by at least 50% or more before the year 1995. After this, the report makes the incorrect assumption that "It is essential to know the background concentrations of natural compounds to be able to establish this reduction accurately and to be able to use water quality models in which sources and effects are coupled". This statement is based on a misconception - it is interesting to know background concentrations, but they are not needed for the purpose stated above. In order to establish the reductions, one needs to have reliable information on concentrations of the substances in question in the relevant matrices in nature, before the reductions in discharges have been carried out. Then one needs to follow, over several years, how the concentrations in nature decline (if they do decline). Finally, one should preferably also model what decline in concentrations could realistically be expected and compare this with the observed results.

In addition to concentrations, primary and secondary effects should be studied, in particular for nutrients.

The report sets one background value for the respective parameters. Background values are in general highly dependent on natural processes in the area, e.g., different geological, chemical and biochemical processes including natural variations in the rock compositions. Therefore, in all tables, a background value should not be given as an average value but as a range.

It should also be stated more clearly from where the different values have been derived, e.g., for metals, from which rivers, if it was surface or deep sea waters, etc., because due to natural biological processes the deep sea is enriched with dissolved constituents compared with the surface waters. This would make it possible to more correctly apply the values given in the report locally.

It is important that the report is updated taking new literature into account, as newer data generally are more reliable. There will soon be more data available from areas like the Arctic through the AMAP programme, and there has recently been published river data from areas in Siberia.

Some specific comments include the following:

Nutrients

Of the methods described in the methods section, some are more obviously than others intended to be applicable to work on nutrients. The group can accept those, with the exception of method 6 since this method incorrectly assumes that concentrations of nutrients are necessarily low in unpolluted natural sea water.

The sub-chapter on sea water makes a very important statement that intensive farming involving large-scale use of industrially manufactured fertilizers started in the early 1950s. The operational consequence of this statement is that in the absence of data on concentrations of nutrients in a pristine North Sea, reliable analytical data from the period before 1950 could be used as the best approximation of historical reference data (not background data). The sub-chapter is very acceptable with the exception that the legend to Table 4 should state that the concentrations are "historical reference values" and data obtained after 1950 should be omitted.

It is not clear in the sub-chapter on rivers whether the authors have made any distinction between data before and after the early 1950s in the same way. The legends to Tables 1–3 make reference to a number of publications from the years 1920–1992. It is possible, but not obvious, that these publications deal only with "historical" data. The report would have gained a lot in credibility if the presentation had included clear reference to the years that these data and estimations refer to, in the same way as was done for Table 4.

This criticism should not detract from the fact that the chapter on nutrients contains useful information both in the text and the tables.

Metals

The statement on page 32, line 3, "Furthermore and unlike for nutrients, advection of Atlantic water across the shelf break cannot be considered as a source of trace metals to the North Sea" might need to be modified. An ongoing EU-project "OMEX", dealing with the exchange of deep-sea water and the shelf, would presumably give valuable information as to whether the Atlantic waters can also act as a source of metals.

Chapter 5, Paragraph 3: It is not correct to use results of metal concentrations from "old" deep sea water as background concentrations, e.g., for the North Sea. Even if the deep sea water was "old", the metals/contaminants could have been transported to the area more recently. In addition, natural processes could have taken place which also might have an influence on the present concentrations in the deep sea areas.

Chapter 5, Paragraphs 7/8: Models should always be tested through field investigations.

Some of the values in the table on page 32 were questioned, the Pb concentration in Atlantic waters being

too high, and also the Zn value given as 0.13 ± 0.40 . The river values according to Zuurdeeg were also surprisingly high as background values.

As for other matrices, it would not be possible to set one background value for blue mussels, as this would depend both on the area where they live as well as the different conditions of the mussel during the different seasons.

Organics

The report considers three groups of organic compounds: those with no natural sources (e.g., DDT, toxaphene); those for which there may be minor natural sources (e.g., chlorophenols, dioxins and furans); and those for which natural sources could provide a significant quantity of material (e.g., PAHs). For PAHs, processes of incomplete combustion have represented a source throughout history. The workshop investigated the use of sediment core data to infer background concentrations. Few such data were available from the North Sea, however. Some tentative data were also explored for water, mussels and the atmosphere.

In the discussion it was reported that some additional data concerning PCBs, dioxins and furans in cores were now available in Canada. Degradation of PAHs in deep sediments could also lead to an underestimate of the natural background concentrations. Sediment case studies are now under way in the Skagerrak/Norwegian Trench area, and a report including additional data for PAHs will be available by the end of 1995. There could still be problems in defining historic background concentrations adequately if they are below current limits of detection.

The report heightened the awareness of the scientific community to the scarcity of relevant data with which to address this topic. It may take some years before sufficient new data are available to make a full reassessment either feasible or necessary; until then the sub-chapter on organics can stand.

Comments on Chapter 2: Recommendations and conclusions

Conclusion 1

The definition is in order but has not been applied consistently in the report.

Conclusion 4

This conclusion is not considered to be acceptable since the main material presented in the report is not background concentrations according to the definition in the report. In addition, not all literature has been taken into account.

Conclusion 5

This conclusion is not acceptable. It presents a very surprising idea that background concentrations for the North Sea can be found by determining present-day

concentrations in samples taken from other parts of the world! Clearly, such samples would represent only the current conditions in that particular area. A sample taken today in the North Sea would represent a particular part of the North Sea as it is today, and the pristine conditions in the North Sea would be difficult if not impossible to find (depending on the substance) in any sample.

Conclusion 7

This conclusion is unacceptable in its present form. What the recommended work will establish is probably what is commonly known as reference concentrations.

Conclusion 10

This conclusion is phrased incorrectly if it is (also) intended to deal with nutrient concentrations. As discussed, concentrations of nutrients in unpolluted sea water are frequently high for natural reasons.

Dr Berman noted that the division of the MCWG into three subgroups had the advantage that a heavy agenda can be dealt with, at the expense, however, of cross-fertilization, discussion and exchange of ideas and information between people of different subgroups. He personally would like to sit in at discussions on some subjects in other subgroups. This point of view was shared by other MCWG members. The Chairman agreed to attempt to structure next year's meeting so as to take this remark into account.

10 ANY OTHER BUSINESS

No other matters were raised under this agenda item.

11 RECOMMENDATIONS AND ACTION LIST

The action list and recommendations are given in Annexes 3 and 7, respectively.

12 DATE AND VENUE OF NEXT MEETING

The MCWG discussed the venue and time of the next meeting. The Instituto Hydrografico in Lisbon, Portugal, offered to host the 1996 meeting of the MCWG. The MCWG acknowledged the invitation with appreciation. It was decided to plan the meeting for 10–17 February 1996.

13 CLOSURE OF THE MEETING

Staff members of the Marine Research Institute joined the closing session of the Working Group. On behalf of the MCWG, the Chairman thanked them for their warm hospitality and for the efforts and services they provided.

In addition, the Chairman thanked the subgroup chairmans for their efforts and support, and all members for their hard work.

The Chairman noted in particular that Dr Wells withdrew as chairman of the Organic Subgroup. On behalf of the entire group, he thanked Dr Wells for his extensive contributions to the MCWG and for his personal support. He expressed the hope that Dr Wells would continue his membership of the MCWG.

The Chairman closed the meeting at about 15.00 hrs.

ANNEX 1

MARINE CHEMISTRY WORKING GROUP

Reykjavík, Iceland, 3–7 April 1995

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ANNEX 2

MARINE CHEMISTRY WORKING GROUP

Reykjavík, Iceland, 3–7 April 1995

AGENDA

1. Opening
2. Adoption of the agenda
3. Report of the 82th ICES Statutory Meeting
4. Reports on related activities
 - 4.1 Joint Monitoring Group of OSPARCOM
 - 4.2 Intergovernmental Oceanographic Commission
 - 4.3 ICES
 - 4.4 EU-S,M&T QA pilot project "QUASIMEME"
 - 4.5 Quality assurance in the Baltic Sea
 - 4.6 Other activities
5. Reports on projects and activities in Member Countries
6. Requests from ACME and regulatory agencies
7. Plenary presentations
8. Subgroup activities and discussions
 - 8.1 Trace Metal Subgroup
 - 8.1.1 (C.Res.1994/2:7:1f) Investigate the possibilities of organizing an ICES baseline study on contaminants in the near future
 - 8.1.2 (C.Res.1994/2:7:1g) Review and report on the progress with respect to a project on estuarine behaviour of metals
 - 8.1.3 (C.Res.1994/2:7:1h) Discuss and report on the need for developing methods for the determination of speciated metals in sea water
 - 8.1.4 (C.Res.1994/2:7:1i) Review and report on progress with respect to an interlaboratory study on analyses of trace metals in sea water and, if appropriate, devise a plan and timetable
 - 8.1.5 Compare the general performance of the NOAA and QUASIMEME interlaboratory studies
 - 8.1.6 Review the "Report on Background Concentrations of Natural Compounds" and supplement it with additional information, if available
 - 8.1.7 Review progress on the relationship between trace metal concentrations and lipid contents in biological tissue, discuss (possible) plans for future activities

- 8.1.8 Review the overviews on organotin and organomercury compounds
- 8.1.9 Review "new" contaminants and determine where reviews or overviews would be warranted
- 8.1.10 Any other business raised by the subgroup

8.2 Organic Subgroup

- 8.2.1 (C.Res.1994/2:7:1a) Finalize, in the light of the outcome of the ASMO meeting, a list of organic parameters which can be monitored in biota and sediments on a routine basis and advise on the quality assurance measures for these contaminants (OSPAR 1.1)
- 8.2.2 (C.Res.1994/2:7:1b) Review an assessment of methodology for the determination of lipids in biological tissues and consider the need for an intercomparison exercise for measurements of lipids in marine samples
- 8.2.3 (C.Res.1994/2:7:1c) Evaluate review notes on chlorinated alkanes, monocyclic aromatic hydrocarbons, modern pesticides in marine waters and organotin compounds, and on data management systems for chemicals transported over the sea (HELCOM 2)
- 8.2.4 (C.Res.1994/2:7:1f) Investigate the possibilities of organizing an ICES baseline study on contaminants in the near future
- 8.2.5 (C.Res.1994/2:7:1j) Review, with a view to adopting, an overall assessment of the results of the Intercomparison Programme on the Analysis of CBs in Marine Media
- 8.2.6 (C.Res.1994/2:7:1k) Assess and report on the outcome of the investigation on CB-patterns in marine mammals
- 8.2.7 (C.Res.1994/2:7:1n) Discuss plans for an intercomparison exercise on non-*ortho* CBs in marine media
- 8.2.8 Review the "Report on Background Concentrations of Natural Compounds" and supplement it with additional information, if available
- 8.2.9 Review "new" contaminants and determine where reviews or overviews would be warranted
- 8.2.10 Any other business raised by the subgroup

8.3 Chemical Oceanography Subgroup

- 8.3.1 (C.Res.1994/2:7:1d) Assess and report on the outcome of the ammonia questionnaire prepared in association with the Fifth Intercomparison Exercise on the Analysis of Nutrients in Sea Water
- 8.3.2 (C.Res.1994/2:7:1e) Discuss plans for the Sixth Intercomparison Exercise on the Analysis of Nutrients in Sea Water
- 8.3.3 (C.Res.1994/2:7:1l) Review a note on organophosphorus compounds containing C-P bonds which are suitable to check recoveries
- 8.3.4 (C.Res.1994/2:7:1m) Review and report on the progress made in the determination of dissolved organic carbon
- 8.3.5 Review the "Report on Background Concentrations of Natural Compounds" and supplement it with additional information, if available
- 8.3.6 Any other business raised by the subgroup

9. Plenary discussion of subgroup work

10. Any other business
11. Recommendations and action list
12. Date and venue of next meeting
13. Closure of meeting

ANNEX 3

MARINE CHEMISTRY WORKING GROUP

Reykjavík, Iceland, 3–7 April 1995

ACTION LIST

- | | |
|--|---|
| W. Cofino and W. de Waal | Contact a Dutch organization to provide a computer program for modelling and send an expert to the Workshop on Estuarine Behaviour of Metals. |
| J.F. Chiffauleau | Act as chairman for the Workshop on Estuarine Behaviour of Metals and contact relevant persons. |
| J.R. Larsen | Send the report "The Relationship Between Trace Metal Concentrations and Lipid Contents in Cod Liver" to ICES WGSAM. |
| W. de Waal | Include issues raised by the Trace Metal Subgroup and by the Organic Subgroup into the overview of tributyltin. |
| G. Ducastel | Investigate the possibility to prepare an overview of the recent developments on organo-Hg. |
| P. Michel | Prepare review note on triphenyltin. |
| P. Roose, M. Lebeuf, M. Cleemann, A. Abarnou, M. Haarich, E. Nixon, J. Klungsøyr, J. Biscaya, T. Nunes, T. Alsberg, R.J. Law, S. Berman | Provide information about the national policy regarding organotins to W. de Waal before 1 September 1995. |
| Members Organic Subgroup | Provide R. Law information on relevant national authorities to be contacted in case of accidents at sea before 20 April 1995. |
| R. Law | Send paper on "Sources of data on chemicals transported by sea" via the Chairman to ACME. |
| J. Boon, D. Wells, J. Klungsøyr, P. Leonards, R. Law, E. Storr-Hansen | Compare and contrast different multivariate methods on a common data set of PCBs in different species. |
| R. Law | Prepare review note on Irgarol 1051. |
| J. de Boer | Prepare a note on tris(4-chlorophenyl)methane and tris(4-chlorophenyl)methanol |
| J. Klungsøyr | Act intersessionally as chairman of the Organic Subgroup |
| S. Carlberg | Act intersessionally as chairman of the Chemical Oceanography Subgroup. |
| Members C-O Subgroup, B. Pedersen, W. Cofino | Review report "Quality Assurance Guidelines for the Baltic Monitoring Programme", provide comments to S. Carlberg before 15 May 1995 or 1 September 1995. |
| B. Pedersen | Act as chairman intersessionally of the Trace Metal Subgroup. |
| W. de Waal | Update document on modern pesticides and present it to next year's meeting. |
| W. Cofino | Contact IOC in order to discuss their participation in the MCWG. |

| | |
|--|---|
| B. Pedersen, J.F. Chiffolleau | Arrange a plenary presentation covering metals for the next MCWG meeting. |
| J. Boon, T. Alsberg, P. Roose | Provide W. de Waal information on their lipid research programmes. |
| W. de Waal | Coordinate lipid research programmes. |
| A. Abarnou, P. Roose, E. Nixon, M. Haarich, T. Alsberg | Look into the importance of lipids as co-factor. |
| P. Roose | Coordinate research on lipids as co-factor. |
| A. Aminot, D. Kirkwood | Finalize report on ammonia questionnaire. |
| A. Aminot | Report on stability of silicate samples. |

ANNEX 4

MARINE CHEMISTRY WORKING GROUP

Reykjavík, Iceland, 3–7 April 1995

A Comparison of the General Performance of the NOAA and QUASIMEME Interlaboratory Studies for Trace Metals

The comparison of the results of the two interlaboratory studies proved to be rather more difficult than anticipated. The main reason for the difficulty lies in the differences in the samples used in the two studies and their trace metal concentrations.

In this discussion I assume that all members of the MCWG are familiar with QUASIMEME but not with the NOAA protocols.

The NOAA exercises are in their tenth year and we are now preparing the samples for NOAA/9. For the last several years the participants have been asked to analyze an unknown sediment and a marine tissue along with a designated appropriate certified reference material for each. Five replicate results are required for Al, Cr, Fe, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Hg and Pb for both matrices, plus Be, Si, Mn, Sb and Tl for the sediments. The purpose of the NOAA study is to define a group of laboratories which is apparently competent to analyze a material for a particular analyte and to determine the 95 percent confidence interval for the determination. QUASIMEME's purpose is apparently somewhat different in determining whether a laboratory can analyze an analyte to within a preconceived variance from an assigned value (Z score).

In order to help provide benchmarks for accuracy the NRC laboratory also analyzes each of the samples for most of the analytes by two different analytical methods. Where possible, one set of results was produced using isotope dilution inductively coupled plasma mass spectrometry. However, if the value assigned by NRC does not differ significantly from the derived mean of the *t* selected group the latter value replaces the assigned value for evaluation purposes. It has been several years since there has been any significant difference between these values except for some difficult determination like tin in a biological tissue.

Therefore, one purpose of the exercise was to arrive at an accepted value for each analyte concentration for each unknown sample in order to evaluate laboratory biases. The overall mean concentration for each metal was calculated from the mean of laboratory replicates and the NRC data. These means were assumed to be normally distributed, which may not be a valid assumption at very low concentrations, but for the purpose of this exercise it is felt to be adequate. A successively applied Student *t*

test at the 95 percent confidence level was used to identify outliers. This approach was pioneered by this laboratory in the 1980s when we coordinated several intercomparison studies for the MCWG.

The majority of laboratories in the NOAA studies employ HF in the decomposition of sediments and this is a policy fostered by NOAA. However, about five of about 40 sediment participants in the 1994 exercise did not use HF. Their results were combined with the others and were usually seen to be rejected in the *t* selection as being significantly low.

In order to compare the two studies a choice had to be made. Either the NOAA data had to be recalculated using robust statistic or the QUASIMEME data had to be recalculated using the Student *t* test to identify outliers. I chose the latter approach because, frankly, I have been unable to understand robust statistics nor was I successful in an attempt to apply it using a QUASIMEME program supplied to me.

Differences in QUASIMEME Results Due to Recalculation

Tables I to IV show the QUASIMEME trace metal results for 1994 using both robust statistics and what I call *t* selection. Where partial and total decomposition values for sediments have been calculated I have also calculated a combined value because this what would have been done in the NOAA study. The rejection of outliers by the *t* test almost invariably leads to lower coefficients of variation (CV) for the mean. Calculations of Cvs are affected by rounding.

For the Sediment QTM006MS the means differ significantly from those calculated by robust statistics for Al, Cd and Hg and are rather closer to the assigned values. They are also significantly different from the "total" Cu and Pb values but are lower than the assigned values for these analytes. This is understandable because they contain "partial" results. There is apparently a group of more than 20 laboratories in strong agreement regarding the concentration of Zn with a CV of 2 percent.

For the Sediment QTM007MS, only the Al values are significantly different and the *t* selected mean for Al is almost identical to the assigned value.

For the biological tissues there are only significant differences for the means for Cd and Pb in the plaice muscle. These are both analytes for which there are indicative values rather than assigned values. The Ni values for the plaice sample have a bimodal distribution above and below the mean with very few near the mean. This results in a large CV by any method of calculation.

It should be noted that results from a group of laboratories producing a CV greater than 50 percent can not possibly be normally distributed unless some of the results are less than zero concentration. This is often the result of the sample concentrations being too close to the limits of detection for some of the participants. The *t* selection usually obviates this problem.

Some Comparisons of QUASIMEME and NOAA Results

As stated above, the biggest problem in comparing results between NOAA and QUASIMEME lies in the large differences in trace metal concentrations in the samples used. In general, the European samples have rather lower trace metal concentrations in sediments, fish muscle and mussels.

Tables V to VIII attempt comparisons assuming that all results were calculated in the NOAA manner. In general, we have to assume that the competence of the *t* selected laboratories on either side of the North Atlantic is comparable.

It would be interesting to arrange for the two studies to use identical samples sometime in the near future.

Table I Sediment - QTM006MS (mg/kg)

| | Assigned Value | N | Robust Statistics | | | t Selection | | | |
|-----------------------|----------------|----|-------------------|-----------|--------|-------------|-------|-----------|--------|
| | | | Mean | Std. Dev. | CV - % | Rejections | Mean | Std. Dev. | CV - % |
| Aluminum | 29300 | 30 | 25430 | 9278 | 36.5 | 11 | 30300 | 2100 | 6.8 |
| Cadmium | 0.03 | 42 | 0.041 | 0.028 | 69.1 | 10 | 0.028 | 0.008 | 31 |
| Mercury | 0.024 | 34 | 0.028 | 0.015 | 52.8 | 12 | 0.020 | 0.006 | 26 |
| Zinc | 30.5 | 45 | 30.6 | 2.6 | 8.4 | 23 | 30.6 | 0.6 | 2.0 |
| Arsenic | 6.1 | 15 | 6.1 | 1.2 | 19.1 | 2 | 6.2 | 0.9 | 14 |
| Copper ^p | 3.2 | 15 | 3.0 | 0.9 | 29.7 | 2 | 3.0 | 0.7 | 23 |
| Copper ^t | 4.59 | 33 | 4.1 | 0.8 | 20.4 | 3 | 4.1 | 0.7 | 18 |
| Copper ^c | | 48 | | | | 6 | 3.7 | 0.8 | 21 |
| Lead ^p | 10.1 | 14 | 8.0 | 5.1 | 64.3 | 1 | 9.9 | 2.2 | 24 |
| Lead ^t | 17.1 | 33 | 16.1 | 2.8 | 17.7 | 10 | 16.7 | 1.0 | 6.2 |
| Lead ^c | | 47 | | | | 2 | 14.4 | 3.9 | 27 |
| Chromium ^p | 19.0 | 6 | 19.0 | 11.0 | 58.2 | 0 | 19.0 | 9.7 | 51 |
| Chromium ^t | 35.0 | 17 | 35.0 | 8.2 | 23.5 | 3 | 34.1 | 5.5 | 16 |
| Chromium ^c | | 23 | | | | 5 | 33.6 | 6.5 | 19 |
| Nickel ^p | 8.7 | 6 | 8.7 | 1.1 | 12.8 | 0 | 8.7 | 1.0 | 11 |
| Nickel ^t | 12.0 | 17 | 12.0 | 1.3 | 11.2 | 5 | 11.6 | 0.5 | 4.9 |
| Nickel ^c | | 23 | | | | 11 | 11.6 | 0.5 | 4.9 |

^p - partial decomposition ^t - total decomposition ^c - combined results

Table II Sediment - QTM007MS (mg/kg)

| | Assigned Value | N | Robust Statistics | | | t Selection | | | |
|---------------------|----------------|----|-------------------|-----------|--------|-------------|-------|-----------|--------|
| | | | Mean | Std. Dev. | CV - % | Rejections | Mean | Std. Dev. | CV - % |
| Aluminum | 36400 | 30 | 32736 | 7925 | 24.2 | 8 | 36500 | 2900 | 7.9 |
| Cadmium | 1.46 | 45 | 1.4 | 0.3 | 21.6 | 19 | 1.4 | 0.2 | 6.2 |
| Mercury | 0.384 | 35 | 0.378 | 0.074 | 19.6 | 7 | 0.38 | 0.05 | 13 |
| Zinc | 170 | 45 | 165 | 13 | 7.7 | 5 | 167 | 10 | 5.8 |
| Arsenic | 16.6 | 15 | 16.6 | 1.9 | 11.3 | 1 | 16.4 | 1.5 | 9.2 |
| Copper | 24.6 | 47 | 23.5 | 2.4 | 10.1 | 2 | 23.6 | 2.2 | 9.2 |
| Lead | 49.8 | 46 | 47.5 | 7.6 | 16.0 | 10 | 48.4 | 4.4 | 9.0 |
| Chromium | 79.3 | 23 | 79.3 | 22.7 | 28.6 | 2 | 78.6 | 19.6 | 25 |
| Nickel ^p | 17.4 | 6 | 17.4 | 1.3 | 7.7 | 0 | 17.4 | 1.2 | 6.8 |
| Nickel ^t | 22.3 | 19 | 22.3 | 3.8 | 17.2 | 1 | 22.0 | 3.2 | 15 |
| Nickel ^c | | 25 | | | | 1 | 20.8 | 3.5 | 17 |

^p - partial decomposition ^t - total decomposition ^c - combined results

Table III Plaice Muscle - QTM004BT (mg/kg)

| | Assigned Value | N | Robust Statistics | | | t Selection | | | |
|----------|---------------------|----|-------------------|-----------|--------|-------------|--------|-----------|--------|
| | | | Mean | Std. Dev. | CV - % | Rejections | Mean | Std. Dev. | CV - % |
| Cadmium | 0.0069 ⁺ | 39 | 0.0087 | 0.0055 | 63 | 13 | 0.0061 | 0.0018 | 30 |
| Mercury | 0.062 | 38 | 0.062 | 0.017 | 28 | 15 | 0.060 | 0.012 | 9.6 |
| Zinc | 5.48 | 41 | 5.82 | 0.84 | 14 | 7 | 5.62 | 0.58 | 10 |
| Arsenic | 6.06 | 16 | 6.06 | 1.72 | 28 | 3 | 5.70 | 1.53 | 27 |
| Copper | 0.22 | 42 | 0.323 | 0.186 | 58 | 13 | 0.22 | 0.04 | 19 |
| Lead | 0.043 ⁺ | 38 | 0.055 | 0.046 | 84 | 20 | 0.019 | 0.008 | 41 |
| Chromium | 0.174 | 20 | 0.174 | 0.098 | 56 | 3 | 0.15 | 0.07 | 44 |
| Nickel | 0.142 | 17 | 0.142 | 0.103 | 72 | 1 | 0.14 | 0.10 | 72 |

⁺ - indicative value only

Table IV Mussel - QTM005BT (mg/kg)

| | Assigned Value | N | Robust Statistics | | | t Selection | | | |
|----------|----------------|----|-------------------|-----------|--------|-------------|-------|-----------|--------|
| | | | Mean | Std. Dev. | CV - % | Rejections | Mean | Std. Dev. | CV - % |
| Cadmium | 0.051 | 42 | 0.058 | 0.021 | 36 | 12 | 0.053 | 0.010 | 19 |
| Mercury | 0.024 | 38 | 0.025 | 0.008 | 30 | 13 | 0.023 | 0.003 | 13 |
| Zinc | 16.4 | 41 | 16.8 | 1.8 | 11 | 13 | 16.5 | 0.8 | 5.1 |
| Arsenic | 1.29 | 16 | 1.29 | 0.32 | 24 | 4 | 1.29 | 0.16 | 12 |
| Copper | 1.60 | 42 | 1.70 | 0.33 | 19 | 7 | 1.61 | 0.25 | 16 |
| Lead | 0.465 | 42 | 0.469 | 0.123 | 26 | 15 | 0.44 | 0.03 | 7.8 |
| Chromium | 0.660 | 20 | 0.660 | 0.207 | 31 | 3 | 0.68 | 0.15 | 21 |
| Nickel | 0.518 | 19 | 0.518 | 0.105 | 20 | 2 | 0.50 | 0.08 | 16 |

Table V A Comparison using *t* Selection: QUASIMEME and NOAA (1992)- mg/kg

| | N | Sediment - QTM006MS | | | | N | Sediment R (NOAA/6) | | | |
|-----------------------|----|---------------------|-------|-----------|--------|----|---------------------|-------|-----------|--------|
| | | Rejections | Mean | Std. Dev. | CV - % | | Rejections | Mean | Std. Dev. | CV - % |
| Aluminum | 30 | 11 | 30300 | 2100 | 6.8 | 22 | 6 | 21900 | 2070 | 9.5 |
| Cadmium | 42 | 10 | 0.028 | 0.008 | 31 | 27 | 5 | 0.14 | 0.03 | 18 |
| Mercury | 34 | 12 | 0.020 | 0.006 | 26 | 17 | 3 | 0.038 | 0.016 | 33 |
| Zinc | 45 | 23 | 30.6 | 0.6 | 2.0 | 31 | 4 | 44.2 | 5.3 | 12 |
| Arsenic | 15 | 2 | 6.15 | 0.85 | 14 | 23 | 3 | 6.2 | 1.1 | 18 |
| Copper ^p | 15 | 2 | 2.96 | 0.69 | 23 | | | | | |
| Copper ^t | 33 | 3 | 4.08 | 0.72 | 18 | | | | | |
| Copper ^c | 48 | 6 | 3.71 | 0.77 | 21 | 31 | 6 | 9.8 | 0.9 | 9.1 |
| Lead ^p | 14 | 1 | 9.86 | 2.22 | 24 | | | | | |
| Lead ^t | 33 | 10 | 16.7 | 1.0 | 6.2 | | | | | |
| Lead ^c | 47 | 2 | 14.4 | 3.9 | 27 | 27 | 2 | 10.4 | 2.5 | 24 |
| Chromium ^p | 6 | 0 | 19.0 | 9.7 | 51 | | | | | |
| Chromium ^t | 17 | 3 | 34.1 | 5.5 | 16 | | | | | |
| Chromium ^c | 23 | 5 | 33.6 | 6.5 | 19 | 29 | 9 | 37.5 | 5.9 | 16 |
| Nickel ^p | 6 | 0 | 8.7 | 1.0 | 11 | | | | | |
| Nickel ^t | 17 | 5 | 11.6 | 0.5 | 4.9 | | | | | |
| Nickel ^c | 23 | 11 | 11.6 | 0.5 | 4.9 | 27 | 3 | 20.6 | 1.4 | 6.8 |

^p - partial decomposition ^t - total decomposition

^c - combined results

Table VI A Comparison using *t* Selection: QUASIMEME and NOAA (1994)- mg/kg

| | Sediment QTM007MS | | | | | Sediment U (NOAA/8) | | | | |
|---------------------|-------------------|------------|-------|-----------|--------|---------------------|------------|-------|-----------|--------|
| | N | Rejections | Mean | Std. Dev. | CV - % | N | Rejections | Mean | Std. Dev. | CV - % |
| Aluminum | 30 | 8 | 36500 | 2900 | 7.9 | 36 | 18 | 51600 | 1900 | 3.6 |
| Cadmium | 45 | 19 | 1.43 | 0.09 | 6.2 | 35 | 10 | 1.44 | 0.15 | 10.4 |
| Mercury | 35 | 7 | 0.383 | 0.048 | 13 | 28 | 6 | 0.56 | 0.07 | 12 |
| Zinc | 45 | 5 | 167 | 10 | 5.8 | 40 | 6 | 205 | 12 | 5.8 |
| Arsenic | 15 | 1 | 16.4 | 1.5 | 9.2 | 31 | 3 | 16.0 | 2.3 | 14 |
| Copper | 47 | 2 | 23.6 | 2.2 | 9.2 | 40 | 9 | 72.7 | 4.0 | 5.5 |
| Lead | 46 | 10 | 48.4 | 4.42 | 9.0 | 39 | 6 | 113 | 10 | 8.7 |
| Chromium | 23 | 2 | 78.6 | 19.6 | 25 | 38 | 11 | 50.8 | 6.0 | 12 |
| Nickel ^p | 6 | 0 | 17.4 | 1.2 | 6.8 | | | | | |
| Nickel ^t | 19 | 1 | 22.0 | 3.2 | 15 | | | | | |
| Nickel ^c | 25 | 1 | 20.8 | 3.5 | 17 | 36 | 3 | 22.8 | 2.5 | 11 |

^p - partial decomposition ^t - total decomposition

^c - combined results

Table VII A Comparison using *t* Selection: QUASIMEME and NOAA (1992)- mg/kg

| Error! Bookmark not defined. | N | Plaice Muscle - QTM004BT | | | | N | Flounder Muscle Q (NOAA/6) | | | |
|------------------------------------|----|--------------------------|--------|-----------|--------|----|----------------------------|--------|-----------|--------|
| | | Rejections | Mean | Std. Dev. | CV - % | | Rejections | Mean | Std. Dev. | CV - % |
| Cadmium | 39 | 13 | 0.0061 | 0.0018 | 30 | 18 | 6 | 0.0078 | 0.0009 | 11 |
| Mercury | 38 | 15 | 0.060 | 0.012 | 9.6 | 23 | 5 | 0.068 | 0.007 | 9.8 |
| Zinc | 41 | 7 | 5.62 | 0.58 | 10 | 29 | 7 | 5.11 | 0.32 | 6.3 |
| Arsenic | 16 | 3 | 5.70 | 1.53 | 27 | 22 | 4 | 26.8 | 2.5 | 9.8 |
| Copper | 42 | 13 | 0.22 | 0.04 | 19 | 28 | 8 | 0.72 | 0.08 | 12 |
| Lead | 38 | 20 | 0.019 | 0.008 | 41 | 20 | 3 | 0.096 | 0.025 | 27 |
| Chromium | 20 | 3 | 0.15 | 0.07 | 44 | 27 | 8 | 1.48 | 0.23 | 15 |
| Nickel | 17 | 1 | 0.14 | 0.10 | 72 | 21 | 5 | 0.78 | 0.15 | 19 |

Table VIII A Comparison using *t* Selection: QUASIMEME and NOAA (1993)- mg/kg

| | N | Mussel - QTM005BT | | | | N | Mussel S (NOAA/7) | | | |
|----------|----|-------------------|-------|-----------|--------|----|-------------------|-------|-----------|--------|
| | | Rejections | Mean | Std. Dev. | CV - % | | Rejections | Mean | Std. Dev. | CV - % |
| Cadmium | 42 | 12 | 0.053 | 0.010 | 19 | 38 | 14 | 0.15 | 0.01 | 6.4 |
| Mercury | 38 | 13 | 0.023 | 0.003 | 13 | 24 | 3 | 0.011 | 0.002 | 16 |
| Zinc | 41 | 13 | 16.5 | 0.8 | 5.1 | 40 | 12 | 25.7 | 0.9 | 3.5 |
| Arsenic | 16 | 4 | 1.29 | 0.16 | 12 | 32 | 9 | 2.50 | 0.22 | 9.0 |
| Copper | 42 | 7 | 1.61 | 0.25 | 16 | 40 | 11 | 0.76 | 0.04 | 5.4 |
| Lead | 42 | 15 | 0.44 | 0.03 | 7.8 | 34 | 10 | 0.21 | 0.03 | 13 |
| Chromium | 20 | 3 | 0.68 | 0.15 | 21 | 29 | 11 | 0.093 | 0.026 | 29 |
| Nickel | 19 | 2 | 0.50 | 0.08 | 16 | 31 | 8 | 0.16 | 0.03 | 17 |

MARINE CHEMISTRY WORKING GROUP

Reykjavík, Iceland, 3-7 April 1995

CHLORINATED ALKANES IN THE MARINE ENVIRONMENT

INTRODUCTION

Chlorinated alkanes are a large group of compounds and it can be assumed that not all members are relevant for the marine environment. GESAMP (1990) made a selection based on criteria such as log K_{ow} , toxicity, persistence, production, and use of the chemical. The resulting list of potentially harmful substances contained mainly low molecular weight (C_1 - C_3) chlorinated alkanes such as chlorinated methanes (e.g., dichloromethane, chloroform, carbon tetrachloride), chlorinated ethanes (e.g., 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane), chlorinated ethenes (e.g., 1,1,2,2-tetrachloroethylene, 1,1,2-trichloroethylene) and epichlorohydrin (1-chloro-2,3-epoxypropane).

The compounds in question exhibit similar physico-chemical properties, have a widespread use, and are produced in large quantities. Due to their persistence and volatility, they may be transported over considerable distances (Krysell, 1989). A number of these compounds therefore been used as tracers for atmospheric mixing and ocean flux studies (Fogelqvist *et al.*, 1982; Krysell and Wallace, 1988; Krysell, 1992). It can therefore be expected that a certain amount will enter the oceans through equilibrium partitioning. Biodegradation (mostly aerobic) has been reported but the data are somewhat conflicting, varying from practically none to considerable degradation (Howard, 1991; Howard *et al.*, 1991). No significant adsorption to sediments is expected, especially not in sediments with a low organic carbon content, and no significant bioconcentration is expected (Howard, 1991). However, concentrations in biota (Dickson and Riley, 1976) and sediments (Bianchi *et al.*, 1991) are significantly higher than those in the surrounding environment.

Most of the above compounds have been intensively studied in ground- and fresh-water systems. However, much less is known about their presence and behaviour in the marine environment. This paper is deliberately limited to findings in the marine environment.

CHEMICAL AND PHYSICAL PROPERTIES

An overview of the most important physico-chemical properties of a number of chlorinated alkanes can be found in Table A5.1. All compounds are liquids at room temperature, but will exist primarily in the vapor phase as a result of their relatively high vapor pressure. This

property has led them to be important atmospheric contaminants. It can be expected that atmospheric transport followed by equilibrium partitioning will cause a widespread distribution in the environment, especially since residence times in the atmosphere are relatively high. It is believed (Howard, 1991) that as a result of their water solubility, Henry's Law constant and vapor pressure, no significant adsorption to soil will occur. The compounds are believed to be rapidly removed from soil by evaporation or leached out into ground water, where their fate remains unknown. The relatively low log K_{ow} would also suggest that no significant bioconcentration will occur.

SOURCES

Natural sources

No natural sources are known for the members of this group of compounds with the exception of chloroform, which is a plant volatile (Graedel, 1978).

Artificial sources

All members of the group are important industrial products or intermediates and are used in a variety of roles such as degreaser, fire extinguisher, grain fumigant, solvent, coupling agent in anti-knock gasoline, dilution agent for pesticides, floatation agent, paint remover, metal degreaser and dry cleaning agent (IARC, 1979; Drury and Hammons, 1979; Khan and Hughes, 1979; U.S. EPA, 1979, 1980; Vershueren, 1983; Wallace *et al.*, 1987).

Contamination of the environment will take place as a result of fugitive emissions during production and use of the chemicals or through waste water and effluents of the following industries: paint and ink industries, metal industries, non-ferrous metal industries, organic chemical industries (petroleum refining, pesticide production, rubber industries, plastic industries), pharmaceutical industries, and cleaning industries (Drury and Hammons, 1979; Johns, 1976; Khan and Hughes, 1979; Singh *et al.*, 1979; U.S. EPA, 1980, 1981; Vershueren, 1983). Chloroform is also produced during the chlorination of drinking water, cooling water, and municipal waste water (IARC, 1979; U.S. EPA, 1975, 1984). Annual production quantities for a number of chlorinated hydrocarbons can be found in Table A5.2.

Table A5.1. Relevant physico-chemical parameters for a number of chlorinated (C_1-C_2) hydrocarbons (after Howard, 1991; van Leeuwen *et al.*, 1992).

| Component | BP ¹ (°C) | MP ² (°C) | MW ³ (g) | log K _{ow} ⁴ | S ⁵ (mg/l) | Vapor pressure (mm Hg) | H ⁶ (atm·m ³ /mole) |
|---|-------------------------|-------------------------|------------------------|-------------------------------------|--------------------------|---------------------------|--|
| carbon tetrachloride CCl ₄ | 76.54 | -23 | 153.84 | 2.83 | 805 | 113.8 at 20°C | 3.04E-2 at 24.8°C |
| chloroform CHCl ₃ | 61.7 | -63.5 | 119.39 | 1.97 | 7950 | 246 at 25°C | 4.35E-3 at 25°C |
| dichloromethane CH ₂ Cl ₂ | 39.75 | -95.1 | 84.94 | 1.25 | 13000 | 434.9 at 25°C | 2.68E-3 |
| 1,1-dichloroethane CH ₃ CHCl ₂ | 57.3 | -96.98 | 98.96 | 1.79 | 5060 | 227 at 25°C | 5.87E-3 |
| 1,2-dichloroethane CH ₂ ClCH ₂ Cl | 83.47 | -35.36 | 98.96 | 1.48 | 8524 | 78.7 at 20°C | 9.77E-4 |
| tetrachloroethane CHCl ₂ CHCl ₂ | 146.5 | -36 | 167.86 | 2.3 | 2962 | 6.1 at 25°C | 4.55E-4 at 25°C |
| tetrachloroethylene C ₂ Cl ₄ | 121 | -19 | 165.82 | 3.4 | 150.3 | 18.49 at 25°C | 1.49E-2 |
| 1,1,2-trichloroethane CHCl ₂ CH ₂ Cl | 113.8 | -36.5 | 133.42 | 2.07 | 4420 | 30.3 at 20°C | 1.2E-3 at 20°C |
| 1,1,1-trichloroethane CCl ₃ CH ₃ | 74.1 | -30.4 | 133.42 | 2.49 | 1495 | 123.7 at 25°C | 8E-3 |
| trichloroethylene CCl ₂ CHCl | 87 | -73 | 131.40 | 2.42 | 1100 | 69.0 at 25°C | 1.03E-2 |
| pentachloroethane CCl ₃ CHCl ₂ | 161 | -29 | 202.29 | 3.05 | 480 | 3.5 at 25°C | 1.94E-3 at 25°C |

¹Boiling point, ²Melting point, ³Molecular weight, ⁴Log octanol/water partition coefficient, ⁵Solubility in water, ⁶Henry's Law Constant

Table A5.2. Annual production quantities for a number of chlorinated hydrocarbons (Howard, 1991).

| Chemical | Annual Production Quantities (tonnes) |
|-----------------------|--|
| monochloroethane | 304 000 (1976) |
| 1,1,1-trichloroethane | 286 000 (1976) |
| 1,2-dichloroethane | 3.6 million (1976) |
| carbon tetrachloride | 266 000 |

ANALYSIS

Volatiles are extracted from the matrices by liquid-liquid extraction or by volatilization. Eklund *et al.* (1978) used a batchwise liquid-liquid extraction in a funnel with pentane for the extraction of volatiles from sea water (see also Fogelqvist *et al.*, 1982; and Fogelqvist, 1985, in Krysell, 1989). Fogelqvist and Krysell (1986) used a liquid-liquid extraction in a segmented flow directly coupled to the on-column injector of the gas chromatograph for the analysis of sea water. This on-line extraction method requires minimum sample handling and thus guarantees a minimum of contamination.

Most other analytical methods are based on the volatilization of the compounds in question, using either static (equilibrium) (Helz and Hsu, 1978) or dynamic (non-equilibrium) headspace techniques (Bellar and Lichtenberg, 1974; Bianchi *et al.*, 1989, 1991; Borén *et*

al., 1982; Grob, 1973; Grob and Grob, 1974; Grob *et al.*, 1975; Grob and Zürcher, 1976). The contaminants in the sample are mobilized by vacuum extraction techniques, heating the sample, purging the sample with an inert gas such as He or N₂, or a combination of both methods.

The resulting gas phase is then immediately analysed (static headspace techniques) or an additional concentration step is performed (dynamic headspace techniques). To this purpose, off-line or on-line cold traps, solid traps (Tenax, activated carbon, silica gel or combinations) or a combination are used to concentrate the contaminants prior to analysis. A variant of the latter is the use of the gas chromatography (GC) column, cooled down to temperatures around -90°C, as the trap (P/WCC: Purging and Whole Column Cryotrapping) (Cohran, 1987; Pankow and Rosen, 1988; Pankow, 1990; Pankow and Rounds, 1991). Analysis is then performed through desorption of the traps and immediate injection in a gas chromatograph with an appropriate

detector (electron capture detector, Hall detector, or mass spectrometer).

DISTRIBUTION AND LEVELS IN THE MARINE ENVIRONMENT

Few data are available on the presence and distribution of these compounds in the marine environment, compared to other types of compounds such as polychlorinated biphenyls (PCBs). This is probably the result of problems that are associated with the analysis of the compounds and the assumption that the group in question should not be considered as a direct threat to the marine environment.

Water

Concentrations in sea water are generally low, in the ng l⁻¹ range or below, but exceptional concentrations up to 200 µg l⁻¹ have been reported (Table A5.3).

Evaporation appears to be the principal removal process for chlorinated alkanes, with half-lives ranging from several days to several years (Howard, 1991). The majority of data for removal processes is found in studies concerning ground water, fresh water, and drinking water (Wilson *et al.*, 1986). Biodegradation, hydrolysis, and photo-oxidation rates are considered to be insignificant in comparison with evaporation processes (Howard, 1991). Adsorption to sediments and bioconcentration in aquatic organisms are also not considered to be important removal processes (Howard, 1991). Table A5.4 gives an overview of both estimated and calculated half-lives for a number of chlorinated alkanes in aqueous systems. The half-lives reported in the table are the net result of the different processes mentioned above. Aerobic conditions will generally result in shorter half-lives, due to increased biodegradation.

Table A5.3. Concentrations of several chlorinated hydrocarbons in marine and estuarine water.

| Chemical | Location | Concentration | References |
|-----------------------|-------------------------|-------------------------------|---|
| carbon tetrachloride | Solent Estuary, UK | 10–311 ng l ⁻¹ | Bianchi <i>et al.</i> , 1991 |
| | Humber Estuary, UK | 3.1–18 ng l ⁻¹ | Krysell and Nightingale, 1993 |
| | Weddell Sea, Antarctica | 1.2–1.3 ng l ⁻¹ * | Krysell, 1992 |
| | Rhine Estuary | 0.96–8.1 ng l ⁻¹ | Krysell and Nightingale, 1993 |
| | Tees Estuary, UK | <25–29 ng l ⁻¹ | Dawes and Waldock, 1994 |
| | Wear Estuary, UK | <25–102 ng l ⁻¹ | Dawes and Waldock, 1994 |
| 1,1,1-trichloroethane | Liverpool Bay, UK | max 03.3 µg l ⁻¹ | Pearson and McConnell, 1975 |
| | Solent Estuary, UK | 0.01–1.01 µg l ⁻¹ | Bianchi <i>et al.</i> , 1991 |
| | Weddell Sea, Antarctica | 2 ng l ⁻¹ * | Krysell, 1992 |
| | Humber Estuary, UK | 5.1–53 ng l ⁻¹ | Krysell and Nightingale, 1993 |
| | Tees Estuary, UK | <10–602 ng l ⁻¹ | Dawes and Waldock, 1994 |
| | Wear Estuary, UK | <10–64 ng l ⁻¹ | Dawes and Waldock, 1994 |
| 1,2-dichloroethane | Gulf of Mexico | 0–210 ng l ⁻¹ | Sauer, 1981, in Howard, 1991 |
| | Solent Estuary, UK | 0.04–0.53 µg l ⁻¹ | Bianchi <i>et al.</i> , 1991 |
| | Tees Estuary, UK | 720–4020 ng l ⁻¹ | Dawes and Waldock, 1994 |
| trichloroethylene | Sea water | max 3.6 µg l ⁻¹ | Dyksen and Hess, 1982, in Howard, 1991 |
| | Rhine Estuary | 1.3–74 ng l ⁻¹ | Krysell and Nightingale, 1993 |
| | Wear Estuary, UK | <10–132 ng l ⁻¹ | Dawes and Waldock, 1994 |
| tetrachloroethylene | Sea water | 0.1–0.8 ng l ⁻¹ | Murray and Riley, 1973, Pearson and McConnell, 1975 |
| | Humber Estuary, UK | 0.87–17 ng l ⁻¹ | Krysell and Nightingale, 1993 |
| | Rhine Estuary | 1.3–47 ng l ⁻¹ | Krysell and Nightingale, 1993 |
| | Tees Estuary, UK | <10–175 ng l ⁻¹ | Dawes and Waldock, 1994 |
| chloroform | NE Atlantic Ocean | 4–13 ng l ⁻¹ | Sauer, 1981, in Howard, 1991 |
| | Gulf of Mexico | 4–200 µg l ⁻¹ | Murray and Riley, 1973 |
| | | 20–35 µg l ⁻¹ | Bianchi <i>et al.</i> , 1991 |
| | Tees Estuary, UK | <10–11,500 ng l ⁻¹ | Dawes and Waldock, 1994 |
| | Rhine Estuary | 4.8–91 ng l ⁻¹ | Krysell and Nightingale, 1993 |

*Values reported are calculated from Figure 4 in Krysell (1992) and are therefore an approximation.

Table A5.4. Aqueous half-lives for a number of volatile chlorinated hydrocarbons (Howard *et al.*, 1991).

| Chemical | Aqueous half-life | |
|-----------------------|----------------------------|-----------------------------|
| | Aerobic | Anaerobic |
| chloroform | H: 6 months L: 4 weeks | H: 4 weeks L: 1 week |
| 1,1-dichloroethane | H: 22 weeks L: 32 days | H: 88 weeks L: 128 days |
| 1,2-dichloroethane | H: 6 months L: 100 days | H: 24 months L: 400 days |
| 1,1,1-trichloroethane | H: 39 weeks L: 20 weeks | H: 156 weeks L: 80 weeks |
| trichloroethylene | H: 1 year L: 6 months | H: 4.5 years L: 98 days |
| tetrachloroethylene | H: 1 year L: 6 months | H: 4.5 years L: 98 days |

H= high value, L= low value

Sediments

Little is known of the fate and concentrations of chlorinated alkanes in marine sediments. Howard (1991) expected that evaporation from water will be the principal pathway for removal of chlorinated alkanes. Based on their physico-chemical properties, he also stated that sorption to sediments should be insignificant in comparison. However, O'Connor and Connolly (1980) in Bianchi *et al.* (1991) stated that sorptive action by sediments was directly involved in the removal of volatile organic compounds from overlying water, regardless of the sediment type. Similarly, Bianchi *et al.* (1991) demonstrated, during a case study in the Solent Estuary, that volatile organic compounds are ubiquitous in the estuary. They concluded that sediments have the

potential to accumulate and concentrate much higher levels than might normally be found in the water column. A distinctive seasonal variation was also observed, with the lowest concentrations in the period July–August and the highest concentrations in October–January. Apparently, higher temperatures during summer cause evaporation from the surface water to be dominant over deposition and sorption to sediments. Concentrations increase during autumn and winter as a result of lower temperatures combined with increased organic loads. Table A5.5 gives an overview of concentrations of a number of compounds in marine sediments and water. The concentrations in the sediments are generally higher than those in the surrounding water, confirming a concentration gradient between water and sediment.

Table A5.5. Concentrations of a number of volatile chlorinated hydrocarbons in the

Solent Estuary (Bianchi *et al.*, 1991).

| Chemical | Concentrations in water (ng l ⁻¹) | Concentrations in sediment (ng g ⁻¹) |
|-----------------------|--|---|
| carbon tetrachloride | <10–311 | 0.075–1.9 |
| dichloromethane | 15–1000 | 0.020–2.7 |
| 1,1,1-trichloroethane | <5–2790 | 0.070–31 |
| 1,2-dichloroethane | 15–955 | 0.070–11 |
| trichloroethylene | <10–603 | 0.070–4 |
| tetrachloroethylene | <10–343 | 0.085–20 |
| chloroform | 10–7500 | 0.097–23 |

Biota

Very few data are available on the presence and distribution of these compounds in marine biota. A number of authors (Dickson and Riley, 1976; Pearson and McConnell, 1975) have analysed biological tissues for the presence of these short-chained chlorinated hydrocarbons. Concentrations in marine fish and invertebrates vary up to 1100 ng g⁻¹ and 1040 ng g⁻¹, respectively. Their results (Table A5.6) clearly

demonstrate that the concentrations in biota are significantly higher than those in sediments or water (see above), indicating a certain degree of bioconcentration.

However, the potential for bioconcentration or biomagnification is considered to be very low (Howard, 1991; Dickson and Riley, 1976; Neeley *et al.*, 1974;

Pearson and McConnell, 1975; McConnell *et al.*, 1975; U.S. EPA, 1978) since calculated or estimated

bioconcentration factors (BCFs) are generally low (between 0.3 and 226, see Table A5.7), especially compared to other well-known environmental contaminants such as PCBs (BCFs up to 50 000, Veith *et al.*, 1979). As a general rule, it can be stated that bioconcentration increases with the degree of chlorination. It should be noted that the data in Table A5.6 date back to the 1970s and may therefore not reflect current conditions.

Even though the potential for bioconcentration is thought to be low, toxicity data suggest that the selected compounds should be considered as important environmental contaminants.

TOXICOLOGY

A variety of toxic responses, mainly in the liver and kidney, have been described (Della Porta *et al.*, 1961; Klaassen and Plaa, 1967, 1969; National Cancer Institute, 1976; Nielsen and Larsen, 1965; Recknagel *et al.*, 1973; Reuber and Glover, 1967). Humans are exposed by inhalation, skin contact, and the intake of contaminated water and food. Moreover, most members of the group are suspected or confirmed carcinogenic substances (ref.: Priority Toxic Pollutants). This also implies that even though the potential to bioconcentrate is low, the consequences may be important.

Table A5.6. Concentrations of a number of chlorinated hydrocarbons in marine biota.

| Chemical | Biota | Concentrations (ng g ⁻¹) | References |
|-----------------------|--|--------------------------------------|--|
| chloroform | marine fish (various species) | 5-851 | Dickson and Riley, 1976 Pearson and McConnell, 1975 |
| | marine invertebrates (various species) | 2-1040 | Dickson and Riley, 1976 Pearson and McConnell, 1975 |
| 1,1,1-trichloroethane | marine fish (various species) | 2-26 | Dickson and Riley, 1976 Pearson and McConnell, 1975 |
| | marine invertebrates (various species) | 0-34 | Dickson and Riley, 1976 Pearson and McConnell, 1975 |
| trichloroethylene | marine fish (various species) | 0.66-1100 | Pearson and McConnell, 1975 |
| | marine invertebrates (various species) | 2-250 | Pearson and McConnell, 1975 |
| tetrachloroethylene | marine fish (various species) | 0.3-479 | Pearson and McConnell, 1975 |
| | marine invertebrates (various species) | 0.5-176 | Pearson and McConnell, 1975 |
| carbon tetrachloride | marine fish (various species) | 3-209 | Dickson and Riley, 1976 |
| | marine invertebrates (various species) | 2-114 | Dickson and Riley, 1976 |

Table A5.7. Calculated or estimated bioconcentration factors (BCFs) of some chlorinated C₁-C₂ hydrocarbons.

| Chemical | BCF | References |
|-----------------------|-----------|---|
| carbon tetrachloride | 10-100 | Pearson and McConnell, 1975 |
| chloroform | 1.6-10.35 | Anderson and Lusty, 1980 Barrows <i>et al.</i> , 1980 |
| trichloroethylene | 2-25 | Dickson and Riley, 1976 Pearson and McConnell, 1975 |
| 1,2-dichloroethane | 0.3-8 | Barrows, <i>et al.</i> , 1980 Howard and Evenson, 1976, in Howard, 1991 |
| 1,1,1-trichloroethane | 8.9 | Davies and Robs, 1984, in Howard, 1991 |
| tetrachloroethylene | 38.9-226 | Neely <i>et al.</i> , 1974 Barrows, <i>et al.</i> , 1980 Lyman <i>et al.</i> , 1982 |

REFERENCES

Anderson, D.R., and Lusty, E.B. 1980. Acute toxicity and bioaccumulation of chloroform to four species of fresh water fish. NUREG/CR089, pp. 8-26. Pacific Northwest Laboratories, Richland, WA.

Barrows, M.E., Petrocelli, S.R., Macek, K.J., and Carroll, J.J. 1980. Bioconcentration and elimination of selected water pollutants by bluegill sunfish (*Lepomis macrochirus*). In Dynamics of exposure and hazard

assessment of toxic chemicals, pp. 379-392. Ann Arbor Press, Ann Arbor, Michigan.

Bellar, T.A., and Lichtenberg, J.J. 1974. Determining volatile organics at the µg/l level by gas chromatography. Journal of the American Water Works Association, 66:739.

Bianchi, A.P., Varney, M.S., and Phillips, J. 1989. Modified analytical technique for the determination of trace organics in water using dynamic headspace and gas

- chromatography-mass spectrometry. *Journal of Chromatography*, 467:111-128.
- Bianchi, A.P., Varney, M.S., and Phillips, J. 1991. Analysis of volatile organic compounds in estuarine sediments using dynamic headspace and gas chromatography-mass spectrometry. *Journal of Chromatography*, 542:413-450.
- Borén, H., Grimvall, A., and Sävenhed, R. 1982. Modified stripping technique for the analysis of trace organics in water. *Journal of Chromatography*, 252:139.
- Cohran, J.W. 1987. Selective water removal in purge/GC analysis of volatile aromatics in aqueous samples. *Journal of High Resolution Chromatography and Chromatography Communication*, 10:573.
- Dawes, V.J., and Waldock, M.J. 1994. Measurement of volatile organic compounds at UK national monitoring plan stations. *Marine Pollution Bulletin*, 28 (5):291-298.
- Della Porta, G., Terracini, B., and Shubick, P. 1961. Induction with carbon tetrachloride of liver cell carcinomas in hamsters. *Journal of the National Cancer Institute*, 26:4.
- Dickson, A.G., and Riley, J.P. 1976. The distribution of short-chain halogenated aliphatic hydrocarbons in some marine organisms. *Marine Pollution Bulletin*, 7(9):167-169.
- Drury, J.S., and Hammons, A.S. 1979. Investigations of selected environmental pollutants 1,2-dichloroethane. U.S. EPA-560/2-78-006, pp. 20-78. Environmental Protection Agency, Washington, D.C.
- Eklund, G., Josefsson, B., and Roos, C. 1978. Determination of volatile halogenated hydrocarbons in tap water, sea water and industrial effluents by glass capillary gas chromatography and electron capture detection. *Journal of High Resolution Chromatography and Chromatography Communication*, 1:34.
- Fogelqvist, E., and Krysell, M. 1986. The anthropogenic and biogenic origin of low molecular weight halocarbons in a polluted fjord, the Idefjorden. *Marine Pollution Bulletin*, 17(8):378-382.
- Fogelqvist, E., Josefsson, B., and Roos, C. 1982. Halocarbons as tracer substances in studies of the distribution patterns of chlorinated waters in coastal areas. *Environmental Science and Technology*, 16:479-482.
- GESAMP. 1990. Review of potentially harmful substances: Choosing priority organochlorines for marine hazard assessment. GESAMP Reports and Studies, No. 42.
- Graedel, T.E. 1978. Chemical compounds in the atmosphere. Academic Press, New York. 324 pp.
- Grob, K. 1973. Organic substances in potable water and in its precursor: Part I. Methods for their determination by gas-liquid chromatography. *Journal of Chromatography*, 84:243-255.
- Grob, K., and Grob, G. 1974. Organic substances in potable water and in its precursor: Part II. Applications in the area of Zürich. *Journal of Chromatography*, 90:303.
- Grob, K., Grob, K., Jr., and Grob, G. 1975. Organic substances in water and in its precursor: Part III. The closed loop stripping procedure compared with rapid lipid extraction. *Journal of Chromatography*, 106:299.
- Grob, K., and Zürcher, F. 1976. Stripping of trace organic substances from water: Equipment and procedure. *Journal of Chromatography*, 117:285.
- Helz, G.R., and Hsu, R.Y. 1978. Volatile chloro- and bromocarbons in coastal waters. *Limnology and Oceanography*, 23 (5):858-869.
- Howard, P.H. 1991. Handbook of environmental fate and exposure data for organic chemicals. Volume 2 (Solvents), 3rd ed., pp. 85-91, 100-109, 146-152, 153-160, 418-429, 450-460. Lewis Publishers, Incorporated, Chelsea, Michigan.
- Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M., and Michalenko, E.M. 1991. Handbook of environmental degradation rates, 2nd ed. Lewis Publishers, Incorporated, Chelsea, Michigan.
- IARC. 1979. Some halogenated hydrocarbons. IARC, 20:402-407.
- Johns, R. 1976. Air pollution assessment: 1,2-dichloroethane. VA:MTR-7164. The Mitre Corporation. 34 pp.
- Khan, Z.S., and Hughes, T.W. 1979. Source assessment: Chlorinated hydrocarbon manufacture. U.S. EPA-600/2-79-019g, pp. 48-66. Environmental Protection Agency, Washington, D.C.
- Klaassen, C.D., and Plaa, G.L. 1967. Relative effects of various chlorinated hydrocarbons on liver and kidney function in dogs. *Toxicology and Applied Pharmacology*, 10:119.
- Klaassen, C.D., and Plaa, G.L. 1969. Comparison of the biochemical alterations elicited in livers from rats treated with carbon tetrachloride, chloroform, 1,1,2-trichloroethane and 1,1,1-trichloroethane. *Biochemical Pharmacology*, 18:2019.

- Krysell, M. 1989. Halocarbons as marine tracers: Determination and applications. Department of Analytical and Marine Chemistry, Chalmers University of Technology and University of Göteborg.
- Krysell, M. 1992. Carbon tetrachloride and methyl chloroform as tracers of deep water formation in the Weddel Sea, Antarctica. *Marine Chemistry*, 39:297-310.
- Krysell, M., and Nightingale, P.D. 1993. Low molecular weight halocarbons in the Humber and Rhine estuaries determined using a new purge and trap gas chromatographic method. *Continental Shelf Research*,
- Krysell, M., and Wallace, D.W.R. 1988. Arctic Ocean ventilation studied with a suite of anthropogenic halocarbon tracers. *Science*, 242:746-749.
- Lyman, W.J., Reehl, W.F., and Rosenblatt, D.H. 1982. Handbook of chemicals property estimation methods. Environmental behavior of organic compounds. New York.
- McConnell, G., Ferguson, D.M., and Pearson, C.R. 1975. Chlorinated hydrocarbons and the environment. *Endeavour*, 34:13-18.
- Murray, A.J., and Riley, J.P. 1973. The determination of chlorinated aliphatic hydrocarbons in air, natural waters, marine organisms and sediments. *Nature*, 242:37-38.
- National Cancer Institute. 1976. Carcinogenesis bioassay of trichloroethylene. U.S. Department of Health, Education and Welfare, Washington, D.C.
- Neely, W.B., Branson, D.R., and Blau, G.E. 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. *Environmental Science and Technology*, 8:1113-1115.
- Nielsen, V.K., and Larsen, J. 1965. Acute renal failure due to carbon tetrachloride poisoning. *Acta Medical of Scandania*, 178:363.
- Pankow, J.F. 1990. Development of purge and trap with whole column cryotrapping for the analysis of ground water contaminated with organic compounds. U.S. EPA Report 90(8):29. Environmental Protection Agency, Washington, D.C.
- Pankow, J.F., and Rosen, M.E. 1988. Determination of volatile compounds in water by purging directly to a capillary column with whole column cryotrapping. *Environmental Science and Technology*, 22:398.
- Pankow, J.F., and Rounds, S.A. 1991. Direct sample-to-column purging with whole column cryotrapping (P/WCC) for the determination of volatile organic compounds in water. *Monitoring water in the 1990s: Meeting new challenges*, pp. 267-275. American Society for Testing and Materials, Philadelphia.
- Pearson, C.R., and McConnell, G. 1975. Chlorinated C₁ and C₂ hydrocarbons in the marine environment. *Proceedings of the Royal Society of London*, 189:305-332.
- Recknagel, R.O., Ugazio, G., Koch, R.R., and Glende, E.A., Jr. 1973. New perspectives in the study of experimental carbon tetrachloride liver injury. Williams and Wilkins, Baltimore.
- Reuber, M.D., and Glover, E.L. 1967. Cholangiofibrosis in the liver of buffalo strain rats injected with carbon tetrachloride. *British Journal of Experimental Pathology*, 48:319.
- Singh, H.B., Sulas, L.J., Shigeishi, H., and Scribner, E. 1979. Atmospheric distribution sources and sinks of selected halocarbons, hydrocarbons, SF₆ and N₂O. U.S. EPA-600/3-79-107. 34 pp. Environmental Protection Agency, Washington, D.C.
- U.S. EPA. 1975. Development document for interim final effluent limitations guidelines and new source performance standards for the significant organic products segment of the organic chemical manufacturing point source category. EPA-440/1-75/045. Environmental Protection Agency, Washington, D.C.
- U.S. EPA. 1978. In-depth studies on health and environmental impacts of selected water pollutants. EPA Contract No. 68-01-4646. Environmental Protection Agency, Washington, D.C.
- U.S. EPA. 1979. Source assessment: Chlorinated hydrocarbons manufacture. EPA-600/2-79-019G. Environmental Protection Agency, Washington, D.C.
- U.S. EPA. 1980. An exposure and risk assessment for dichloroethanes. Final draft report, pp. 3.1-3.10. Environmental Protection Agency, Washington, D.C.
- U.S. EPA. 1981. Treatability manual. EPA-600/2-82-001A, pp. I.12.23.1-I.12.23.5. Environmental Protection Agency, Washington, D.C.
- U.S. EPA. 1984. Health assessment document for chloroform. EPA-600/8-84-004A, pp. 3.4-3.28. Environmental Protection Agency, Washington, D.C.
- van Leeuwen, C.J., van der Zandt, P.T.J., Aldenberg, T., Verhaar, H.J.M., and Hermens, J.L.M. 1992. Application of qsars, extrapolation and equilibrium partitioning in aquatic effects assessment: I. Narcotic industrial pollutants. *Environmental and Toxicological Chemistry*, 11:267-282.

Veith, G.D., Defoe, D.L., and Bergstedt, B.V. 1979. Measuring and estimating the bioconcentration factor of chemicals in fish. *Journal of the Fisheries Research Board of Canada*, 36:1040–1048.

Verschueren, K. 1983. Handbook on environmental data on organic chemicals, pp. 118–191 and p. 486. Van Nostrand Reinhold Company, New York.

Wallace, L.A., Pellizari, E.D., Leaderer, B., and Zelon, H.S. 1987. Emissions of volatile organic compounds from building materials and consumer products. *Atmosphere and Environment*, 21:385–393.

Wilson, B.H., Smith, G.B., and Rees, J.F. 1986. Biotransformation of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material: A microcosm study. *Environmental Science and Technology*, 20:997–1002.

ACKNOWLEDGEMENT

This review note has been prepared by P. Roose, Fisheries Research Station, Ankerstraat 1, 8400 Oostende, Belgium.

ANNEX 6

MARINE CHEMISTRY WORKING GROUP

Reykjavík, Iceland, 3–7 April 1995

BENZENE AND ITS C₁–C₂ ALKYL DERIVATIVES IN THE MARINE ENVIRONMENT

INTRODUCTION

Benzene and C₁ and C₂ alkylated benzenes have similar physico-chemical properties, are important industrial products with large annual production amounts, and behave in a similar way in the marine environment. They are well-known atmospheric pollutants mainly associated with the use and combustion of fossil fuels. Atmospheric deposition and industrial wastewater discharges are the principal routes of entry of these compounds into the marine environment. The compounds are readily degraded in the atmosphere through reactions with photochemically produced hydroxyl radicals, and residence times in the atmosphere are therefore short. Biodegradation (mostly aerobic) is reported for all members of the group, with half-lives varying from several days to several weeks. No significant adsorption to sediments is expected, especially to sediments with a low organic carbon content, and no significant bioconcentration is expected to occur (Howard, 1990, 1991).

CHEMICAL AND PHYSICAL PROPERTIES

Table A6.1 gives an overview of the most important physico-chemical properties of these compounds. At room temperature they exist as liquids with a relatively high vapour pressure. This property, in combination with their production during the combustion of fossil fuels, has resulted in their being important atmospheric contaminants. Although the residence times of mono-aromatic hydrocarbons in the atmosphere are short, a proportion will reach the oceans and seas through equilibrium partitioning and wet deposition. Howard (1991) reported that little adsorption to soil will occur due to the high water solubility and vapour pressure of

these compounds. They are rapidly removed from soil by evaporation or leached out into ground water. Biodegradation in ground water has been demonstrated in the presence of oxygen (Barker *et al.*, 1987). The relatively low log K_{OW} would also suggest that no significant bioconcentration will occur.

SOURCES

Natural sources

Benzene and its C₁ and C₂ alkyl derivatives are natural constituents of crude oil (Graedel, 1978; IARC, 1982; NAS, 1980; Vershueren, 1983) and are produced as plant volatiles or during volcanic eruptions and forest fires (Graedel, 1978).

Artificial sources

These chemicals are important industrial intermediates and are used in the production of paints, varnishes, glues, and styrene, and as solvents (Fishbein, 1985; Graedel, 1978; Hawley, 1977; IARC, 1982; NAS, 1980; Vershueren, 1983; Walker, 1976). Contamination of the environment results from emissions and spills during their production and use as a chemical intermediate and during processes of petroleum refining, coke processing, and ore mining (Graedel, 1978; IARC, 1982; NAS, 1980). Wastewaters from these industries are another source of contamination. A significant amount will also enter the environment during production, venting, transport, and combustion of gasoline and diesel oil or emissions from residential wood-burning stoves and fireplaces (NAS, 1980). Annual production amounts can be found in Table A6.2.

Table A6.1. Relevant physico-chemical parameters for benzene and alkylated benzenes (after Howard, 1990, 1991; van Leeuwen *et al.*, 1992).

| Component | BP ¹ (°C) | MP ² (°C) | MW ³ (g) | log K _{OW} ⁴ | S ⁵ (mg l ⁻¹) | Vapour pressure (mm Hg at 25°C) | H ⁶ (atm·m ³ /mole) |
|------------------|-------------------------|-------------------------|------------------------|----------------------------------|---|------------------------------------|--|
| benzene | 80.1 | 5.5 | 78.11 | 2.13 | 1791 | 95.19 | 5.43 x 10 ⁻³ |
| toluene | 110.6 | -95 | 92.13 | 2.73 | 534.8 | 24.8 | 5.94 x 10 ⁻³ |
| <i>o</i> -xylene | 144.4 | -25 | 106.17 | 3.12 | 175 | 6.6 | 5.1 x 10 ⁻³ |
| <i>m</i> -xylene | 139.3 | -47.4 | 106.17 | 3.20 | 146 | 8.3 | 7.68 x 10 ⁻³ |
| <i>p</i> -xylene | 137 | 13–14 | 106.17 | 3.15 | 156 | 8.7 | 7.68 x 10 ⁻³ |
| ethylbenzene | 136.2 | -94.97 | 106.16 | 3.15 | 161 | 9.53 | 8.44 x 10 ⁻³ |

¹Boiling point, ²Melting point, ³Molecular weight, ⁴Log octanol/water partition coefficient, ⁵Solubility in water, ⁶Henry's Law Constant

Table A6.2. Annual production quantities for benzene, toluene, and ethylbenzene in the U.S.A. (Howard, 1991).

| Chemical | Annual Production Quantities (tonnes) |
|--------------|---------------------------------------|
| benzene | 4 million |
| toluene | 2.5 million |
| ethylbenzene | 3000 |

ANALYSIS

Traditional liquid extraction techniques (Law *et al.*, 1991) or static (equilibrium) and dynamic (non-equilibrium) headspace techniques (Bellar and Lichtenberg, 1974; Bianchi *et al.*, 1989, 1991; Borén *et al.*, 1982; Grob, 1973; Grob and Grob, 1974; Grob *et al.*, 1975; Grob and Zürcher, 1976) are used to isolate these compounds. Dynamic headspace techniques (purge and trap) offer the advantage of an additional concentration step. This concentration step is, in many cases, necessary to obtain adequate sensitivity for environmental samples. Chemicals in the sample are mobilized by heating and/or purging the sample with inert gases such as He or N₂ or by using vacuum extraction techniques. The resulting gas phase is subsequently injected into a gas chromatograph (static headspace techniques) equipped with a suitable detector (in most cases a mass spectrometer), or an additional concentration step is performed (dynamic headspace techniques). Components in the carrier gas are subsequently concentrated using off-line or on-line cold traps, solid traps (Tenax, activated carbon, silica gel or combinations) or a combination of these, prior to injection into a gas chromatograph.

DISTRIBUTION AND LEVELS IN THE MARINE ENVIRONMENT

Data on the presence and distribution of these chemicals in the marine environment are generally sparse. This is probably due both to difficulties associated with the analysis, and the assumption that they are not considered to be a danger to the marine environment.

Water

Concentrations in sea water are generally low, in the ng l⁻¹ range or below, but exceptional concentrations up to 400 µg l⁻¹ have been reported (Table A6.3). Evaporation is thought to be one of the principal processes of removal, but biodegradation can be equally important

(Howard, 1990, 1991; Wakeham *et al.*, 1983). The predominant process will depend on water temperature, mixing conditions, the existence of acclimated micro-organisms, and the presence of oxygen. Degradation half-lives for benzene and the alkylated benzenes can be found in Table A6.4. Adsorption to sediments and bioconcentration in aquatic organisms are not considered to be important removal processes (Howard, 1991), although some adsorption to sediments may be expected. The half-lives are the net result of all the processes that lead to degradation in aquatic systems and are an estimate of the highest and lowest rates of removal (Table A6.4). The differences between the half-lives under aerobic and anaerobic conditions are mainly the result of different biodegradation processes. Aerobic conditions will generally enhance biodegradation.

Sediment

Concentrations reported in sediments are given in Table A6.5. Although adsorption to sediments is thought to be unimportant, some adsorption might occur (Howard, 1991). Bianchi *et al.* (1991) demonstrated that benzene, alkylated benzenes, and other volatile organic compounds were ubiquitous in the Solent Estuary. They concluded that sediments have the potential to accumulate and concentrate much higher levels than might normally be found in the water column. A distinctive seasonal variation was also observed, with the lowest concentrations in the period July–August and the highest concentrations in October–January. Higher temperatures during summer cause evaporation from the surface water to dominate over deposition and sorption to sediments. Concentrations increase during autumn and winter as a result of lower temperatures combined with increased organic loads. This was in agreement with the statement of O'Connor and Connolly (1980) cited in Bianchi *et al.* (1991) which claimed that sorptive action by sediments was directly involved in the removal of volatile organic compounds from overlying water, regardless of the sediment type.

Table A6.3. Marine and estuarine water concentrations of benzene and alkylated benzenes.

| Chemical | Location | Concentrations | Reference |
|---------------------------------|----------------------------------|--|--|
| benzene | Gulf of Mexico | 5–15 ng l ⁻¹ | Sauer, 1981 in Howard, 1991 |
| | Solent Estuary, UK | 0.100–55 µg l ⁻¹ | Bianchi <i>et al.</i> , 1991 |
| toluene | Gulf of Mexico | 3–376 ng l ⁻¹ | Sauer, 1978, 1981 in Howard, 1991 |
| | Solent Estuary Vineland Sound | 0.010–400 µg l ⁻¹ 10–54 ng l ⁻¹ | Bianchi <i>et al.</i> , 1991 Sauer, 1978, 1981 in Howard, 1991 |
| <i>m</i> - and <i>p</i> -xylene | Gulf of Mexico | 2.7–24.4 ng l ⁻¹ | Sauer, 1978, 1981 in Howard, 1991 |
| | Vineland Sound | 4.5–66 ng l ⁻¹ | Sauer, 1978, 1981 in Howard, 1991 |
| <i>m</i> -xylene | Solent Estuary | 15–955 ng l ⁻¹ | Bianchi <i>et al.</i> , 1991 |
| <i>o</i> -xylene | Vineyard Sound | 1.8–2.5 ng l ⁻¹ | Gschwend <i>et al.</i> , 1982 |
| | Solent Estuary | 0.010–400 µg l ⁻¹ | Bianchi <i>et al.</i> , 1991 |
| | Gulf of Mexico | 1–30 ng l ⁻¹ | Sauer, 1978, 1981 in Howard, 1991 |
| ethylbenzene | Gulf of Mexico | 0.50–5.0 µg l ⁻¹ | Sauer, 1978, 1981 in Howard, 1990 |
| | Solent Estuary | 0.010–312 µg l ⁻¹ | Bianchi <i>et al.</i> , 1991 |

Table A6.4. Aqueous half-lives for benzene and alkylated benzenes (Howard *et al.*, 1991).

| Chemical | Aqueous half-life | |
|------------------|-------------------|--------------|
| | Aerobic | Anaerobic |
| benzene | H: 16 days | H: 24 months |
| | L: 5 days | L: 16 weeks |
| toluene | H: 22 days | H: 30 weeks |
| | L: 4 days | L: 8 weeks |
| <i>o</i> -xylene | H: 4 weeks | H: 12 months |
| | L: 1 week | L: 6 months |
| <i>m</i> -xylene | H: 4 weeks | H: 16 weeks |
| | L: 1 week | L: 1 week |
| <i>p</i> -xylene | H: 4 weeks | H: 16 weeks |
| | L: 1 week | L: 4 weeks |
| ethylbenzene | H: 10 days | H: 228 days |
| | L: 3 days | L: 176 days |

H= high value, L= low value

Table A6.5. Concentrations of benzene and alkylated benzenes in the Solent Estuary (Bianchi *et al.*, 1991).

| Chemical | Concentration in water ng l ⁻¹ | Concentration in sediment ng l ⁻¹ |
|------------------|--|---|
| benzene | 0.10–55 | 0.3–97 |
| toluene | 0.01–400 | 0.55–480 |
| <i>o</i> -xylene | 0.010–400 | 0.87–480 |
| <i>m</i> -xylene | 15–955 | 0.07–11 |
| ethylbenzene | 0.01–312 | 0.51–201 |

Biota

Few data are available on the concentrations and distribution of benzene and alkylated benzenes in marine biota. Table A6.6 gives an idea of concentrations that were determined in several marine species.

Concentrations are low and in the same range as those in sediments. A conclusion might be that this group of chemicals shows little tendency to bioconcentrate. Similar results were expected from calculated and estimated bioconcentration factors (BCFs) (Howard, 1991).

Table A6.6. Concentrations of benzene and alkylated benzenes in marine biota.

| Chemical | Species | Concentration | Reference |
|--------------|--|---------------|---|
| benzene | oyster (<i>Crassostrea virginica</i>): Lake Pontchartrain | 220 ng/g | Ferrario <i>et al.</i> , 1985 |
| | clam (<i>Rangia cuneata</i>): Lake Pontchartrain | 260 ng/g | Ferrario <i>et al.</i> , 1985 |
| toluene | oyster (<i>Crassostrea virginica</i>): Lake Pontchartrain | 3.4 ng/g | Ferrario <i>et al.</i> , 1985 |
| | clam (<i>Rangia cuneata</i>): Lake Pontchartrain | 11–18 ng/g | Ferrario <i>et al.</i> , 1985 |
| | marine fish (in a petroleum contaminated harbour, Japan) | 5 µg/g | Tsani-Bazaca, <i>et al.</i> , 1981 in Howard, 1991 |
| ethylbenzene | bottom fish | 100 ng/g | Nicola, 1987, in Howard, 1990 |

It is very likely that the physico-chemical properties, such as log K_{OW} , of the selected aromatics are not the only factors influencing bioconcentration. Rapid metabolism prevents bioaccumulation and can result in detoxification or toxic activity. In the case of benzene, metabolism is a prerequisite for toxicity (Kalf *et al.*, 1987). The environmental impact of benzene lies in its presence and widespread distribution rather than its potential to bioconcentrate.

TOXICOLOGY

Of these chemicals, only benzene has been confirmed as a carcinogen (leukemic agent) in humans (Verschuere, 1983). Uptake by humans will occur primarily from inhalation of contaminated air and ingestion of contaminated water. Consumption of fish need not be considered as an important source, since the chemical has a low potential for bioconcentration. Carcinogenicity of the alkylated benzenes is suspected, but not proven. Benzene and toluene have been shown to adversely affect aquatic organisms (Verschuere, 1983). Exposure of marine organisms to these compounds via their food is likely to be low, but data are non-existent.

REFERENCES

Barker, J.F., Patrick, G.C., and Major, D. 1987. Natural attenuation of organic hydrocarbons in a shallow sand aquifer. *Ground Water Monitoring Review*, 7:64–72.

Bellar, T.A., and Lichtenberg, J.J. 1974. Determining volatile organics at the µg/l level by gas chromatography. *Journal of the American Water Works Association*, 66:739.

Bianchi, A.P., Varney, M.S., and Phillips, J. 1989. Modified analytical technique for the determination of trace organics in water using dynamic headspace and gas chromatography-mass spectrometry. *Journal of Chromatography*, 467:111–128.

Bianchi, A.P., Varney, M.S., and Phillips, J. 1991. Analysis of volatile organic compounds in estuarine sediments using dynamic headspace and gas chromatography-mass spectrometry. *Journal of Chromatography*, 542:413–450.

Borén, H., Grimvall, A., and Sävenhed, R. 1982. Modified stripping technique for the analysis of trace organics in water. *Journal of Chromatography*, 252:139.

Ferrario, J.B., Lawler, G.C., Deleon, I.R., and Laster, J.L. 1985. Volatile organic pollutants in biota and sediments of Lake Pontchartrain. *Bulletin of Environmental and Contaminant Toxicology*, 34:246–255.

Fishbein, L. 1985. An overview of environmental and toxicological aspects of aromatic hydrocarbons. I. Benzene. *Science and the Total Environment*, 43:165–183.

- Graedel, T.E. 1978. Chemical compounds in the atmosphere. Academic Press, New York.
- Grob, K. 1973. Organic substances in potable water and in its precursor. I. Methods for their determination by gas-liquid chromatography. *Journal of Chromatography*, 84:243-255.
- Grob, K., and Grob, G. 1974. Organic substances in potable water and in its precursor. II. Applications in the area of Zürich. *Journal of Chromatography*, 90:303.
- Grob, K., Grob, K. Jr., and Grob, G. 1975. Organic substances in water and in its precursor. III. The closed loop stripping procedure compared with rapid lipid extraction. *Journal of Chromatography*, 106:299.
- Grob, K., and Zürcher, F. 1976. Stripping of trace organic substances from water. Equipment and procedure. *Journal of Chromatography*, 117:285.
- Gschwend, P.M., Zafirion, O.C., Mantoura, R.F.C., Schwarzenbach, R.P., and Gagosian, R.B. 1982. Volatile compounds at a coastal site. 1. Seasonal variations. *Environmental Science and Technology*, 16:31-38.
- Hawley, G.G. 1977. The condensed chemical dictionary. 9th ed.
- Howard, P.H. 1990. Handbook of environmental fate and exposure data for organic chemicals: Large production and priority pollutants, Vol. 1, pp. 325-334. Lewis Publishers, Inc. Chelsea, Michigan.
- Howard, P.H. 1991. Handbook of environmental fate and exposure data for organic chemicals: Solvents, Vol. 2, pp. 29-39, 435-444, 505-515, 516-525, 526-535. Lewis Publishers, Inc. Chelsea, Michigan.
- Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M., and Michalenko, E.M. 1991. Handbook of environmental degradation rates. 2nd ed. Lewis Publishers, Inc. Chelsea, Michigan.
- IARC. 1982. Some industrial chemicals and dyestuffs. *Monograph*, 29:99-106.
- Kalf, G.F., Post, G.B., and Snyder, R. 1987. Solvent toxicology: Recent advances in the toxicology of benzene, the glycol ethers, and carbon tetrachloride. *Annual Review of Pharmacological Toxicology*, 27:399-427.
- Law, R.J., Fileman, T.W., and Matthiessen, P. 1991. Phthalate esters and other industrial organic chemicals in the North and Irish Seas. *Water Science and Technology*, 24 (10):127-134.
- NAS. 1980. The alkyl benzenes.
- van Leeuwen, C.J., van der Zandt, P.T.J., Aldenberg, T., Verhaar, H.J.M., and Hermens, J.L.M. 1992. Application of qsars, extrapolation and equilibrium partitioning in aquatic effects assessment. I. Narcotic industrial pollutants. *Environmental and Toxicological Chemistry*, 11:267-282.
- Verschueren, K. 1983. Handbook of environmental data on organic chemicals, pp. 118-191. Van Nostrand Reinhold Company, New York.
- Wakeham, S.G., Davis, A.C., and Karas, J.A. 1983. Mesocosm experiments to determine the fate of volatile organic compounds in coastal sea water. *Bulletin of Environmental Contamination and Toxicology*, 31:582-584.
- Walker, P. 1976. Air pollution assessment of toluene, pp. 1-22. VA: 46-92 MTR-7215. Mitre Corp., McLean.

ACKNOWLEDGEMENT

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ANNEX 7

MARINE CHEMISTRY WORKING GROUP

Reykjavík, Iceland, 3–7 April 1995

RECOMMENDATION LIST

Recommendation 1

The MCWG recommends that a workshop should be organized on estuarine behaviour of metals preceding directly the next MCWG meeting, chaired by J.F. Chiffolleau.

Recommendation 2

The MCWG recommends that an interlaboratory study for the analysis of trace metals in sea water be organized by B. Pedersen (project manager), S. Berman, J.F. Chiffolleau and J. Olafsson. A contribution in the costs is to be requested from the participants.

Recommendation 3

It is recommended that MCWG is given the permanent task to manage a list of contaminants which can be monitored in biota and sediments on a routine basis, including information on actual analytical proficiency obtained from interlaboratory studies.

Recommendation 4

The MCWG recommends that the paper 'Review of results of the intercomparison programme on the analysis of CBs in marine media' be published in the *ICES Cooperative Research Report* series together with the report on step 4 of the intercomparison programme.

Recommendation 5

The MCWG (W. Cofino, Chairman) should accept the offer made by the Instituto Hydrografico in Lisbon to host the next meeting in Portugal. This meeting should be held from 10–16 February 1996 to carry out the following tasks:

- a) to review the planning of the Sixth Intercomparison Exercise on the Analysis of Nutrients in Sea Water (NUTS 6);
- b) to review the progress in an interlaboratory study on trace metals in sea water;
- c) to review the status of the EU - QUASIMEME project and its implications for the work of the MCWG;
- d) to review the outcome of the QUASIMEME interlaboratory study on planar CBs in marine media;
- e) to review the outcome of the Workshop on Estuarine Behaviour of Metals;
- f) to review the results of the coordinated research on lipids;
- g) to review and report on the results of coordinated investigations on lipids as co-factors;
- h) to assess the review notes on modern pesticides, Igarol 1051, tris(4-chlorophenyl)methane and tris(4-chlorophenyl)methanol, triphenyltin, butyltin and organo-mercury;
- i) to nominate a new chairman for the working group;
- j) to review the progress on chemical associations of various metals and liver lipid types;
- k) to update, where appropriate, the list of contaminants which can be monitored routinely on a routine basis, including a discussion about actual analytical proficiency based on recent interlaboratory studies;
- l) to review the progress on a joint study to compare and contrast different multivariate methods on a common data set.

