Advisory Committee on the Marine Environment

ICES CM 1997/Env:2
Ref: D+E

REPORT OF THE

MARINE CHEMISTRY WORKING GROUP

Ostende, Belgium
3–8 March 1997

International Council for the Exploration of the Sea

Conseil International pour l'Exploration de la Mer

Palægade 2–4 DK–1261 Copenhagen K Denmark

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1 OPENING OF THE MEETING

The Chairman, Dr B. Pedersen, opened the meeting of the Marine Chemistry Working Group (MCWG) at 10.00 hrs on 3 March 1997. Dr W. Vyncke, Director of the Rijksstation voor Zeevisserij in Oostende, welcomed the Working Group on behalf of the Institute.

Working Group participants introduced themselves and briefly described their main area(s) of research. The list of participants is given in Annex 1.

2 ADOPTION OF THE AGENDA

The terms of reference for this meeting of the Marine Chemistry Working Group (ICES C.Res.1996/2:15:1) were to:

a) review and finalise draft guidelines for monitoring PAHs in biota and, with WGMS, in sediments [OSPAR 1997/1.1];

b) review the outcome of the Sixth Intercomparison Exercise on Trace Metals in Sea Water;

c) assess the need for and possibilities to organise an interlaboratory study on organotin analysis;

d) review the progress of studies looking into the associations between metals and lipids in biological tissues and report on the implications for marine monitoring;

e) review the final guidelines prepared by the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea [HELCOM 1996/3];

f) review progress in the collaborative study on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe);

g) review and report on progress on a joint study to compare and contrast the different results of using multivariate methods on a common data set on PCBs in fish-eating marine mammals;

h) review the performance for metals of laboratories in recent NOAA and QUASIMEME interlaboratory studies, and derive indicators for performance which can be used in the design of monitoring programmes as a representative estimate for between-laboratory variability;

i) review the overview papers on chlorinated solvents and benzene, toluene, and xylene (BTX) in fish, chlorinated dioxins and furans in sediments, the formation of hexachlorobenzene (HCB) metabolites, toxaphene, Irgarol 1051 and phenyltins [HELCOM 1996/2];

j) update, where appropriate, the list of contaminants which can be monitored on a routine basis, including a discussion about actual analytical proficiency based on recent interlaboratory studies;

k) review the paper on bioaccumulation and biomagnification of PCBs in the food chain, with the aim of facilitating a more detailed request on the transfer of halogenated compounds in food chains by HELCOM [HELCOM 1996/9];

l) review papers on units for nutrients and oxygen, total nitrogen methods, the reliability of old nutrient data, and particulate organic carbon (POC) in anoxic waters;

m) review the paper on quality assurance of data to be loaded in a database, and prepare general guidelines for this activity;

n) review the paper on methods for oxygen determination and their quality assurance and provide guidance for OSPAR;

o) review descriptions of members' protocols for quality control procedures on nutrient analysis;

p) review the updated paper on DOC/TOC in sea water including estuaries;

q) based on a response from the IWC on cetacean diets, provide information on contaminant levels in these prey species.

In addition, together with WGEAMS [ICES C.Res.1996/2:15:4(f)], MCWG should also review information gathered intersessionally on variance components in seabird egg analysis.

The Chairman had incorporated all of these items into the agenda.

Shortly before the meeting, the Chairman was informed by the ICES Environment Secretary, J. Pawlak, that term of reference (q) 'to provide information on contaminant levels in prey species in cetacean diets' had been withdrawn from the work programme as no information had been received from the International Whaling Commission (IWC). J. Pawlak had also informed the Chairman about an item arising from the 1997 meeting of the OSPAR Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (SIME 1997, i.e., to review the Report of the OSPAR/ICES Workshop on the Overall Evaluation and Update of Background/Reference Concentrations for Nutrients and Contaminants in Sea Water, Biota and

Sediment. Hence, this item is on the agenda of all three Subgroups.

Prior to the meeting, the Chairman had also received a copy of the first draft report of the ICES/HELCOM Baseline Study of Contaminants in Baltic Sea Sediments from J. Pawlak. Although MCWG was not requested to review the report, a copy of it was distributed to the Chairmen of the Subgroups to be dealt with as they felt appropriate.

Two new plenary lectures, one by R. Law and one by M. Leermakers, were suggested to be added to the agenda in addition to the planned presentations by P. Roose and M. Lebeuf.

MCWG adopted the agenda, with the suggested changes. The annotated agenda is provided in Annex 2.

The six plenary presentations were scheduled as follows: two for Tuesday, 3 March by K. Stange and R. Law; two for Wednesday, 4 March by G. Rimkus and M. Leermakers; and two for Thursday, 5 March by P. Roose and M. Lebeuf.

The work was carried out in three Subgroups. The members and guest participants were grouped as follows:

Chemical Oceanography Subgroup

S. Carlberg (Chairman), A. Aminot, L. Føyn, D. Kirkwood, M. Krysell, K. Mäkelä, K. Nagel, J. Ólafsson, O. Vagn Olsen;

Trace Metals Subgroup

G. Asmund (Chairman), B. Pedersen, G. Audunsson, S. Berman, V. Besada Montenegro, J.F. Chiffoleau, W. Cofino, M. Leermakers, J.R. Larsen (also in Organics Subgroup), K. Parmentier, G. Vlachonis;

Organics Subgroup

J. Klungsøyr (Chairman), A. Abarnou, J. Biscaya, J. de Boer, B. Jansson, P. Henschel, R.J. Law, M. Lebeuf, E. McGovern, G. Rimkus, P. Roose, K. Stange, D. Wells, A. Van der Zande.

3 REPORT OF THE 84TH ICES STATUTORY MEETING

The Chairman informed the participants that all of the tasks requested for consideration by the MCWG at the 1996 ICES Annual Science Conference (84th Statutory Meeting) had been incorporated into the draft agenda. The MCWG was informed by Stig Carlberg that there had not been time at the last Statutory Meeting to present and discuss the reports of the different working groups reporting to ACME. A different procedure was planned for the next Statutory Meeting in order to ensure that sufficient time was allocated to handle the reports.

4 REPORTS ON RELATED ACTIVITIES

4.1 OSPAR and HELCOM

Official requests from the regulatory Commissions have been included in the agenda. For HELCOM, advice is requested:

- regarding organotins;
- on the final guidelines prepared by the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea,
- on the bioaccumulation and biomagnification of halogenated compounds in the food chain.

For OSPAR, guidelines for monitoring PAHs are requested.

4.2 Intergovernmental Oceanographic Commission (IOC)

No items were raised by the members on this agenda item.

4.3 ICES

No additional points were raised by ICES at the meeting.

J.R. Larsen, ICES Environment Data Scientist, and S. Carlberg, in his capacity as Chairman of ACME, briefly informed MCWG about the present and future structure of ICES committees and working groups. This topic was further discussed informally in the Subgroups.

4.4 EU QA Pilot Project 'QUASIMEME'

D. Wells gave an overview of the EU project QUASIMEME which was finalized in March 1996. A full report of this project will be published as a special issue of the Marine Pollution Bulletin in early summer 1997. The QUASIMEME project has continued on a subscription basis for participating laboratories. Membership in the new QUASIMEME Laboratory Performance Studies is open to all institutes. Institutes in the Baltic countries, Poland, and Russia have also been invited to participate and have been supplied test materials according to their selected requirements. About 120 laboratories worldwide have now joined the scheme. A brief review of both QUASIMEME Projects is provided in Annex 3.

4.5 EU SMT Project 'Quality Assurance of Sampling and Sample Handling (QUASH)'

W. Cofino outlined the outcome of the successful bid to the EU to provide funding for the 'QUASH' project. The coordinators of each of the workgroups gave an overview of the various aspects of the programme. Further details of the project are given in an article on QUASH, attached as Annex 4.

4.6 Other Activities

S. Berman reported the following information:

1) *(ISO/REMCO) ISO's Committee on Reference Materials*

ISO Guide 34—Quality System Guidelines for the Production of Reference Materials—was issued last spring. This document sets out guidelines for the producers of reference materials on the interpretation of ISO Guide 25 and the ISO 9000 series with respect to the production of reference materials.

This is driven by two factors: the need to produce high quality reference materials and the need to guide accreditation bodies when producers seek accreditation under Guide 25 or registration under ISO 9002.

The end result should be more reliable and better reference materials for the user laboratories.

2) *International Committee on Weights and Measures*

Several years ago, and about 100 years after its founding, the International Committee on Weights and Measures (CIPM) became aware of the fact that there are chemical standards as well as physical standards. As a result, the Consultative Committee on the Quantity of Matter (CCQM) was established in 1993, one of eight standing committees of the CIPM. The others all deal with physical standards.

This is a committee at the highest level of chemical metrology drawing its representation from the national laboratories of participating nations.

Among the first tasks of the CCQM is to intercompare national laboratories using fundamental methodologies such as isotope dilution mass spectrometry. Once intercomparabilty is established among national laboratories, then the traceability of work in the laboratories of various countries can be more readily achieved for all phases of chemical analysis. A major factor driving this work is world trade and international monitoring programmes.

3) *North American Metrology Agreement (NORAMET)*

The establishment of the North American Free Trade Agreement (NAFTA) among Canada, Mexico, and the United States resulted in a parallel metrology agreement among the national laboratories of the three countries (National Research Council of Canada (NRC), Centro Naçional de Metrologia of Mexico, and the US National Institute of Standards and Technology(NIST)).

Of nine standing committees of NORAMET, one deals with chemical measurement.

The three national laboratories are in the process of intercomparing themselves beginning with trace measurements in the environment. This process has already been going on for many years in an unofficial and highly successful cooperative programme between NRC and NIST. This cooperation has now been intensified and expanded.

5 REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES

L. Føyn gave a short presentation of some results from a Norwegian cruise in November-December 1996. These results clearly illustrate that Atlantic water with high nitrate concentrations enters the North Sea via two pathways, through the Channel and over the northern boundary.

6 REQUESTS FROM ACME AND REGULATORY COMMISSIONS

Requests from ACME were included in the agenda.

7 PLENARY PRESENTATIONS

7.1 Mercury in the Marine Environment

M. Leermakers gave a presentation on the presence of mercury in the marine environment. The biogeochemical cycle of mercury was discussed, including the behaviour of mercury species in the Scheldt Estuary. The lecture demonstrated the importance of correct speciation analysis of the different Hg compounds when studying the fate of mercury in the environment. Artifact formation of methylmercury during extraction of environmental samples by distillation could be one serious mistake in the analysis. The presentation also clearly illustrated the need to understand the biogeochemical cycle of mercury in order to be able to design a good monitoring programme and to make reasonable estimates of mercury fluxes to the sea.

7.2 AMAP, an Example of a Newly Established Monitoring and Assessment Programme

K. Stange gave an overview of the Arctic Monitoring and Assessment Programme (AMAP). The programme started in 1991 and there is no special convention for the programme but the eight countries bordering the Arctic Ocean have signed a multilateral agreement. The programme covers not only the presence and fate of organic contaminants, radionuclides, and metals in the marine environment, but also includes other components of the environment, e.g., the atmosphere, fresh water and effects on human beings. The assessment of the Arctic area is based on existing data and on new data compiled under the framework of AMAP. Other members of MCWG involved in the programme supplemented K. Stange's presentation. The first phase of AMAP will end in June 1997 with a Ministerial Conference and Scientific Symposium in Tromsø, Norway. More information about AMAP is available on the World Wide Web (www).

7.3 Sea Empress Oil Spill: Impact on Fisheries and Marine Life

R. Law gave a presentation on the impact of the oil spill of the '*Sea Empress*' in February 1996. Approximately 70,000 tonnes of crude oil were spilled in an area with very important fishing activity.

The impact of the oil spill was closely followed in several projects, e.g., oil/PAH concentrations were measured regularly in different fish species, shellfish, and plants. Biological effects studies were also performed. Criteria for recovery of the area were set up and used for deciding on removal of fishery restrictions. The effects on fisheries were less than predicted and most fishing was resumed about six months after the spill.

7.4 Synthetic Musk Compounds in the Aquatic Environment

G. Rimkus gave a presentation on synthetic musk compounds in the aquatic environment. Synthetic musk fragrances (nitro musks or polycylic musk compounds) are especially used in soaps, cosmetics, and laundry detergents. The world-wide production is >1000 tonnes/year for the two types of musk compounds and there is only little knowledge about the bioaccumulation and toxicology of these compounds. However, certain of these musk compounds (MA and ATTN) are no longer produced because of their toxicity. The compounds were detected early in rainbow trout in Denmark, and were later found in several fish species as well as in water samples and in sediment and sewage sludge. The presentation clearly illustrated the need to continuously develop new methods in order to be able to register and follow the fate of new anthropogenic compounds entering the aquatic environment.

The presentations 'Determination and presence of volatile organic compounds in marine biota' given by P. Roose and 'Chlorinated dioxins and furans in the lower St. Lawrence estuary' presented by M. Lebeuf are covered in Sections 8.1.9.4 and 8.1.9.5, respectively.

8 SUBGROUP ACTIVITIES AND DISCUSSIONS

For the sake of clarity, the outcome of the discussions on topics requested by ACME will be presented in Section 8.1. Then, the discussions about the items arising from the SIME 1997 meeting (see Section 4.1, above) will be reported in Section 8.2. Finally, any additional items discussed in the subgroups will be dealt with in Sections 8.3 to 8.5.

8.1 Topics Requested by ACME

8.1.1 Review and finalise draft guidelines for monitoring PAHs in biota and, with WGMS, in sediments [OSPAR 1997/1.1]

This item resulted from a request from OSPAR [OSPAR 1997/1.1] for guidelines on the determination of PAHs in biota and sediments; aspects of this request have also been passed to the Working Group on Marine Sediments in Relation to Pollution (WGMS) and the Working Group on Environmental Assessment and Monitoring Strategies (WGEAMS) for consideration at their 1997 meetings. The Organics Subgroup considered a draft paper produced by WGMS at its 1997 meeting, and suggested that a tighter focus was needed in order to meet the needs of OSPAR. The document should focus on analytical aspects and the selection of PAH determinands relative to the sources (combustion/oil and oil products) to be investigated, and should also reflect the experience of recent intercomparison and field studies. For sampling procedures and strategy, it should, in principle, be possible to refer to general guidance for organochlorine analysis; in order for more specific information to be provided regarding PAHs, the aims of the monitoring programme would need to be more clearly defined.

A revised draft will be prepared shortly after MCWG 1997 which incorporates the recommendations of the Organics Subgroup. This will be circulated for comment by e-mail to all members of the Subgroup, and also to F. Smedes and K. Stange, who will comment on behalf of WGMS and WGEAMS, respectively. A final version incorporating all of the comments will then be prepared for submission to ACME 1997.

8.1.2 Review the outcome of the Sixth Intercomparison Exercise on Trace Metals in Sea Water

The Trace Metals Subgroup reviewed the draft report on the ICES Seventh Round Intercomparison Exercise for

Trace Metals in Sea Water (this exercise was originally incorrectly titled 'Sixth' instead of 'Seventh'). The report was presented by S. Berman. The outcome of the exercise is briefly summarised here together with some of the suggested amendments.

Forty laboratories (71 % of those receiving samples) submitted data. About 25 % of the respondent laboratories have demonstrated an ability to competently analyse a good majority of trace metals of interest in this exercise. Six laboratories, for whatever reasons, analyse for only a small number of trace metals but do it well. Only about one third of the laboratories appear to be quite competent regarding the analysis of the samples for all three of the trace metals that had previously been mandatory in the former OSPAR Joint Monitoring Programme, namely, copper, zinc, and cadmium. A disappointing forty percent of the respondent laboratories could not demonstrate the ability to adequately analyse both samples for the three trace metals. There are a number of competent procedures for the extraction of trace metals from sea water. The study could not discern significant differences in the efficacy of these separation methods. Also, there are a number of competent instrumental methods for the measurement of trace metal concentrations after extraction from sea water. The study could not discern significant differences in the efficacy of these instrumental procedures Many laboratories do not appear to be using procedures of adequate sensitivity for the analysis of metals in sea water. However, their reported procedures are often not much different from laboratories producing good quantitative results.

Laboratory contamination and/or poor control of reagent blanks and/or improper calibration procedures appear to be major sources of error in many laboratories. Clean facilities, equipment, and reagents are prerequisites for the successful analysis of trace metals in sea water. Good laboratory practices are essential. The trace metal concentration levels in the two intercomparison samples were very similar except for cobalt, for which there is a factor of ten difference. However, 95 % confidence intervals were in general smaller for sample B. This may be related to the lower total organic carbon content of sea water, resulting in more efficient extraction of the trace metals. Also the difference in salinity may be a factor.

Suggestions for amendments to the report were made regarding the process of evaluating the performance of the participants and regarding some of the conclusions made by the authors. The accepted values for the trace metal concentrations and their associated confidence intervals may also be changed slightly in the revised version as some recalculations were foreseen. Figures 1 to 3 as well as the error in the labelling for the Z-scores shown in Appendix E also need to be corrected. These and all other amendments made will be incorporated into the final version of the report.

MCWG recommended that the final report should be published in the *ICES Cooperative Research Report* series and it was anticipated that the final report will be available for distribution to the participants within the next two months.

8.1.3 Assess the need for and possibilities to organise an interlaboratory study on organotin analysis

The requirement for an interlaboratory study on the measurement of organotins in the marine environment was discussed, and it was agreed that it is timely that an initiative on these compounds is undertaken. D. Wells introduced the QUASIMEME scheme for 1997/1998 which includes a development exercise for organotins. This exercise will begin with a series of standard solutions and a mussel tissue. The compounds that will be studied are the mono-, di-, and tributyl and phenyltins. In addition, the ethyl and pentyl derivatives will be available as a quality check on the derivative techniques that many laboratories use in their methods for the determination of these species. In the near future, QUASIMEME plans to develop the organotin programme to include sediment and water matrices.

MCWG agreed that this was a welcome development. QUASIMEME agreed to keep MCWG fully informed on the development and outcome of this programme. MCWG agreed that, in view of the QUASIMEME initiative in this area, there is no need for an ICES interlaboratory study on organotins.

8.1.4 Review the progress of studies looking into the associations between metals and lipids in biological tissues and report on the implications for marine monitoring

Section 6 of the 1997 report of the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM), 'Review and report on investigations concerning appropriate bases for expressing metal concentrations in fish livers', with an accompanying note by a note by a member of the Subgroup, was reviewed by the Trace Metals Subgroup.

The conclusion of the discussion was that it is necessary to compensate, by some kind of normalization, for the influence of the fat content of fish livers on the trace metal concentrations. However, in the report from WGSAEM it was concluded that a normalization procedure for the influence of the fat content as applied here only resulted in a decrease in the variance of the data for zinc. The Subgroup therefore concluded that zinc analyses of fish liver should be expressed on a lean weight basis when comparisons of results are made in time or space, at least for certain fish species. Other elements should be expressed on a wet weight basis.

The influence of fish size, liver size, and fat content of fish liver on trace element concentrations is being studied in an Icelandic project. The Icelandic results will be available for MCWG at its next meeting.

8.1.5 Review the final guidelines prepared by the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea [HELCOM 1996/3]

M. Krysell (SGQAC Chairman) introduced the final draft of Guidelines prepared by the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC) for the three Subgroups of MCWG before the Guidelines were reviewed by the Subgroups. A general remark was made that the Guidelines under consideration will be updated every year, e.g., for next year, it is expected that there also will be Guidelines for Hg in sea water and biological tissues.

The Chemical Oceanography Subgroup proposed several amendments to the text where clarification was needed. M. Krysell will take care of these amendments.

It was made clear that the organic contaminant section of the Guidelines has not been revised by SGQAC since it was reviewed at the 1996 MCWG meeting. It was therefore not necessary to consider this section of the document again.

The Trace Metals Subgroup was asked to concentrate on Annex H (trace metals in sea water), as this annex had not yet undergone external review, and also since the rest of the trace metals section had not changed substantially since it was reviewed at the last MCWG meeting.

The detailed comments of the Chemical Oceanography Subgroup to Annex H of the Guidelines are given in Annex 5.

MCWG noted that a wealth of important information has been assembled in the Guidelines and that this document will be of great value to the Baltic laboratories. MCWG fully supports publication of the Guidelines by HELCOM.

8.1.6 Review progress in the collaborative study on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe)

J. de Boer has sent out reference compounds to several laboratories represented in the MCWG but only a few have been able to report any results on environmental levels, although many are in the process of producing such data.

P. Roose reported preliminary results from analyses of these compounds in sediment and fish tissue. All samples were taken from the coast of Belgium and the results indicate concentrations of TCPM in sediment to be in the range of 0.8 to 3.9 ng g^{-1} dw and TCPMe between 0.4 and 1.7 ng g^{-1} dw. In most samples the concentration of TCPM exceeded that of TCPMe, which is in agreement with previously published results. The concentrations of TCPM and TCPMe found in flounder were 28 and 120 ng g^{-1} lw (n = 1), respectively, in shrimp 17 and 42 ng g^{-1} lw (n = 1), in mussel 26 and 91 ng g^{-1} lw (n = 2), in eel 8 and 25 ng g^{-1} lw (n = 2) and in dab 13 and 83 ng g^{-1} lw (n = 2). None of these compounds could be detected (limit of detection estimated at 0.1 ng g^{-1} lw) in cod muscle. In all samples in which the compounds were detected, the level of TCPMe was higher than that of TCPM, which is not in agreement with earlier results. This may be due to an interference in the chromatogram, and steps will be taken to verify the results intersessionally.

M. Harich, from the Bundesforschungsanstalt für Fischerei in Hamburg, had sent data on TCPM and TCPMe in cod liver and mussel. Both samples were from the QUASIMEME programme and the mussel sample level of TCPM was 130 ng g^{-1} ww and of TCPMe 90 ng g^{-1} ww. In cod liver, only TCPMe was analysed and shown to contain 21000 ng g^{-1} ww. These concentrations are higher than those reported by J. de Boer *et al.* (1996).

It was recommended that the laboratories involved in this study continue to work intersessionally and report any new data to J. de Boer before the end of 1997 to improve the database for a new assessment at the next MCWG meeting. Some intercomparison studies will also be undertaken in order to ensure that the data from all the laboratories are comparable.

The paper discussed at the 1996 MCWG meeting on TCPM and TCPMe has been published (Reviews of Environmental Contamination and Toxicology, 150, 1996, 95–106) and reprints were delivered by J. de Boer, who also provided another paper concerning the analysis and environmental concentrations of these compounds (Environmental Pollution 93, 1996, 39–47). He also delivered reprints of a report on the effects on rats following exposure to TCPM (Poon *et al.*, Chemosphere 34, 1997, 1–12). In this study, rats were fed a diet containing 1, 10, or 100 ppm TCPM and, at the higher doses (10 and/or 100 ppm), a number of different effects were found.

8.1.7 Review and report on progress on a joint study to compare and contrast the different results of using multivariate methods on a common data set on PCBs in fish-eating marine mammals

The first phase of this study, in which data were combined from a number of laboratories in order to study biotransformation, has now been completed and a paper has been accepted for publication. The second phase will involve the development of a common dataset which will be used to test the applicability and utility of a number of multivariate statistical techniques. It has not been possible to make any progress since the 1996 MCWG meeting on the second phase, and the project will be carried forward and a report on progress will be made at the 1998 MCWG meeting.

8.1.8 Review the performance for metals of laboratories in recent NOAA and QUASIMEME interlaboratory studies, and derive indicators for performance which can be used in the design of monitoring programmes as a representative estimate for between-laboratory variability

S. Berman and D. Wells introduced the key developments and statistical outcomes of the recent NOAA and QUASIMEME interlaboratory performance studies, respectively. The details of the outcome of these studies can be found in the respective reports of these programmes; the NOAA studies will be published shortly by NOAA and the QUASIMEME project results will be published in a special issue of the Marine Pollution Bulletin expected in summer 1997, as well as in reports already submitted to the ICES Secretariat.

From the presentations, it was clear that the following conclusions can be made:

1) Regular laboratory performance studies are an important tool for establishing the quality of data from participating laboratories.

2) Most laboratories which participated in either exercise have improved over the years. Because the NOAA programme has been in operation for a longer period, there is clearer evidence in the NOAA exercise for this improvement in analysis of trace metals in both biota and sediment.

3) The requirements and the original aims of the two programmes are different, as are the method(s) of data analysis and assessment. Therefore, it is considered that there is no real value in making a detailed comparison of the results of the two schemes.

The QUASIMEME information on QA for the laboratories gives the mean, Z-score, and P-score from the laboratory performance studies. The Z-score and P-score can easily be calculated from the NOAA data if required. The scores are based on a declared level of acceptable bias (currently at 25% for a Z-score of 2). The required level of laboratory performance for a particular monitoring programme can be set by the programme and the new Z-score calculated on the basis of that performance criteria, if different from that set by QUASIMEME. The assessments can then be made according to the level required by the monitoring programme.

8.1.9 Review the overview papers on chlorinated solvents and benzene, toluene, and xylene (BTX) in fish; chlorinated dioxins and furans in sediments; the formation of hexachlorobenzene (HCB) metabolites; toxaphene; Irgarol 1051; and phenyltins [HELCOM 1996/2]

8.1.9.1 Review note on Irgarol 1051

R. Law presented a revision of the review paper on Irgarol 1051, initially presented at MCWG 1996. The information presented on the historic usage of TBT in the introduction has been reduced, as recommended by MCWG 1996. Current discussions within the International Maritime Organization (IMO) may lead to further restrictions on the use of antifouling paints on larger vessels, which is likely to further increase usage of copper- and zinc-based paints which now often incorporate Irgarol 1051 in their formulation. New information provided in the updated review includes results from a study of Irgarol 1051 levels at a marina in Sweden, and data on the usage of Irgarol 1051 in Ireland, Belgium, and Denmark. Information on the usage of Irgarol 1051 in Norway is to be added to the document, but data on usage in Germany are unavailable. It was suggested that sediment data, although limited, be included in Table 1 of the paper. There is little information available as to the levels which will cause harmful biological effects, but the mode of action is likely to be additive with other triazines (such as simazine and atrazine).

Preliminary studies in The Netherlands detected low levels in water (approx. 1–40 ng l^{-1}). A. van der Zande commented that he had been shown results by Ciba-Geigy Ltd. (The Netherlands) pertaining to a study in eastern Sweden where levels of Irgarol 1051 in water were seen to increase to several hundred ng l^{-1} in the boating season but decrease in winter. These data have not been published in the open literature, but they are in line with other information presented in the review paper. He also received an abstract from Ciba-Geigy relating to Irgarol 1051 toxicity which has been copied to R. Law.

MCWG recommended that the review paper should be finalised and forwarded to ACME for review, with a view to including it in their 1997 report.

8.1.9.2 Review note on the formation of hexachlorobenzene (HCB) metabolites

B. Jansson presented a review on the metabolism of HCB as an example of the metabolism of a persistent organochlorine compound. HCB was chosen because it is a single compound, persistent, and relatively well studied. It is a ubiquitous contaminant in the environment due to its use as a pesticide, as an intermediate in chemical processes, and due to its formation as a combustion product. The review outlines major and minor metabolites detected in anaerobic sediment, in fry of steelhead trout, in *Saccharomyces cervisiae* expressing human cytochrome P450 3A4, and in excreta from rats. At least 42 different metabolites have been reported, including chlorobenzenes, chlorophenols such as pentachlorophenol (PCP), and compounds containing thiol, methylthioether, methyl sulphone and methyl sulphoxide groups.

The studies were generally carried out under experimental conditions in the laboratory. The difficulty in assessing HCB metabolism in the environment was recognised, particularly as PCP and its metabolites, as well as some lower chlorinated benzenes, occur independently of HCB.

MCWG recommended that this review should be included as an annex to the MCWG 1997 report (Annex 6) and that it should be considered by ACME as an example of the complexity of behaviour of even a single persistent organic contaminant in the marine environment.

8.1.9.3 Review note on toxaphene

J. de Boer presented a comprehensive discussion paper on toxaphene in the marine environment. Toxaphene is an insecticide used primarily in cotton growing but also as a pesticide. It is a complex mixture mostly consisting of chlorinated bornanes (CHBs). The cumulative global production of toxaphene, estimated at 1.3 million tonnes, is higher than that of PCBs, and the complexity of congeners in toxaphene greatly exceeds that of PCBs. Of the toxaphene congeners identified in technical toxaphene mixtures, only a fraction occur at significant concentrations in fish tissue.

Strict German tolerance levels for total toxaphene of 0.1 mg kg^{-1} lipid weight for fatty fish (> 10 % fat) and 0.1 mg kg^{-1} wet weight for lean fish (< 10 % fat) are due to be changed to 0.1 mg kg^{-1} wet weight for the sum of CHB26, CHB50, and CHB62 in all fish. Results presented contained values in excess of the current German limit for many samples.

There is a need for additional information on the carcinogenicity of toxaphene and it should be noted that specific congeners may exhibit greater toxicity than total toxaphene.

Normally the determination of total toxaphene can be achieved using GC/ECD, but GC/NCI-MS (negative chemical ionization mass spectrometry) is recommended for better sensitivity and accuracy. It is necessary to separate the PCB and toxaphene fractions prior to GC analysis. To achieve congener-specific analysis, more advanced techniques such as high resolution mass spectrometry (HRMS) or multi-dimensional gas chromatography (MDGC) are required, with comprehensive multi-dimensional gas chromatography (CMDGC) being particularly promising. MDGC data were used to demonstrate that a 'heart cut' of a single peak, identified as CHB26, separated into a number of peaks for which CHB26 was not the primary component. This illustrates the requirement for congener-specific analysis.

There are currently no certified reference materials available, but a number of specific congeners are commercially available as solutions. A stepwise development exercise is being initiated under the QUASIMEME II programme in 1997 and will involve the analysis of specific CHB congeners.

MCWG recommended that the review paper should be finalised and forwarded to ACME for review, with a view to including it in their 1997 report. MCWG further recommended that toxaphene be considered for future routine monitoring programmes, once the present analytical difficulties have been overcome. Steps are being taken to overcome these problems.

8.1.9.4 Determination and presence of volatile organic compounds in marine biota

P. Roose gave a presentation on the determination and presence of volatile organic compounds in marine biota. The coupling of a commercial purge and trap apparatus to a GC/MS (gas chromatograph mass spectrometer) formed the basis for the development of a suitable analytical technique for the determination of volatile organic compounds (VOCs) in marine biota.

Firstly, the interspecies and interspecimen variability was studied for dab (*Limanda limanda*) and whiting (*Merlangius merlangus*) from Belgian waters. A large variability was seen in the concentrations of VOCs in individuals of the same population. The distribution of the concentrations was investigated using a variant of the Kolmogorov-Smirnov test and normal probability plots, and it was concluded that the concentrations of VOCs seemed to be normally distributed in the different tissue types of two species. These results should, however, be interpreted with some caution, as the sample size was relatively small for these particular types of statistical tests. No distinct relationship was observed between the fat content of tissues and the concentration of the individual VOCs, although this was clearly the case for the PCBs. It seems, therefore, that VOCs behave and distribute differently from PCBs. No significant

relationship could be established between the concentration of the individual VOCs and the length of the organism, and it was therefore concluded that biomagnification does not occur in the species studied. This is further supported by the fact that the concentrations in organisms from different levels of the food chain are generally not significantly different. The concentrations in liver and muscle tissue of fish showed no significant correlation. The observation was made that concentrations of VOCs in the liver of dab, the main site of metabolization, were generally higher.

8.1.9.5 Chlorinated dioxins and furans in the lower St. Lawrence Estuary

M. Lebeuf gave a presentation on polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF) in sediment cores from the lower St. Lawrence Estuary (LSLE). This clearly illustrated the value of using sediment cores as a monitoring tool in this specific area. In summary, the LSLE represents an important zone of permanent accumulation of PCDD/PCDF within the St. Lawrence system. The trend of PCDD/PCDF accumulation in sediments matches the evolution of atmospheric transport of these compounds. The dominant source is characterised by a PCDD/PCDF distribution pattern representative of atmospheric inputs. Fluvial inputs of PCDD/PCDF to the LSLE predominate over direct atmospheric deposition.

8.1.10 Update, where appropriate, the list of contaminants which can be monitored on a routine basis, including a discussion about actual analytical proficiency based on recent interlaboratory studies

The Trace Metals Subgroup prepared a new list of trace elements that can be monitored on a routine basis in biota, sediments, and water, based on information from recent intercomparison exercises as well as the availability of certified reference materials. This list is attached as Annex 7.

There are sufficient intercomparison exercises available (both QUASIMEME and NOAA) for the routine analysis of Zn, Cu, Pb, Cd, Hg, Cr, Ni, and As in biota; Zn Cu, Pb, Cd, Hg, Cr, Ni, As, and Al in sediments; and Zn, Cu, Pb, Cd, Cr, Ni, As, Fe, and Mn in sea water. NOAA has also successfully measured the following elements: Ag, Se, Sb, Fe, and Sn in biota; Si, Be, Tl, Ag, Se, Sn, Sb, Fe, and Mn in sediments. Additional elements and species of interest are Ag, Se, organotin compounds, arsenic speciation (As(III), As(V), MMA, DMA, TMA, arsenocholine, arsenobetaine), MMHg in biota and sediments; Hg and MMHg, Se speciation (Se (II), Se (IV), Se (VI)) and Cr speciation (Cr(III), Cr(VI)) in water. For these additional elements and species, no monitoring should be carried out until successful intercalibrations have been performed. Arsenic speciation, and the analysis of methylmercury and organotin compounds in biota and sediments are currently in a preparatory phase in the QUASIMEME proficiency testing schemes.

The Organics Subgroup also discussed the updating of the list of organic contaminants which can be monitored on a routine basis, as given in Annex 6 of the 1996 MCWG report (ICES CM 1996/Env:2). It was felt that the table should be revised, and that a new procedure should be implemented in order to routinely update the list prior to each MCWG meeting, so as not to take up time needed for Subgroup discussion of other issues. It was proposed that tables for organic compounds, trace metals, and nutrients should be prepared by a small group prior to the MCWG meeting and circulated to Subgroup members by e-mail. This arrangement will be implemented for the MCWG meeting in 1998.

The following terms of reference were set for the group:

1) The information produced should cater to the needs of all interested parties (e.g., HELCOM, OSPAR, AMAP, and ICES).

2) The team should provide an annual update based on current information on QA/QC for chemical determinands in the marine environment, especially those of interest for marine monitoring programmes.

3) The list of determinands should include (groups of) compounds of interest to international monitoring programmes as well as new contaminants.

4) Subgroups of compounds should be specified where necessary (e.g., PCB congeners, unsubstituted or alkylated PAHs, etc.)

5) Data from international interlaboratory studies should be presented with the appropriate references.

6) A list of currently available certified reference materials should be included.

7) Information should be given on the capability of laboratories in the analysis of the determinands concerned. This should include overall information on the state-of-the-art, a range of CV% values, and the basis of the assessment parameters.

The group will comprise of D. Wells (who will act as the coordinator), S. Berman, E. McGovern, A. Aminot, and M. Lebeuf. The updated information will be circulated by e-mail to all Subgroup members before 1 January 1998, and comments should be returned to the group before 1 February 1998, after which the team will finalise the summary for MCWG 1998.

The new procedure suggested by the Organics Subgroup was accepted by MCWG.

8.1.11 Review the paper on bioaccumulation and biomagnification of PCBs in the food chain, with the aim of facilitating a more detailed request on the transfer of halogenated compounds in food chains by HELCOM [HELCOM 1996/9]

A. Abarnou presented a summary of the review note on 'Bioaccumulation: chemical and biological factors governing the transfer of organic compounds in food chains'. The document gives a general overview of (i) the processes of bioaccumulation; (ii) chemical factors; and (iii) biological factors acting on bioaccumulation. MCWG deemed it impractical to provide too many examples of bioaccumulation. On the other hand, A. Abarnou expressed his interest to continue to address this issue if more precise requests are formulated by HELCOM.

MCWG recommended that the review note should be forwarded to ACME after a minor revision and included as an annex to the 1997 ACME report.

A. Abarnou will also present information on the modelling of PCB bioaccumulation in the Seine Estuary at MCWG 1998. MCWG also supported the initiative by A. van der Zande to present his results on problems and limitations in the determination of dissolved concentrations of highly hydrophobic compounds and bioconcentration in mussels from the Mussel Watch Programme in The Netherlands.

8.1.12 Review papers on units for nutrients and oxygen, total nitrogen methods, the reliability of old nutrient data, and particulate organic carbon in anoxic waters

The paper, 'Units and unit symbols and their use in chemical oceanography', by A. Aminot was reviewed by the Chemical Oceanography Subgroup.

The paper examines the basic SI units applicable to chemical oceanography, along with past and present uses of these units. MCWG agreed that the paper be included in this report as Annex 8. Some suggestions for clarification purposes were made.

As examples of correct usuage in chemical oceanography, MCWG noted that volume could be expressed either in litres (l) or cubic decimetres (dm^3) and that the amount of substance is expressed on a mole basis. Salinity is now, by definition, a dimensionless quantity but it can be reported, e.g., as 35.000 (PSS78) thereby referring to the Practical Salinity Scale 1978. Nutrient concentrations should be reported in the unit $\mu mol\ dm^3$ or the uhit $\mu mol\ l^{-1}$. The current practice is to report dissolved oxygen as $ml\ l^{-1}$, as in the standard oceanographic tables.

A paper entitled, 'Review of methodology for the determination of total-N in sea water', by D. Kirkwood reviews and examines present-day methods. It is attached as Annex 9. A preliminary version of this paper was presented at the QUASIMEME workshop in Crieff, Scotland, in 1996. It is encouraging to note that a fair number of workers have made thorough investigations of the technique and the recovery of nitrogen in the oxidation step.

O. Vagn Olsen gave an introduction to his paper on the reliability of old nutrient data and presented the statistical tool used (SAS GLM). The investigation on some data from the northern North Sea and the Skagerrak indicates that a substantial amount of the old (from 1960 and onwards) phosphate and nitrate data may be of comparable quality among laboratories and that there was no reason to exclude these data.

The data on total phosphorus and total nitrogen could not be evaluated by any statistical analysis because the dataset was too small.

Ammonia and silicate showed less comparability in this investigation. It was decided that the work should continue and that more conclusions on this data screening method should be presented at the next MCWG meeting.

8.1.13 Quality assurance of data to be loaded in a database, and general guidelines for this activity

No paper was available for discussion, but the ICES Environment Data Scientist, J.R. Larsen, outlined the changes being made to the ICES Environmental Data Bank and the requirements for input to the process from MCWG. J.R. Larsen presented an outline of the present procedure for the reporting of quality assurance information to the ICES Environmental Data Bank. MCWG noted that a significant part of the information is reported in user-defined (free text) fields.

MCWG recommended that this practice in principle be replaced by a system where the data supplier chooses from a list of defined options.

Codes have earlier been developed for the analytical methods, but for sampling, storage, and pre-treatment some intersessional work will be needed to develop the necessary coding scheme.

The Trace Metals Subgroup prepared a provisional list of information that should accompany marine chemical data to serve as an example (Annex 10, Sections 1, 2, 3). The Subgroup also prepared a provisional description of a system for the reporting of information on the sampling, pre-treatment, preservation, and storage of samples of sea water, sediments, and biota.

The Trace Metals Subgroup also reviewed the way information on analytical methods is reported for trace metals under the QUASIMEME programme (Annex 10, section 7). The Subgroup found that the style is useful, and recommended that it be appliedgenerally for the reporting of analytical methods information.

It was emphasized that the lists and coding system is provisional and should be carefully reviewed before final recommendations are made. This work should be done intersessionally. If possible, the work should be carried out in cooperation with the QUASH programme.

The Chemical Oceanography Subgroup concurred that there was little to be gained by high levels of detail, and that a simple differentiation of 'colorimetic' and 'others' would at least distinguish between present-day technology and possible future developments. It was further recommended that for the sampling of sea water there should be a clarification as to whether sampling was done with pumping systems or as discrete samples from, e.g., hydrocast bottles.

The intersessional work should be carried out in close co-operation with members of all Subgroups in order to ensure that the final system is compatible with the needs of all concerned.

A small working group consisting of J.R. Larsen (Chairman), G. Asmund, J. Klungsøyr, S. Carlberg, and D. Wells volunteered to work intersessionally on the item and report back at the next MCWG meeting.

8.1.14 Review the paper on methods for oxygen determination and their quality assurance and provide guidance for OSPAR

The paper on quality assurance of oxygen measurements by A. Aminot was presented and discussed by the Chemical Oceanography Subgroup. Some corrections and additions were made to the paper, which is now attached as Annex 11 to this report. It was well written and provided important guidance to the monitoring community.

It is of interest to note that the UNESCO Joint Panel on Oceanographic Tables and Standards recommended an algorithm and produced oxygen saturation tables in 1973, but in 1986 the panel made a new recommendation for an improved algorithm, but no new tables were produced. It seems probable that the 1986 recommendations may have escaped the attention of many in the oceanographic community, who will then still be using the outdated 1973 oxygen saturation tables.

8.1.15 Review descriptions of protocols for quality control procedures on, e.g., nutrients data

The Chemical Oceanography Subgroup took the view that there are three distinct stages in the overall quality assurance of, e.g., nutrients data.

Stage 1: Sample handling and analytical chemistry

This covers all operations from arrival of the hydrocast bottle on board ship, to the production of concentration data for individual nutrients. The most evident drawback in this area is the continued lack of CRMs for nutrients in sea water. Nutrients chemists are therefore unable to demonstrate their level of quality control by the use of Shewart and CUSUM charts, etc., in the manner that is customary for chemists measuring contaminants in sediments and biota where suitable CRMs are available.

The nearest approach available to the nutrients chemist is to check on the consistency of autoanalyser performance by keeping a record of absorbance/concentration data for calibration solutions by way of Shewart and CUSUM charts. This can be a very effective early warning system of instrumental and chemical malfunction. It is hoped that the forthcoming QUASH programme will contribute quantitatively and significantly to the understanding of how sample handling prior to the actual chemical analysis can affect data quality.

Stage 2: Critical examination of the data

The oceanographic consistency of data can be examined in a variety of ways. There is no substitute for the well-trained eye and, combined with computer-generated property/property plots, anomalies can be readily identified. N/P ratios and nutrient/salinity plots are particularly useful. The Subgroup concurred that if no specific and satisfactory evidence can be found for rejecting outlying data points they must be retained, yet flagged in some way, otherwise phenomena such as 'The Great Salinity Anomaly' and certain Baltic events, for example, the reduced silicate concentration in the water might be overlooked. One way of flagging such data has been developed by IGOSS and is presented in Table 8.1.15.1.

Table 8.1.15.1. Method for flagging outlying data points developed by IGOSS.

0 – No quality control	No quality control has been performed.
1 – Correct	Appears to be correct.
2 – Inconsistent	Appears to be inconsistent with other elements.
3 – Doubtful	Appears to be doubtful.
4 – Erroneous	Appears to be erroneous. The flag indicates a value outside the permitted range.
5 – Corrected	The value has been corrected. The flag indicates a change has been made by the operator. Only obvious errors are corrected. The previous value is not saved.
8 – Inter-/extrapolated	Reserved. Local definition: The value is inter-/extrapolated by observer. Methods unspecified.
9 – Missing	The value of the element is missing.

MCWG had the view that with the access to state-of-the-art computers there would be no need to store data which have been interpolated or extrapolated. Such data should be created only when they are needed.

Fully computerised scrutiny of data is possible in the more straightforward cases, for example, nitrite cannot be greater than the sum of nitrate plus nitrite: likewise, total-N should be not less than the sum of nitrate, nitrite, and ammonia.

Specific combinations of data are important, for example, appropriate salinity data are vital to the interpretation of nutrients data. Therefore, no nutrient data should be considered acceptable without accompanying salinity data.

Stage 3: Suitability of data for the intended purpose

At the third stage, the emphasis is on the user of the data. The user has to be familiar with the data sets, the requirements under which they were collected, and the quality assurance information available in support of the data sets. Based on this, the user must decide whether the data meet the requirements of his intended study, e.g., a time trend assessment. Thus, the actual use and evaluation of the data are likely to reveal quality problems—if there still are any.

The use of the data should, therefore, be seen as the final check of their quality.

8.1.16 Review the updated paper on DOC/TOC in sea water including estuaries

The Chemical Oceanography Subgroup reviewed a paper by M. Krysell on the use of organic carbon in chemical oceanography, which was originally presented at last year's MCWG meeting. The paper has now been extended with references to estuarine studies. The extension does not affect the conclusions that were drawn last year, they remain the same; we cannot see any reason why organic carbon should be included in monitoring programmes, even though the data may be very useful in targeted experiments. The paper is attached as Annex 12.

8.1.17 Based on a response from the IWC on cetacean diets, provide information on contaminant levels in these prey species, in collaboration with WGEAMS

As no clarification of this request had been forthcoming from IWC, the item was dropped from the Agenda at the request of the ICES Environmental Secretary.

8.1.18 In collaboration with WGEAMS, review information gathered intersessionally on variance components in seabird egg analysis

There had been little intersessional activity on the topic of variance components in the analysis of seabird eggs. The Chairman had received copies of papers from M. Haarich regarding the use of seabird eggs in environmental monitoring programmes in Germany. K. Stange informed the Subgroup about related agenda items discussed by WGEAMS in 1995 and 1996. Seabird eggs are monitored routinely within the German and Swedish national programmes and are also included in the OSPAR JAMP as a voluntary matrix for the analyses of metals and organic contaminants. None of the Subgroup members present were involved in the analysis of seabird eggs. The Subgroup felt, therefore, that they had insufficient information and expertise to discuss variance components in seabird egg analysis. To take this work forward, a plenary lecture on this topic at next year's meeting was suggested. B. Jansson offered to make arrangements for a presentation by Anders Bignert from the Museum of Natural History in Stockholm on the experiences with the use of guillemot eggs in the Swedish national monitoring programme, including the aspect of variance components. The members of the Subgroup were encouraged to submit any relevant information from their countries on the analysis of seabird eggs to B. Jansson. K. Stange agreed to supply information from the 1995 and 1996 WGEAMS reports, and also from the 1997 WGEAMS meeting which would also consider this topic.

8.2 Review the Report of the ICES/OSPAR Workshop on the Overall Evaluation and Update of Background/Reference Concentrations for Nutrients and Contaminants in Sea Water, Biota and Sediment

K. Stange had attended the Workshop on background concentrations and explained how the report was produced. In spite of a request from the 'workgroup for background concentrations' for relevant data to be submitted prior to the meeting, few data were provided, and so the group (20 participants) used only those data available at the meeting. These data were compiled from data sets for the most 'pristine' or remote sites, and selected concentration ranges for specific locations.

An earlier report on this subject had already been reviewed by MCWG. MCWG had also supported the idea of a second workshop at their 1996 meeting. However, strong doubts about the possibility of establishing background concentrations of nutrients were also expressed at that meeting. MCWG also pointed out at their 1996 meeting the importance of having the definitions of background and reference concentrations well established by the second workshop.

In the report of the previous workshop, the terms 'background concentrations' and 'reference concentrations' were inadequately defined and a major part of the criticism of that report, centered on the fact that reference concentrations were presented as background concentrations. In the new report, the authors argued that 'it was felt to be too sophisticated' to distinguish between the two. In a general sense, this is really a step backwards in the development of environmental science.

Once more, the task given to the Workshop fails to make it sufficiently clear that for nutrients, there are no background concentrations available. Annex 6 of the Workshop report, which concerns nutrients, mentions briefly the existence of physical processes in the sea. However, the authors have failed to see the consequences of this and the fact that the marine system is highly dynamic, e.g., for the effects of eutrophication it is the flux of nutrients rather than absolute concentrations that is of importance.

It is inappropriate to consider nutrients together with, e.g., chlorobiphenyls, in the manner of the terms of reference of the workshop. The concept that the great bulk of the North Atlantic Ocean can be considered 'pristine' from the point of view of anthropogenic influences is easily grasped by the non-scientist. This leads to the expectation that in 'pristine' areas all substances that can cause environmental problems occur in low concentrations.

However, for nutrients, it is not widely appreciated that for nitrate, Atlantic concentrations are far in excess of those in the North Sea, and result from completely natural biogeochemical processes.

Physical processes, such as upwelling in coastal areas, can displace large water volumes and cause rapid changes in the nutrient concentrations by bringing in, e.g., Atlantic water; consequently, the natural range of nutrient concentrations in a certain area can be quite large and include high concentrations. Contamination by nutrients from anthropogenic sources will not necessarily make significant changes to the concentration range for the nutrients. Consequently, the use of so-called 'background concentrations' would be misleading since they will not reveal any changes caused by anthropogenic sources.

The inclusion of any nutrients data whatever in a report entitled 'background concentrations of natural compunds' has great potential to mislead. The report, as it stands, will not prevent future investigators with pollution-driven motives from referring erroneously to the nutrients data therein as 'background concentrations'.

The concept of 'background concentrations' was considered to be appropriate for metals and organic contaminants, although the terms 'background' and 'reference concentrations' were confusing, as they still have not been clearly defined.

In addition to these general objections, MCWG made the following comments and suggestions:

- It might be preferable to use the term 'minimum values' for these types of compounds in a defined area and for a well-defined matrix, taking into account relevant cofactors such as species, sex, length, and age for biota, and grain size distribution and organic carbon content for sediments.

- It could be argued that for man-made compounds, like PCBs, the background or minimum concentration should be zero. If this is not acceptable, then we should better speak of 'present minimum concentrations values in surface sediments and biota'.

- Errors during sampling, handling, and analysis can always occur due to contamination problems when the samples contain low concentrations. This can influence the concentration range found in 'pristine areas' and, hence, create problems of assessing 'correct' background concentrations.

- Levels of confidence were not given for the data, although it was emphasized that it is not acceptable to provide and use any data without their associated uncertainty.

- It is important that an assessment should only be undertaken by experts (including analytical chemists) who have a clear awareness of the quality and limitations of the data being used and the necessity of using all available relevant data (including cofactors).

- It is not possible to define one background concentration for the entire OSPAR Convention Area since large regional variability can occur. The background concentrations must therefore be defined on a regional basis.

- Regional differences can be illustrated, e.g., for trace metals in blue mussels. It appears that the background concentrations given for trace metals in mussels are much lower than those found in remote areas (pristine) in Iceland and Greenland, which are also part of the Convention Area.

- Background data from Iceland and Greenland and other areas are recommended to be incorporated in the report in order to make it usable for more regions. Also, information from other matrices, e.g., contaminants in seabird eggs, is recommended to be included.

- A normalization procedure is generally necessary for sediment data, although it may cause a loss of precision in the data.

- It is recommended to use data from the winter season and from depths between 10 m and 100 m as background concentrations for trace metals in sea water. This has to be clarified in the text if this has been the case, e.g., in the title of Table 1 on trace metals in sea water.

8.3 Other Issues: Trace Metals Subgroup

8.3.1 Mercury speciation

At the 1996 MCWG, M. Leermaker presented a report on mercury speciation in sea water. The report has now been updated to cover mercury bioaccumulation in marine fish and the revised report was presented by M. Leermaker.

MCWG found this paper very informative and made some comments on the manuscript, such as:

- include a few references about analytical methods;

- review the list of references;

- include more data about mercury concentrations in fish in other areas.

Several members of the group will send M. Leermakers data from their areas as soon as possible. MCWG recommended that the paper, after minor revisions and after it had been reviewed by G. Asmund and G. Audunsson, should be forwarded to ACME for information and appended to their 1997 report.

8.3.2 Chairman for the Trace Metals Subgroup

G. Asmund was re-elected with acclamation as Chairman for next year's meeting and the intersessional period.

8.4 Other Issues: Organics Subgroup

8.4.1 Review of an overview on polychlorinated diphenyl ethers

J. de Boer presented an overview on polychlorinated diphenyl ethers (PCDEs) describing sources, analysis, environmental levels, and effects of these compounds. The Subgroup made some comments on the manuscript and recommended that it should, after minor revisions, be forwarded to ACME for information on these compounds, and recommended that it be appended to their 1997 report.

8.4.2 Any other business

J. Klungsøyr was confirmed as Chairman of the Organics Subgroup for MCWG 1998 and the intersessional period by acclamation.

The paper SIME 97/6/1-E, reporting the results of the OSPAR DIFFCHEM survey, was tabled for comment. The programme involved the collection of sediment samples from 22 estuaries in western Europe and the determination of PAHs, chlorinated paraffins, polybrominated diphenylethers, polybrominated biphenyls, and alkylphenols and alkylphenol ethoxylates.

This survey has provided valuable information on the presence, in sediments, of a range of contaminants not presently included routine collaborative monitoring programmes; the idea of screening for the presence of contaminants in the environment before establishing a routine programme is a good one. The Subgroup looked forward to seeing a revised text incorporating all the results and a more substantial treatment of the significance of the data and any recommended action to be taken by OSPAR.

Another paper, 'The use of lipids as a cofactor in organochlorine analysis of biota', was received too late for consideration, but will be tabled during MCWG 1998.

MCWG 1998: Topics for plenary lectures

Dr Anders Bignert has agreed to present a lecture on the Swedish seabird contaminant monitoring study which utilises guillemot eggs. D. Wells agreed to coordinate a

presentation describing progress within the QUASIMEME and QUASH (sample handling) programmes. J.R. Larsen agreed to make a presentation on the new structuring of the ICES Environmental Data Bank and its capabilities, in order to stimulate discussion and critical review of the developments to date.

Review Notes for MCWG 1998

G. Rimkus agreed to prepare a review note on synthetic musk compounds in the marine environment and B. Jansson a review note on chlorinated paraffins.

In the proposed restructuring of the ICES committee system, MCWG should report to the Oceanography Committee rather than to ACME. The Subgroup felt that this was not a logical move and that it is important to maintain the direct link between MCWG and ACME; a link which was established when MCWG was transferred from the Hydrography Committee.

8.5 Other Issues: Chemical Oceanography Subgroup

The Chemical Oceanography Subgroup discussed work items for next year's meeting and agreed that the following items should be considered:

1) report on progress in the application of high temperature techniques for the determination of total nitrogen in sea water (K. Nagel);

2) statistical tools to demonstrate the reliability of old nutrient data (O. Vagn Olsen);

3) review a paper on particulate organic carbon (POC) in anoxic water (M. Krysell);

4) demonstration of one or more screening softwares for chemical data to be entered into databases (M. Krysell and others);

5) review a paper on quality assurance aspects in the determination of chlorophyll in sea water (A. Aminot);

6) collate and review information on the fate of nutrients in estuaries (all Subgroup members);

7) collate and review information on experience with the use of automated *in situ* systems for observation of chemical variables (all Subgroup members).

Two plenary presentations were suggested: one on the impact and fluxes of materials carried with a glacial outburst flood caused by volcanism, near Skeidasandur, November 1996, by J. Ólafsson; and one on the Impact of Rhine overflow water on the Skagerrak and the Kattegat, by M. Krysell.

The Subgroup re-elected with acclamation S. Carlberg as Chairman intersessionally and for the next meeting.

9 ANY OTHER BUSINESS

Different ways to improve the communication among MCWG members were discussed. An e-mail post box system supported by the ICES Secretariat was suggested. J.R. Larsen offered to investigate the possibilities to set up and test such a system.

MCWG also informally discussed the outcome of the proposed restructuring of the ICES committee system in the Subgroups (see Section 8.4.2).

10 ACTION LIST AND RECOMMENDATIONS

The Action List and Recommendations are given in Annexes 13 and 14, respectively.

11 DATE AND VENUE OF NEXT MEETING

MCWG discussed the venue and dates of the next meeting. The Swedish Meteorological and Hydrological Institute, SMHI, offered to host the 1998 meeting of the MCWG in cooperation with the University of Stockholm. MCWG acknowledged the invitation with appreciation. It was decided to plan the meeting for 2–6 March 1998.

12 CLOSURE OF THE MEETING

Staff members of the host institute joined the closing session of the Working Group. On behalf of MCWG, the Chairman, B. Pedersen, thanked them for their warm hospitality, the superb organization, and for the support and services they provided.

In addition, she thanked the Subgroup Chairmen for their efforts and support, and all participants for their hard work.

The Chairman then closed the meeting at approximately 13.30 hrs.

ANNEX 1

LIST OF PARTICIPANTS

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ANNEX 2

AGENDA

1 OPENING OF THE MEETING

2 ADOPTION OF THE AGENDA

3 REPORT OF THE 84TH ICES STATUTORY MEETING

4 REPORTS ON RELATED ACTIVITIES

5 OSPAR AND HELCOM
- 5.1 Official requests have been included in the agenda.
- 5.2 Intergovernmental Oceanographic Commission (IOC)

6 ICES
- 6.1 The MCWG is requested to review an updated version of the report 'Background concentrations of natural compounds'. The item is on the agenda for all Subgroups.
- 6.2 Laboratory Performance Study 'QUASIMEME II'
  - 6.2.1 Dr Wells has been requested to provide an update.
- 6.3 EU-BCR QA project 'QUASH'
  - 6.3.1 The co-ordinators of the project have been requested to inform about the programme
- 6.4 Other Activities
  - 6.4.1 Members who wish to make a presentation under this item should prepare a note for MCWG

7 REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES
- 7.1 All members who wish to make a presentation on this item should prepare a note for MCWG

8 REQUESTS FROM ACME AND REGULATORY AGENCIES
- 8.1 Requests from ACME which have arisen prior to this agenda being produced, have been included

9 PLENARY PRESENTATIONS
- 9.1 AMAP, an example of a newly established monitoring assessment programme.
  Kari Stange (and other members of the MCWG)
- 9.2 Synthetic musk compounds in the aquatic environment..
  G. Rimkus *(Lebensmittel- und Veterinäruntersuchungsamt Schleswig-Holstein, Neumünster, Germany)*

10 SUBGROUP ACTIVITIES AND DISCUSSIONS
- 10.1 Trace Metal Subgroup
  - 10.1.1 (C. Res. 1996/2:15:1 b) Review and report on the outcome of the Intercomparison Exercise on the Analysis of Trace Metals in Sea Water. *(In Lisbon it was agreed that B. Pedersen, G. Asmund and S. Berman would organise this exercise)*
  - 10.1.2 (C.Res.1996/2:15:1 d) Review the progress of studies looking into the associations of various metals and lipids in biological tissues and report on possible implications for monitoring. *(In Lisbon, it was agreed that G. Asmund would make information available from a Danish-Norwegian-Icelandic study on associations between metals and lipids*)
  - 10.1.3 (C.Res.1996/2:15:1 j) Update where appropriate the list of contaminants which can be monitored on a routine basis, including a discussion about actual analytical proficiency based on recent interlaboratory studies
  - *10.1.4* (C.Res.1996/2:15:1 c) Assess the need for and possibilities to organise an interlaboratory study on organotin analysis *(In Lisbon, it was decided that D. Wells and W. Cofino should sent out a questionnaire on organotin analysis and contemplate about the possibilities to organise an interlaboratory study in this field)*
  - 10.1.5 (C.Res.1996/2:15:1 e) Review the final guidelines prepared by the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea [HELCOM 1996/3].
  - 10.1.6 (C.Res.1996/2:15:1 m) Review the paper on quality assurance of data to be loaded in a database, and prepare a general guideline for this activity

10.1.7 (C.Res.1996/2:15:1 h) Review the performance of metals of laboratories in recent NOAA and QUASIMEME interlaboratory studies, and derive indicators for performance which can be used in the design of monitoring programmes as a representative estimate for between-laboratory variability.

10.1.8 (C.Res.1996/2:15:1 q) Based on a response from the IWC on cetacean diets, provide information on contaminant levels in these prey species, in collaboration with WGEAMS.

10.1.9 (C.Res.1996/2:15:4 f) In collaboration with WGEAMs, review information gathered intersessionally on variance components in seabird egg analysis.

10.1.10 Review and report on an updated version of the report 'Background concentrations of natural compounds'

10.1.11 Assess the review note on mercury speciation in biota prepared by M. Leermakers. *(In Lisbon, it was agreed that M. Leermakers should supplement her review on mercury speciation in sea water by including also mercury in biota).*

10.1.12 Any other business raised by the subgroup *(Among others, the Trace Metals Subgroup needs to appoint a chairperson to deal with matters which may arise intersessionally and who can chair the subgroup next year).*

10.2 Organics Subgroup

10.2.1 (C.Res.1996/2:15:1 j) Update where appropriate the list of contaminants which can be monitored on a routine basis, including a discussion about actual analytical proficiency based on recent interlaboratory studies

10.2.2 (C. Res. 1996/2:15:1 c) Assess the need for and possibilities to organise an interlaboratory study on organotin analysis *(In Lisbon, it was decided that D. Wells and W. Cofino should sent out a questionnaire on organotin analysis and contemplate about the possibilities to organise an interlaboratory study in this field)*

10.2.3 (C.Res.1996/2:15:1 e) Review the final guidelines prepared by the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea [HELCOM 1996/3].

10.2.4 (C.Res.1996/2:15:1 m) Review the paper on quality assurance of data to be loaded in a database, and prepare a general guideline for this activity

10.2.5 (C.Res.1996/2:15:1 g). Review and report on progress on a joint study to compare and contrast the different results of using multivariate methods on a common data set on PCBs in fish-eating marine mammals *(In Lisbon, it was agreed that D. Wells should prepare a report on Texel meeting for MCWG 1997)*

10.2.6 (C.Res.1996/2:15:1 i). Review the overview papers on chlorinated solvents and benzene, toluene and xylene (BTX) in fish, chlorinated dioxins and furans in sediment, the formation of hexachlorobenzene (HCB) metabolites , toxaphene, IRGAROL 1051 and phenyltins [HELCOM 1996/2] *(In Lisbon, it was agreed that P. Roose will present results of research on the presence of chlorinated solvents and benzene, toluene and xylene (BTEX) in fish, M. Lebeuf to give a presentation on the occurrence of chlorinated dioxins and furans in sediments, including some core-studies, J. de Boer to prepare a short discussion paper on toxaphene including aspects of analysis and tolerance levels, B. Janson to prepare short discussion paper on toxic HCB-metabolites).*

10.2.7 (C.Res.1996/2:15:1 k) Review the paper on bioaccumulation and biomagnification of PCB:s in the food chain, with the aim of facilitating a more detailed request on the transfer of halogenated compounds in food chains by HELCOM[HELCOM 1996/9] (*In Lisbon, it was decided that a group of members of the MCWG would provide a report on general principles (chemical and biological) governing the transfer of halogenated organic contaminants illustrated by a few examples)*

10.2.8 (C.Res.1996/2:15:1 a) Review and finalise draft guidelines for monitoring PAHs in biota, and with WGMS, in sediments including the number of replicate samples per area to characterise the sampling area [OSPAR 1997/1.1].

10.2.9 (C.Res.1996/2:15:4 f) In collaboration with WGEAMs, review information gathered intersessionally on variance components in seabird egg analysis.

10.2.10 (C.Res.1996/2:15:1 q) Based on a response from the IWC on cetacean diets, provide information on contaminant levels in these prey species, in collaboration with WGEAMS.

10.2.11 (C.Res.1996/2:15:1 f) Review the progress in the collaborative study on tris (4-chlorophenyl)methanol (TCMP) and tris(4-chlorophenylmethan(TCPMe). *(In Lisbon, it was agreed that J.de Boer should take the lead in such a study).*

10.2.12 Review and report on an updated version of the report 'Background concentrations of natural compounds

10.2.13 Review an overview on polychlorinated diphenyl ethers (PCDEs) prepared by J.de Boer

10.2.14 Presentation of results of research on the presence of chlorinated solvents and benzene, tolouen and xylene (BTEX) in fish (P. Roose).

10.2.15 Presentation of the occurrence of chlorinated dioxins and furans in sediments, including some core-studies (M. Lebeuf).

10.2.16 Presentation of results of a study on the bioaccumulation and biomagnification of PCB:s in the food chain.(A. Abarnou)

10.2.17 Any other business raised by the subgroup. *(Among others, the organic subgroup needs to appoint a chairperson to deal with matters which may arise intersessionally and who can chair the subgroup next year.)*

10.3 Chemical Oceanography Subgroup

10.3.1 (C.Res.1996/2:15:1 e) Review the final guidelines prepared by the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea [HELCOM 1996/3].

10.3.2 (C.Res.1996/2:15:1 m) Review the paper on quality assurance of data to be loaded in a database, and prepare a general guideline for this activity. *(In Lisbon it was agreed that Mikaell Krysell would give a presentation and possibly demonstrate the methods used at SMHI for quality assurance of data to be loaded in the database).*

10.3.3 (C.Res.1996/2:15:1 o) Review the descriptions of members' protocols for quality assurance and provide guidance for OSPAR *(In Lisbon it was agreed that all members were asked to contribute with descriptions of the quality control procedures used by their labs on nutrient analysis).*

10.3.4 (C.Res.1996/2:15:1) Review papers on units for nutrient and oxygen, and total nitrogen methods, the reliability of old nutrient data, and particulate carbon (POC) in anoxic waters.*(In Lisbon it was decided that Don Kirkwood would present a review of total nitrogen method and Mikaell Krysell a discussion paper on particulate organic carbon, POC in anoxic waters. Ole Vang Olsen would prepare a discussion paper on the reliability of old nutrient data.).*

10.3.5 (C.Res.1996/2:15:n) Review the paper on methods for oxygen determination and their quality assurance and provide guidance for OSPAR (In Lisbon it was agreed that *Alain Aminot would put together a presentation of methods for oxygen determination and the quality assurance of these)*

10.3.6 (C.Res.1996/2:15:p) Review the updated paper on DOC/TOC in sea water including estuaries.

10.3.7 Review and report on an updated version of the report 'Background concentrations of natural compounds

10.3.8 Any other business raised by the subgroup *(Among others, the Chemical Oceanography Subgroup needs to appoint a chairperson to deal with matters which may arise intersessionally and who can chair the subgroup next year).*

11 PLENARY DISCUSSION OF SUBGROUP WORK

12 ANY OTHER BUSINESS

13 RECOMMENDATIONS AND ACTION LIST

14 DATE AND VENUE OF THE NEXT MEETING

15 CLOSURE OF THE MEETING

ANNEX 3

REPORT ON THE PROGRESS OF THE EU PROJECT QUASIMEME AND THE DEVELPOMENT OF THE QUASIMEME II LABORATORY PERFORMANCE STUDIES

The information given in this report are published in the QUASIMEME Bulletin No 4 January 1997 availbale from the QUASMIMEME Project Office.

QUASIMEME Amongst Top European Projects

QUASIMEME has been judged to be amongst the top projects in the European Union's Industrial Technologies Programme (BRITE-EURAM, S,M&T Research). Following a submission of the project's progress by the EU Commission, DG XII, the QUASIMEME project Office was interviewed on the telephone and the European Services Network in Brussels produced an article on QUASIMEME as part of the EU 'Success Stories' in Europe.

QUASIMEME Success Story

Summary of the ESN report

Without accurate chemical data, it is impossible to protect the sea against pollution. Policy decisions based on poor quality data could have devastating social, economic and environmental consequences.

The QUASIMEME project, involving 90 key marine monitoring laboratories from all the maritime member states, has succeeded in determining the current accuracy of their measurements. Using a holistic Quality Assurance approach, it has identified key sources of error, and has made demonstrable progress towards improving the quality of monitoring data.

QUASIMEME has built an effective European marine monitoring network, which will continue on a self-financing basis, providing national and international agencies with increasingly reliable data from the contributing marine institutes.

Over the three years QUASIMEME has not only fulfilled its stated objectives, but has used the resources made available by the EU to establish an international quality system for all marine institutes making chemical measurements for monitoring or research purposes.

At the outset QUASIMEME had three main objectives which have been achieved through a series of stepwise interlaboratory studies in each of the main strands of chemical measurement

QUASIMEME Objectives

1. To establish a comprehensive knowledge of the Quality of Chemical Measurements made in Marine Monitoring Programmes.
2. To understand the basic underlying causes of 'poor' between laboratory agreement.
3. To undertake a stepwise improvement programme to allow each laboratory an opportunity to provide data of a higher quality.

for nutrients in sea water, trace metals in sediment and biota, organochlorine residues in sediment and biota and PAHs in sediment. The feedback has been effective through a series of detailed assessment reports and specialist workshops held at different locations throughout Europe. At each stage of the work, the progress of each group was reviewed and an action plan prepared for the next step of the studies.

Main Achievements of QUASIMEME I (1993–1996)

- Developed a broad based Marine Chemistry Network in Europe which is now extending worldwide.
- Provided a comprehensive knowledge of the quality of chemical measurements in the marine environment.
- Provided more appropriate test materials
- Stabilised sea water for nutrient analysis
- Wet homogenised biological tissue
- Broad range of sediment types
- Established a database for all QUASIMEME Information. These data are transferred electronically by diskette or e-mail.

The QUASIMEME project now has a membership which has extended beyond the ICES Marine Chemistry Working Group to include partners in the Mediterranean and now worldwide. The interlaboratory studies undertaken in the last three years have allowed the scientific assessment group to establish a comprehensive understanding of the key sources of the analytical error in chemical measurements and an overall evaluation of the quality of information provided for environmental assessment. Effectively the Marine Chemistry Network have gone from a position of unknown or 'patchy' knowledge of the quality of data to a level of known quality. These data have also been established using more suitable test materials, especially in the area of biological tissues. Previously, most test materials were dried powders, developed for use as reference material. These powders had the advantage that they were more likely to be stable over longer periods of time, but not directly appropriate for use in testing methods which routinely require wet fish tissue. The new series of wet tissues developed at the DLO- Netherlands Institute for Fisheries Research at IJmiuden for QUASIMEME have allowed the laboratories to fully test their extraction and clean-up techniques on more realistic samples.

The Scientific Group assessments in each of the five sets of interlaboratory studies within QUASIMEME I have achieved some invaluable milestones.

Achievements of the QUASIMEME Scientific Assessment Group

- Established a clear and coherent system of evaluation based on Z scores (ISO 43).
- Clear identification of the 'problem' determinands.
- Low levels of ammonia and phosphate in sea water
- Lead in biota
- CB 29 in biota and sediment
- Clear indication of laboratories that: a) perform consistently at a high standard and; b) laboratories that have demonstrated a significant improvement during the project.
- Established a level of comparability and the best *between laboratory* performance.
- Established realistic targets for bias and precision based on constant and proportional errors.

The assessments have clearly indicated which laboratories now perform to a high, acceptable standard and which laboratories have shown a significant improvement in performance during the three years of the project (Table 1).

In general, the laboratory performance can be classified into four group; a) those who have shown an improved performance, b) those that are consistently good, c) those that are consistently poor and d) those that have declined in performance during the period of the project..

Normal data treatment, either by classical or robust statistical methods (Cofino and Wells, 1994) do not separate or classify the laboratories into groups. Also, any classification based on the comparison of the standard deviation of the group may not be the most sensitive indicator of changes in the quality of individual laboratory data. For example, a number of laboratories within a group may improve with successive interlaboratory studies while a few participants continue to produce poor data of very variable quality. In this case it is quite conceivable that the small number of poor performers are masking the improvement of others by controlling the magnitude of the standard deviation of the whole data set.

An alternative approach to assessing the performance of laboratories is to compare the *proportion* of analyses that can be classified as 'satisfactory' (Thompson and Wood, 1993; ISO/IEC, 1996). Each value (x) obtained by a laboratory is normalized as a Z score using the assigned value (X) and a predefined, allowable bias ( ). Such that:

$$Z = (x - X)/s.d.$$

where s.d. represents the target standard deviation. The laboratory's data are classified as satisfactory when $|Z| < 2$. An overview of the whole data set is given here to summarise the progress of the interlaboratory studies conducted within the project.

The total number of satisfactory scores for each group of determinands were obtained for both the Initial Interlaboratory Studies (Rounds 1 and 2, or 2 and 3) and the Final Interlaboratory Studies (Rounds 4 and 5) and expressed as a percentage of the total number of measurements made for that determinand group by each laboratory, so that, for example:

$$\% \text{ of satisfactory scores (Nutrients)} = (|Z| < 2)^* \ 100/\text{Number of reported values.}$$

The overview in Table 1 indicates that a high proportion of laboratories have shown a measurable improvement in performance for each of the key determinands in each of the matrices tested, particularly for trace metals in sediment and nutrients in sea water. There is also an improvement for a number of laboratories for CBs in cod liver oil, but this is not so evident for CBs in biological tissue. However, the comparison for CBs in biota is not equivalent since the analysis of the whole tissue homogenate was not introduced into the scheme until the third round. The number of laboratories with satisfactory scores ($|Z|<2$) for CBs in biota did not improve significantly over the three rounds (Rounds 3 to 5). In Round 3 the laboratories with acceptable scores ranged from 64-77% for the nine individual CBs, 45–84% for Round 4 and 48–66% for Round 5.

A total of % satisfactory scores for the key mandatory determinands has also been made to assess the overall performance. These data are based on the nutrient, TOxN, ammonia, nitrite and phosphate, the trace metals, (Cd, Cu, Hg, Pb and Zn) and the three most abundant and stable congeners (CBs 138, 153 and 180).

Of the 76 laboratories reporting data for the whole programme, 32 have improved their measurements for these determinands and 18 are consistently good, while 16 were consistently poor and a further 10 have declined in performance. Overall 34 of the 76 laboratories currently produce data which have >80% of the values as being satisfactory.

From the returns of the QUASIMEME questionnaires it was possible to classify the laboratories as a) accredited, b) those actively seeking accreditation and c) those which are not accredited It would appear that there is currently no correlation between performance in the QUASIMEME Laboratory Performance Studies and the status of the laboratory in terms of accreditation. In fact, if there were any trend the data would suggest a negative correlation. Only six out of the 39 laboratories with >80% of satisfactory scores are accredited while 12 out of the 40 laboratories with <80% of satisfactory data are accredited.

Although accreditation requires a quality system to be in place in a laboratory, the scope for accreditation, at present, does not base the quality performance criteria of a laboratory on external quality control tests like QUASIMEME. Instead, each laboratory is permitted to set its own performance criteria. Although it might be expected that an accredited laboratory would perform better that one that is not accredited, it is not automatically the case. A good laboratory can be taking all the correct actions and decisions to produce good data and not be accredited, while an accredited laboratory can document and audit data of a lower quality!

However, there is now a growing tendency for Accreditation Bodies, especially those associated with the European Accreditation of Laboratories (EAL), to include the results of external QC testing, such as QUASIMEME, in the annual assessment of accredited laboratories. Until this link is in force there may be no reason to expect a positive correlation with laboratory performance to an external standard. In general, there is good evidence to suggest that the quality of performance is related to the opportunity to undertake the analysis without the pressure of other immediate tasks or contract studies, where time is at a premium. When staff are given the training, motivation, facilities and reasonable time then they are able produce the data to the required quality.

QUASIMEME has established itself as an international project dedicated to the improvement of Quality Management and Quality Measurement in Marine Institutes. The series of interlaboratory studies undertaken during 1993–1996

clearly demonstrate that laboratories can improve the quality of measurement when given a structured framework in which to test their performance, and an opportunity to obtain constructive feedback through the detailed assessments. In the tailor made workshops, participants discuss their problems and find appropriate solutions to these difficulties. QUASIMEME now provides the programme through which all marine laboratories can obtain the essential external quality assessment information which can be submitted with their environmental data to the national and international monitoring programmes..

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Prepared and Presented by
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Table 1. Overview of performance and improvement of laboratories for the first rounds (1 and 2) and the last rounds (4 and 5).

Determinand group	No. of labs with 80% or more satisfactory results (|Z|<2)	No. of labs with improved performance	No. of labs that are consistently good	No. of labs that are consistently poor	No. of labs that have decline in performance
Nutrients	22	21	8	9	9
Trace metals in sediment	32	27	10	3	8
Trace metals in biota	14	12	8	9	13
CBs in cod liver oil	15	11	9	1	8
CBs in sediment	9	15	4	3	9
All data					
Key mandatory determinands	34	32	18	16	10

Improved performance	% Satisfactory scores in the final two interlaboratory studies improved by more than 10% over those in the first two studies.
Consistently good	% Satisfactory scores >80% for both the first two and final two interlaboratory studies.
Consistently poor	% Satisfactory score <80% for both the first two and final two interlaboratory studies.
Declined performance	% Satisfactory scores in the final two interlaboratory studies declined by more than 10% over those in the first two studies.

QUASIMEME Laboratory Performance Studies (LPS) for 1997–1998

The QUASIMEME II International Laboratory Performance Studies are open to all organizations making chemical measurements in the marine environment, and which provide QA information for national or international monitoring programmes, for individual or collaborative research or for contract studies. The LPSs are designed to support quality management and quality measurement in the participating laboratories. The assessment of the test data may be used (i) to validate internal laboratory QA, (ii) in support of accreditation and (iii) to support QA information submitted with environmental monitoring data to national or international programmes.

The QUASIMEME LPS has the support of the Helsinki Commission (HELCOM), the Oslo and Paris Commissions (OSPAR), Mediterranean Pollution Monitoring and Research Programme (MEDPOL), the Arctic Monitoring and Assessment Programme (AMAP), the International Council for the Exploration of the Seas (ICES) and the European Co-operation for Accredited Laboratories (EAL). The Laboratory Performance Studies meets part of the Quality Assurance objectives of those laboratories which submit environmental data to the marine monitoring programmes.

The QUASIMEME LPS includes many of the key determinands in aqueous, sediment and biological matrices for nutrients, trace metals and organochlorines, organophosphorus, triazine and PAH residues. The concentration range covered reflects those found in estuarine, coastal and open water areas. The QUASIMEME LPS follows an annual timetable, from June to the following May, with a series of tests for each determinand/matrix combinations. To assist participants in their planning, the timetable will be available six months ahead of the first testing period in each year. Each testing period, from receipt of sample to reporting, is around five months and the test report will be available within three months of the deadline for the receipt of results. New test materials with additional determinands may be incorporated into the future programme provided there is sufficient demand for these studies.

During the year, June 1997 to May 1998, the new, additional, determinands will include lithium, scandium, iron and manganese in the measurements of metals in marine sediments . Selenium will be added to the trace metals in biological

tissue. The measurements of PAHs will be offered for measurement in shellfish and 17 chlorinated dioxins and furans will be available for measurement in biological tissue.

There will be three new development exercises. These will be for PAH metabolites in solution and bile extract, toxaphene in solution and biological tissue extract and organo tins in solution and shellfish.

The QUASIMEME LPS is funded by an annual subscription from each participating laboratory and a fee for each group of determinands selected from the programme. In general there are four test materials for each group of determinands in any one year of the LPS. Two test materials are sent to participants on two occasions in the LPS year with five to six months between the commencement of each test period. The cost for each group decreases on a *pro rata* basis, so that the overall cost is lower, per group, for those laboratories who select a greater number of groups.

The fees include the provision of the selected test materials delivered to the laboratory with protocols and information on the analyses required together with a data collector programme, which operates under MS DOS, to record and submit the analytical data and method codes. This method of data submission significantly reduces errors in data transmission and speeds up the reporting and assessment processes.

The Assessment

Each test will be fully assessed and a Z score (bias) and, where appropriate P score (precision), will be calculated. .

The Report

The details of the test report will be sent to all participants. The results remain the property of each participant and full confidentiality is maintained. No information on the performance of any participant is disclosed to any third party. QUASIMEME, however, positively encourages each participant to use their test results and the assessment to support their QA data in the submission of environmental information to national or international marine monitoring programmes.

QUASIMEME LPS Data Submission to third parties.

QUASIMEME LPS operates a confidential service to all participants. However, the data generated by the participants is invaluable to the national and international organisations that collate and assess environmental data for the same chemical determinands.

QUASIMEME encourages all participants to submit their QA data, including their LPS results along with their environmental data. QA data submission, including LPS data, to any third party is the responsibility of that laboratory.

As a service to participants, QUASIMEME will prepare their LPS data for submission to third parties. When this service is selected, QUASIMEME will organise a laboratory's data for the year on a diskette, forward the diskette to the laboratory with a printout for confirmation.

QUASIMEME provides a comprehensive programme of support to laboratories to monitor their QA through external quality assessment and information on improvement in analytical performance.

Matrices and Determinands

The QUASIMEME LPSs offer participants the following test materials which include an extensive range of determinands.

SEA WATER SAMPLES

Some sea water will be provided as filtered samples. In most cases a specific volume of sea water will be provided along with a spiking solution and specific instruction on the preparation of the test sample. Other sea water samples will be provided for analysis 'as received'. Specific information will be given with each set of test materials.

AQ-1 Nutrients in filtered sea water

Open water samples — Nitrate + nitrite (TOxN), Nitrite, Ammonia, Orthophosphate, Silicate, Total -N and Total -P

AQ-2 Nutrients in filtered sea water

Estuarine samples — Nitrate + nitrite (TOxN), Nitrite, Ammonia, Orthophosphate, Silicate, Total -N and Total - P

AQ-3 Metals in sea water

Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Zinc

AQ-4 Metals in sea water

Total mercury. Mercury is offered as a separate determinand since it is necessary to prepare and ship this element separately. All trace metals in sea water come as complete, filtered samples in ca 0.6% nitric acid in sea water.

AQ-5 Chlorinated organics in sea water

α, ß and γ HCH, HCB, HCBD, p,p' DDE, p,p' DDD, p,p' DDT, o,p' DDT, aldrin, endrin, isodrin, dieldrin, Trifluralin, Total Endosulphan (I & II), 1,2,4, TCB, 1,3,5 TCB, 1,2,3 TCB

Samples will be shipped either as pre-spiked material or with a spiking solution in methanol.

AQ-6 Chlorinated volatiles in sea water

Chloroform, Carbon tetrachloride, Trichloroethane, 1,2 Dichloroethane, Trichloroethene, Tetrachloroethene. Samples will be shipped either as pre-spiked material or with a spiking solution in methanol.

AQ-7 Pentachlorophenol in sea water

PCP is offered as a separate determinand since it is usually determined by a different method and requires a separate volume of sample.

AQ-8 Triazines & Organophosphorus compounds in sea water

Simazine, atrazine, azinphos-methyl, azinphos-ethyl, fenthion, malathion, parathion, parathion-methyl, fenitrothion, dichlorvos, diazinon, fenchlorophos.

SEDIMENTS

MS-1 Metals in sediment

Aluminium, Arsenic, Cadmium, Chromium, Copper, Iron, Lithium, Lead, Manganese, Mercury, Nickel, Scandium, Zinc, total organic carbon, inorganic carbonate

MS-2 Chlorinated organics

CB 28, CB 52, CB 101, CB 105, CB 118, CB 138[1], CB 153, CB 156, CB 180, and HCH, HCB, p,p' DDE, p,p' DDD, p,p' DDT, o,p' DDT, aldrin, endrin, isodrin, dieldrin, transnonachlor

MS-3 PAHs

Benzo[a]anthracene, Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[e]pyrene, Benzo[g,h,i]perylene, Chrysene, Fluoranthene, Indeno[1,2,3,cd]pyrene, Phenanthrene, Pyrene

BIOTA

BT-1 Metals

Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Zinc.

BT-2 Chlorinated organics

CB 28, CB 52, CB 101, CB 105, CB 118, CB 138, CB 153, CB 156, CB 180, and HCH, HCB, p,p' DDE, p,p' DDD, p,p' DDT, o,p' DDT, aldrin, endrin, isodrin, dieldrin, transnonachlor

BT-3 Non-ortho CBs, PCDFs & PCDDs

CB 77, CB 126, CB 169

2378-TCDF, 12378 PeCDF, 23478 PeCDF, 123478 HxCDF, 123678HxCDF, 234678 HxCDF, 123789 HxCDF, 1234678 HpCDF, OCDF

2378 TCDD, 12378 PeCDD, 123478 HxCDD, 123678 HxCDD, 123789 HxCDD, 234678 HpCDD, OCDD

BT-4 PAHs

Benzo[a]anthracene, Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[e]pyrene, Benzo[g,h,i]perylene,Chrysene, Fluoranthene, Indeno[1,2,3,cd]pyrene, Phenanthrene, Pyrene

DEVELOPMENT EXERCISE

DE-1 PAH metabolites

A series of standard solutions and fish bile extracts spike with PAH metabolites which can be used to test and validate method development for these adducts.

DE-2 Toxaphene

A series of standard solutions and cleaned-up fish tissue extracts which can be used to test the methods of separation and quantification of toxaphene congeners.

1

"CB 138" is equivalent to CB 138 + CB 163 unless declared otherwise by the participant. Most participants are not separating these congeners on a routine basis at present.

DE-3 Organo tins

A series of solutions containing organo tins in solution and shellfish to test the methods of calibration and sample preparation.

DATA TRANSMISSION

DT-1 Data transmission to ICES

QUASIMEME LPS Data from the requesting laboratory will be prepared on diskette for that laboratory to forward to ICES as part of the QA submission in support of environmental data. This laboratory should normally be submitting data to ICES for OSPAR or HELCOM.

DT-2 Data transmission to UK NMAQC

QUASIMEME LPS Data from the UK requesting laboratory will be prepared on diskette for that laboratory to forward to ICES as part of the QA submission in support of environmental data.

Timetable and Content of the Test Scheme for June 1997 to May 1998

Test Period	Start date	Deadline	Report available
1 (5 months)	June 1 1997	October 30 1997	January 30 1998
2 (4 months)	October 1 1997	January 30 1998	April 30 1998
3 (5 months)	December 1 1997	April 30 1998	July 30 1998
4 (4 months)	April 1 1998	July 30 1998	October 30 1998

Test Period	Group No	No. of tests in a group	Determinand Group	Matrix
AQUEOUS SAMPLES				
1 & 3	AQ-1	2+2[1]	Nutrients	Sea water
1 & 3	AQ-2	2+2	Nutrients	Estuarine water
2 & 4	AQ-3	2+2	Metals (other than Hg)	Sea water
2 & 4	AQ-4	2+2	Mercury	Sea water
2 & 4	AQ-5	2+2	Chlorinated organics	Sea water
2 & 4	AQ-6	2+2	Chlorinated volatiles	Sea water
2 &4	AQ-7	2+2	Pentachlorophenol	Sea water
2 & 4	AQ-8	2+2	Triazines & Organophosphorus organics	Sea water
SEDIMENTS				
1 & 3	MS-1	2+2	Trace metals	Silty Sediment
1 & 3	MS-2	2+2	Chlorinated organics	Silty Sediment
1 & 3	MS-3	2+2	PAHs	Silty Sediment

BIOTA				
1 & 3	BT-1	2+2	Trace metals	Fish & shellfish
1 & 3	BT-2	2+2	Chlorinated organics	Fish & shellfish
1	BT-3	2	Non ortho CBs, PCDDs and PCDFs	Fish & Shellfish
3	BT-4	2	PAHs	Shellfish
DEVELOPMENT EXERCISES				
1	DE-1	2	PAH Metabolites	Soln. & bile
1	DE-2	2	Toxaphene	Soln. & extract
3	DE-3	2	Organotins	Soln & shellfish

ANNEX 4

QUALITY ASSURANCE OF SAMPLE HANDLING

Following the successful development of the EU QUASIMEME I project to a fully self-supporting subscription-based scheme for the Laboratory Performance Studies, a project was initiated to test the quality assurance associated with sampling and sample handling. This project was prepared as a proposal to the EU (S, M & T) under the 4th framework programme in 1995 and accepted in 1996.

The Quality Assurance of Sample Handling (QUASH) was developed as a direct response to the requirements of the Oslo and Paris Commissions (OSPAR), the Helsinki Commissions, (HELCOM) and the Mediterranean Pollution and Research Programme (MEDPOL) to establish an holistic quality management and training programme to improve the sample handling techniques used and the measurement of co-factors in MMPs and to provide data of known quality. These international and the national programmes provide data on mandatory determinands for the Quality Status Reports of the North Sea, Baltic Sea and the Mediterranean marine environment.

The analytical QA of data for these programmes is now covered by the QUASIMEME II LPSs. The additional resources provided by the QUASH project focus on the improvement and control of the total uncertainty of two inter-related, factors; sample handling and the cofactors. The environmental data generated by laboratories are not necessarily of poor quality, but are often unknown quality primarily because the variance associated with sample handling and the measurement of the cofactors are not widely available. These two areas are considered to be the main sources of unquantified error and are currently the weakest link in the quality chain. The magnitude of the total variability is a function of each step from sampling to data interpretation. Since cofactors are frequently used to normalize the data on contaminants in sediment and biota, then the variance resulting from the sampling and measurement of these parameters can have a significant impact on the interpretation of the data.

Poor or misused sampling methods and incorrect sample handling cause gross errors which cannot be corrected by a valid chemical measurement in the laboratory. The main cofactors currently used to normalize the mandatory determinands and to provide an assessment of the environmental impact of these contaminants are lipids for biota, and total organic carbon, iron and aluminium for sediments. Methods which have been fully validated between laboratories are required to provide a similar level of improvement and uncertainty for the cofactors as the determinands themselves.

Guidelines for sampling and sample handling exist, but they can differ between monitoring programmes for the same matrix-determinand combination and have never been fully tested or evaluated for different users in broad based international interlaboratory studies. Although the technology and methodology is available, the agreement between marine laboratories is currently lacking, due to underdeveloped quality systems, and validated methods for sample handling and for the measurement of the cofactors. This situation is compounded by insufficient test materials and QC check samples to validate the sampling methods and operate an holistic QA scheme.

QUASH has been developed as a coordinated project to allow participating laboratories to undertake a stepwise improvement programme to identify and, where possible, correct these problems. The project provides an audit trail to give: i) feedback via critical evaluation as a learning tool; ii) a means to obtain detailed sample handling information; and iii) control through management training and the use of key laboratory-to-field-to laboratory test samples.

The main studies focus on the estimation and control of the uncertainty associated with sample manipulation prior to laboratory analysis. The validation of sampling methods, sample handling techniques used and the measurement of the co-factors are central to obtain reliable marine chemical measurements. Procedures for quality assessment and quality control of sample handling are obtained concurrently to estimate the levels of uncertainty and thus the improved reliability of data on co-factors from sampling to analysis.

The information from these studies supports the development of each laboratory's scope for accreditation for field measurements and establish guidelines for the audit of field manipulations. It provides an holistic quantitative assessment to guarantee the quality of information to achieve objectives of the MMPs and provide recommendations to OSPAR, HELCOM and MEDPOL with respect to guidance on sampling, sample handling and the measurement of cofactors.

The objectives are achieved through a matrix work plan of three programmes and six activities (Table 1). The structure of the programme will network National Coordination Centres (NCCs) in each of the countries involved. The activities, experience and information gained by the NCCs in each work programme are passed to the national institutes through a

series of cascade, second tier workshops held in each country or region (Scheme I) which provides a cost effective scheme to guarantee the quality of information. The QUASIMEME I project had a limited number of participants, which in itself has a number of advantages. However, it was inappropriate to maintain a select number of participants for such international developments and the two tier system allows a broad spectrum of participation at the national level.

The project's six work groups each have three distinct phases.

1) Diagnosis: Assessment of the present state of the uncertainty associated with sample handling.

2) Improvement: The formulation and implementation of corrective actions.

3) Control: The development and implementation of practices and procedure in order to control an adequate level of sample handling.

Each of the six work groups are outlined in Scheme I and Table I. The first four focus on the key areas of the sampling and preservation of nutrients in sea water, sample handling and cofactors in relation to normalization in sediments, the measurement of lipids and water in biological tissue as cofactors and the effects of sample handling on biota. The last two work groups are as a support to provide the necessary test materials and for the execution of the laboratory and field performance studies.

Sampling and sample handling differs markedly from purely analytical work in that considerably greater resources are required to obtain the same level of quantitative feedback to evaluate a field procedure. Large scale intercomparisons (ca >50 laboratories) are difficult to organise due to logistic and financial constraints. For example, considerable resources are needed to organize a study where each monitoring institute transports unwieldy sampling devices such as box corers and/or van Veen grabs and other materials to a single site to undertake a field intercomparison. Also, field procedures of each institute can differ significantly and therefore the sources of error and the magnitude of uncertainty will be quite different between organisations.

In the QUASH project considerable emphasis has, therefore, been given to the prevention of these problems and dedicated exercises in each work package have focused on the important and common sources of uncertainty in sampling procedures, sample handling and the measurement of the cofactors. The uncertainty of the measurement has been minimised by involving dedicated reference laboratories for the individual studies using parameters which can be easily measured with the required bias and precision). Procedures and guidelines for QA and QC of sampling and sample handling described in the current literature are being collated and critically evaluated. Each literature evaluation is combined with the information on uncertainty estimates from the interlaboratory studies to produce a practical, tailor-made set of procedures and practices for QA and QC of sampling and sample handling for the MMPs.

The NCCs are then encouraged to apply the evaluated method and techniques. The information learnt can be elaborated in the context of their own procedures. Following each study the NCCs will organize a workshop in their own country (or region) to implement the conclusions of the international study. These workshops also take the form of an interlaboratory studies along the same principles. Reports of the national activities and conclusions are made to QUASH and the results of the national and international studies are critically evaluated at a technical discussion. Where national marine QA programmes exist the NCCs provide a two way exchange of information and experience to the international marine network.

Table 1. QUASH Working Groups.

QUASH Working Groups	Coordinator
Sampling and Preservation of Nutrients in Sea Water	Stig Carlberg (SMHI, Sweden)
Monitoring Contaminants in Biota: Lipid and Water as Cofactors	Jacob de Boer (RIVO-DLO, IJmuiden, NL)
Sampling of Biological Tissues	Britta Pedersen (NERI, DK)
Sample Handling and Cofactors in relation to Normalization Procedures for Sediments	Geogios Vlachonis (IMBC, Crete)
Preparation of Test Material, Laboratory and Field Performance Studies	Wim Cofino, (IVM, NL)
Laboratory and Field Performance Studies	David Wells (Aberdeen, UK)

The QUASH Team Line-up for the Fieldwork

A successful inception meeting was held at the Vrije University in Amsterdam on 24–25 October 1996. In addition, Foppe Smedes from RIKZ, The Netherlands and Mikael Krysell from SMHI were also invited to join the team as scientific experts.

The QUASH team spent two days preparing the details of the various work-packages and a launch workshop which has been planned for the National Coordination Laboratories (NCLs). These laboratories will play a crucial role in establishing the QUASH activities at a national level. A series of interlaboratory exercises with the NCLs will assess all aspects of sample handling and pretreatment and then information will be passed on at a national level. Workshops will aim to cover each specialist area of the programme and will be very much a 'hands on' design.

The aim of the project is to establish validated methods for sample handling and pretreatment, and to improve the analytical results by identifying and reducing errors due to sampling and sample handling. At present many of the guidelines or recommendations for a QA/QC programme related to sample handling or cofactors have not been verified and documented by interlaboratory trials. The scientific group meet in Amsterdam in October 1996 and covered much of the essential groundwork to lay the plans for the first year and the inception workshop to be held in The Netherlands in April 1997.

ANNEX 5

COMMENTS ON THE 'GUIDELINES'

§H 1 It should be mentioned that class 3 means 3000 particles per cubic meter. The note being European, this explanation should preceed the American one (class 100). However, it should be stipulated that both class types are equal. ($3000/m^3 = 100/ft^3$), and that these conditions are the minimum required to work contamination free.

§H 2 'Suprapur' should be replaced by 'high purity', since the former is a commercial term. For the same reason, 'Nuclepore filters' should be replaced by 'polycarbonate or cellullose acetate filters'.

For applying the term 'high purity' to water, a resistivity of 18M(/cm-1 should be the minimum basis.

Bottles should be stored filled with diluted acid and bagged until use.

Chlorofluorocarbon should be replaced by the general term 'solvents', since there is a wide variety to choose from.

Futhermore, it should be pointed out that these are suggestions, because many methods exist that are equally good. In almost all cases,HCl and HNO^3 are interchangeable.

'LDPE/quartz bottles' should be replaced by 'sampling bottles', because also HDPE, polypropylene, teflon plastics are appropriate.

Teflon Subboiling still is required for distilling HF.

High purity ammonium acetate, citrate or other salts should be mentioned (cfr. §H4).

§H 3 Pumping is also a way of sampling. Use should be made of a peristaltic pump or a teflon piston pump together with a precleaned tubing.

Another way is collection by hand from a rubber boat wearing arm-length gloves, navigating gently upstream, and if possible againt the wind.

Using one of these two methods is suggested to collect surface water .

Avoidance of contamination in the absence of clean lab facilities is impossible, except when the pumping and/or handling can be performed in a closed system. (Berman S *et al.*...)

§H4 On-line filtration during pumping should be mentioned. It should be noticed that rinsing filters with deionised water destroys phytoplankton, a significant part of the particulate phase (especially during bloom). Instead, solutions isotonic to sea water should be used. These solutions can be prepared from high purity NH4 Acetate or NH4 citrate.

§H5 Acidification to a of pH of 1,6 or less is necessary. This requires 1,5 ml acid per liter approximately. Filters can be stored at -18°C (avoiding special freezers), and storage 'up to six months' should become 'at least one year'.

§H6 Special care should be taken to acquire HF of high purity.

Detailed information regarding this section can be found 'in the open literature', instead of the mentioned references.

§H7 Analytical techniques should also mention ICP-MS, ICP-AES and 'Voltammetric Stripping Methods' should be generalised to 'Electrochemical Methods'.

§H8 Title should be 'Quality Control', using 'Blank and Calibration' as a subtitle, and 'reference material' as another (cf. Annex B (p 29), where a sea water standard should be added (e.g., NASS-4)

Recommanded Working standard solutions should not be mentioned.

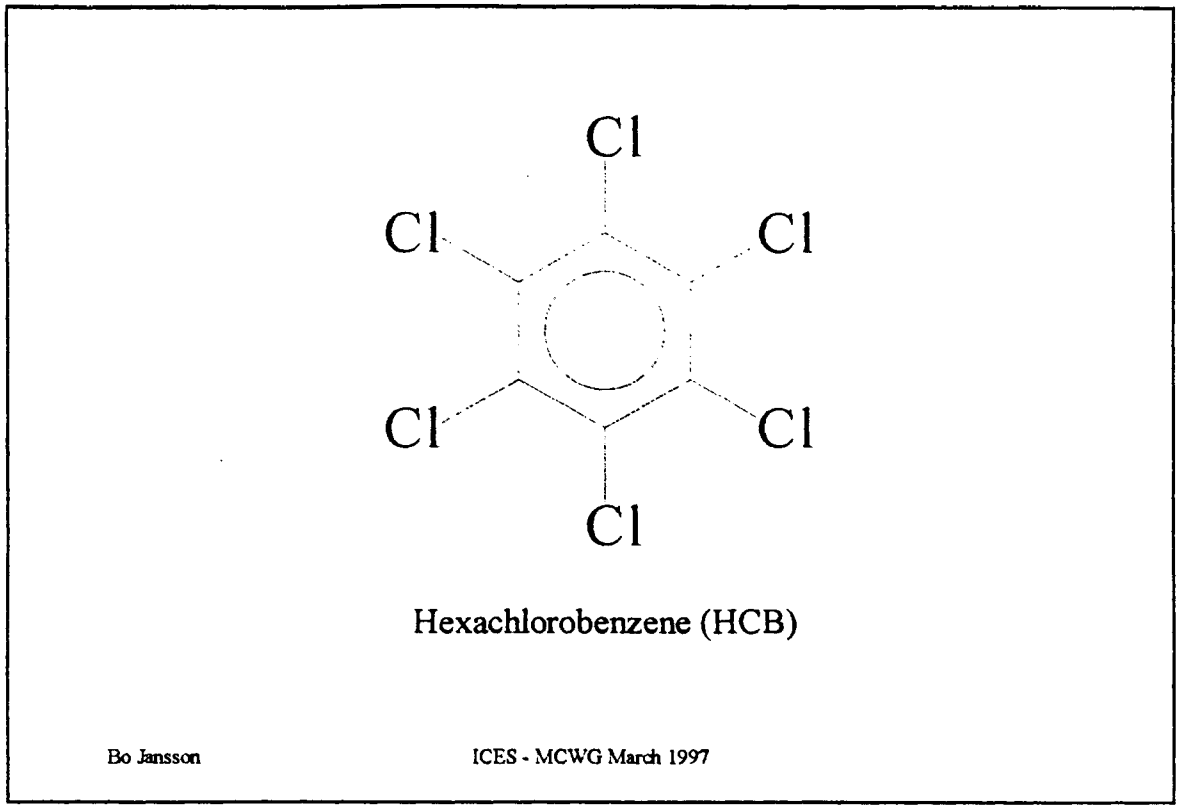
'Precleaned containers' are preferable for storage of standards, since not only LDPE is suitable.

More recent references can be found in the open literature.

ANNEX 6

METABOLISM OF HCB

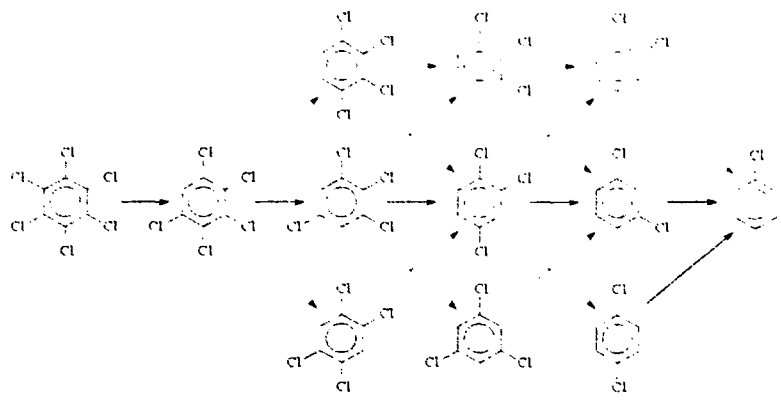
Bo Jansson
Institute of Applied Environmental Research
Stockholm University



Hexachlorobenzene is one of the well recognized Persistent Organic Pollutants (POPs). Chlorine atoms on all carbons and no hydrogen available for attack. But is that really true?

This short overview will show that a large number of metabolites of HCB have been reported and some of these may be of environmental concern.

The material is mainly based on a review article by Brenner (1988) and a manuscript from IPCS (WHO, 1997). A litterature review have disclosed a few recent papers that also have been included.

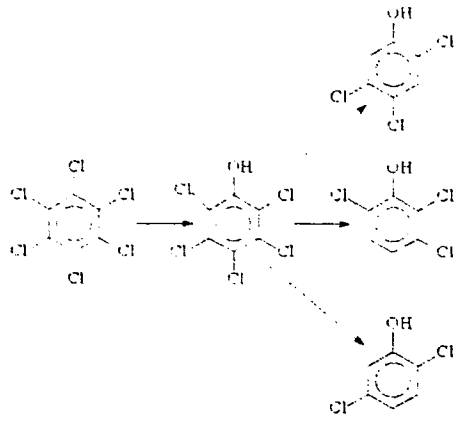


Major (> 50%) and minor (< 50%) pathways for the transformation of HCB under anaerobic conditions. Black arrows show slow processes. (From Susarla et al. 1996)

Bo Jansson ICES - MCWG March 1997

A study of reductive dechlorination ov HCB in anaerobic sediment collected close to a chemical industry (Susarla et al., 1996). Formation of all 12 chlorobenzenes could be seen.

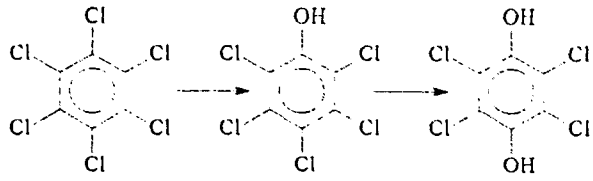
The chlorobenzenes are lipophilic and bioaccumulating. At least the congeners with high clorination degree show biological effects.



Major (50%) and minor (50%) pathways for the transformation of HCB in fry of steelhead trout (*Salmo gairdneri*) (Frankovic et al., 1995).

Bo Jansson ICES - MCWG March 1997

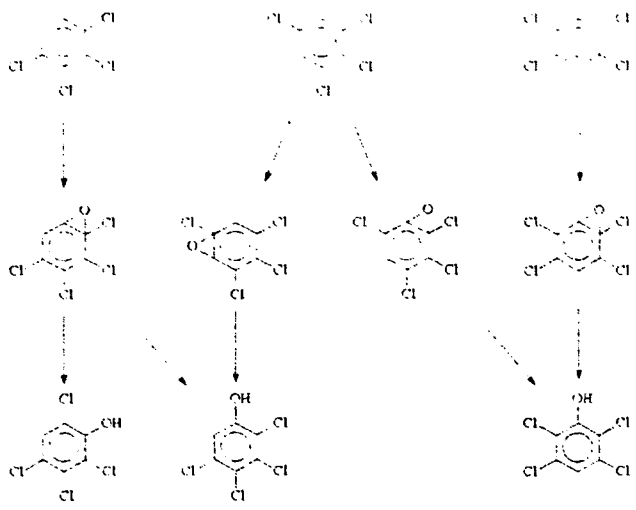
In many species the major metabolites of HCB are chlorophenols. In fry of steelhead trout (*Salmo gairdneri)* pentachlorophenol is the major metabolite and small amounts of lower chlorinated phenols were found.



The biotransformation of HCB in *Saccharomyces cereviviae* expressing human cytochrome P450 3A4 (Mehmood et al., 1996).

Bo Jansson ICES - MCWG March 1997

Biotransformation of HCB was studied in microsomal fractions and whole cells of *Saccharomyces cereviviae expressing* human cytochhrome P450 3A4 (Mehmood et al., 1996). The major metabolite was pentachlorophenol and smaller amounts of tetrachlorohydroquinone were also found. No further breakdown could be seen in this study.

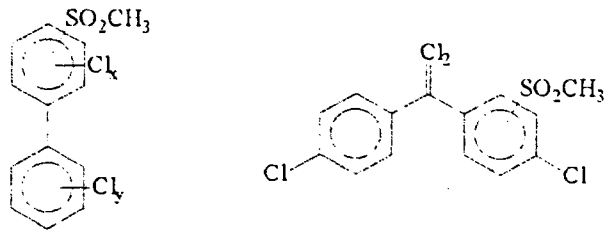


Metabolism of the isomeric tetrachlorobenzenes (Kohli et al. 1976)

Bo Jansson ICES - MCWG March 1997

The formation of chlorophenols from chlorinated benzenes goes via arene oxides intermediates. These are produced by the cytochrom P-450 monooxygenase system.

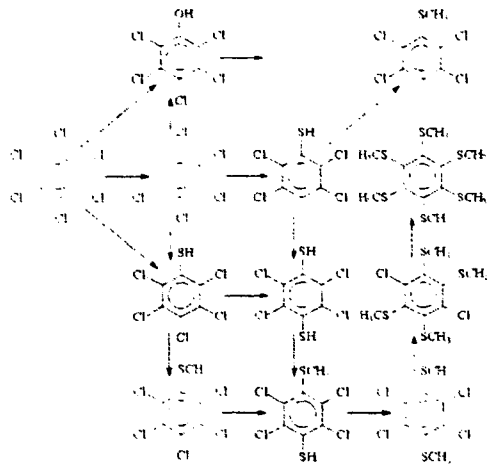
Kohli et al. (1976) studied the metabolism of tetrachloro-benzenes and found the three chlorophenols as products. The formation af these substances may involve a migration of a chlorine atom - NIH shift.



Methylsulfon metabolites of PCB and DDE
(Jensen and Jansson, 1976).

Bo Jansson ICES - MCWG March 1997

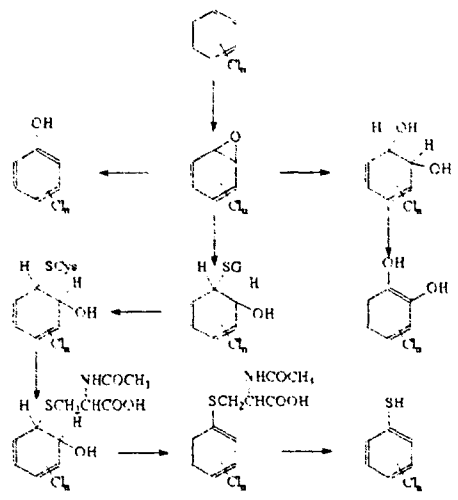
In the mid 1970's we found metabolites of PCB and DDE containing methyl sulfon groups in seal from the Baltic (Jensen and Jansson, 1976). These substances were present at levels of about 10% of the corresponding mother compounds and these metabolites were bioaccumulated. This raised our interest for the mechanism responsible for the production of these metabolites.



Compounds identified in excreta from a rat given hexachlorobenzene. Red compounds were also found in adipose tissue and the magenta compound was found in the liver (Jansson and Bergman, 1978). For some of the compounds the exact conformation is not known.

Bo Jansson ICES - MCWG March 1997

Excreta from rats given HCB were ahown to contain at least 12 different metabolites, some of which were present both in free form and as conjugates (Jansson and Bergman, 1978). Nine of these metabolites contain sulfur groups but neither sulfoxides nor sulfones could be detected. Methylthioether groups were quite common and traces could be analysed of a benzene substituted with six methylthioether groups.

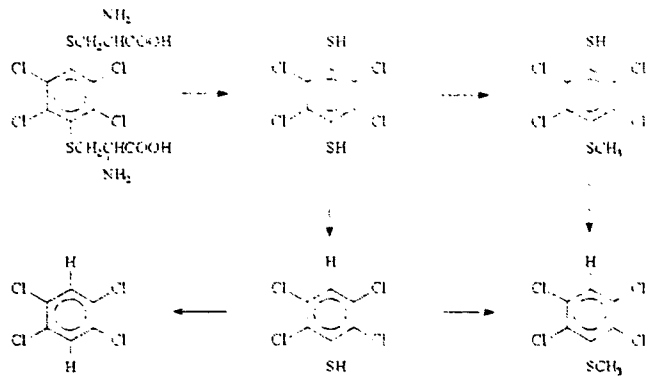


A possible pathway for the formation of HCB metabolites containing thiol groups (Renner, 1988).

Bo Jansson ICES - MCWG March 1997

The formation of sulfur containing metabolites from chlorinated aromatics is expected to go via arene oxides. These react with glutathion and further tranferred to a cysteine product. After acetylation this is fragmented at the S-C bond resulting in a thiol (Renner, 1988).

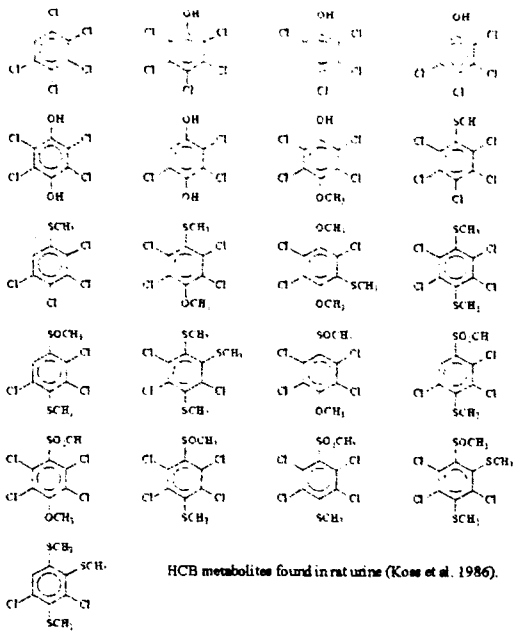
The thiols may be methylated resulting in methylthioethers, which can further be oxidised to the corresponding sulfoxides and sulfones.



Reductive desulfuration of S,S'-(tetrachloro-*p*-phenylene)dicysteine observed in rabbit (Renner, 1988).

Bo Jansson ICES - MCWG March 1997

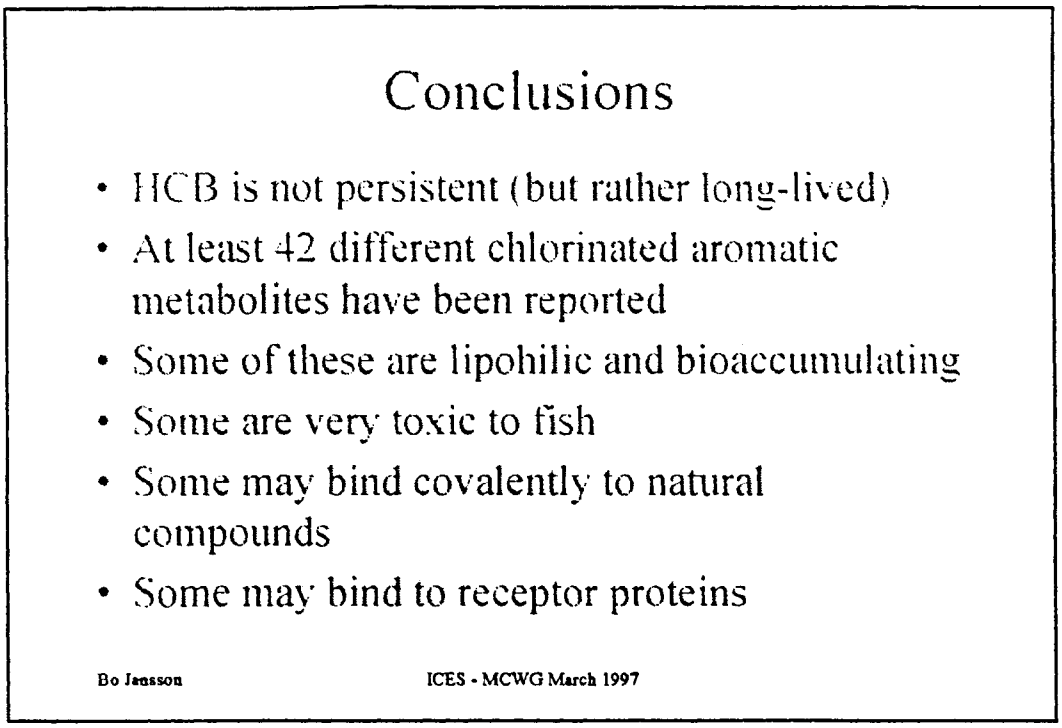
It has also been shown that the thiol groups can be reductively desulfurated to form the corresponding chlorinated hydrocarbon (Renner, 1988).



HCB metabolites found in rat urine (Koss et al. 1986).

Bo Jansson ICES - MCWG March 1997

Koss and co-workers (1986) were able to identify 21 different metabolites of HCB in rat urine. Compounds containing methyl sulfoxides and/or methyl sulfones were found.



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ANNEX 7

TRACE ELEMENTS (AND TRACE ELEMENT COMPOUDS) THAT CAN BE MONITORED IN BIOTA, SEDIMENTS, AND SEA WATER

Table A7.1. Trace elements (and trace element compouds) that can be monitored in biota, sediments and water as well as compounds of interest

BIOTA

Metal	Recent I/C data	QC material
Zn	Quasimeme/NOAA	NRC: DORM-2 (Dogfish muscle)
Cd	Quasimeme/NOAA	DOLT-2 5Dogfish liver)
Pb	Quasimeme/NOAA	TORT-2 (Lobster tissue)
Cu	Quasimeme/NOAA	LUTS-1 (Lobster tissue)
Cr	Quasimeme/NOAA	IAEA 350 (Tuna fish)
Ni	Quasimeme/NOAA	BCR 278 (mussels), BCR 414 (plankton)
As	Quasimeme/NOAA	BCR 422 (Cod muscle)
Hg	Quasimeme/NOAA	NIST: SRM 1566a (Oyster tissue)
Ag	NOAA	"
Se	NOAA	"
Sb	NOAA	Sn
NOAA	Fe	NOAA
MMHg	none	BCR CRM 463, 464 (Tuna fish) All NRC biota
* As compouds	none	DORM-2 (2)
* Organotin compounds	none	NISH (Japan)

SEDIMENTS

Metal	Recent I/C data	QC material
Zn	Quasimeme/NOAA	NRC: BCSS-1, MESS-1, NBS 1646
Cd	Quasimeme/NOAA	BCR 277, BCR 320
Pb	Quasimeme/NOAA	NIST: SRM 1645, SRM 1646, SRM 2704
Cu	Quasimeme/NOAA	
Cr	Quasimeme/NOAA	
Ni	Quasimeme/NOAA	
As	Quasimeme/NOAA	
Al	Quasimeme/NOAA	
Hg	Quasimeme/NOAA	BEST-1
Si	NOAA	
Be	NOAA	
Tl	NOAA	
Sn	NOAA	
Sb	NOAA	
Fe	NOAA	
Mn	NOAA	
Ag	NOAA	
Se	NOAA	
MMHg	none	IAEA 356, BCR 580 (1), PACS-2 (2)
*Organotin compounds	none	BCR 463 (DBT, TBT)

SEA WATER

Metal	Recent I/C data	QC material
Zn	ICES	NRC: NASS -4 (Sea water)
Cd	ICES	SLEW- 2 (Estuarine water)
Pb	ICES	SLRS-3 (River water)
Cu	ICES	
Cr	ICES	"
Ni	ICES	"
As	ICES	"
Fe	ICES	"
Mn	ICES	"
Hg	QUASIMEME (3)	none
*MMHg	none	none
* Ag	none	
* Se	none	none
* Se (-II), Se (IV), Se (VI)	none	none
* Cr (III), Cr(VI)	none	none

* not yet suitable for monotoring
(1) in phase of certification (2) in phase of preparation (3) currently being performed

ANNEX 8

UNITS AND UNIT SYMBOLS: CORRECT USE IN CHEMICAL OCEANOGRAPHY

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1. INTRODUCTION

Most of the information presented here is derived from No 45 of the Unesco Technical Papers in Marine Science (UNESCO, 1985) and from a guide published in French (Moureau, 1980). There is no better way of convincing scientists of the need for using the SI than the following arguments (UNESCO, 1985).

> « Each day standardisation becomes more urgent in all scientific fields. The main aim is to arrive at a uniform scientific language and writing, so as to avoid confusion as far as possible, and to ensure the best possible understanding among men of science.
> In the domain of quantities and units, it is important that this mutual understanding should exist, not only between members of the same scientific discipline, but also, and above all, on an interdisciplinary basis.
> The same physical quantity should be given the same name in all scientific disciplines. The quantity should be clearly defined and its name chosen so as to avoid all possibility of confusion between any neighbouring quantities...
> The worldwide adoption of the Système International d'Unités, with its SI symbols and prefixes, and its very strict rules for writing, is in fact proposed with the aim of contributing to a decisive manner to this effort of standardization. »

The SI was elaborated by the Conférence Générale des Poids et Mesures (CGPM) between 1948 and 1960. Because the metric system was created in France, the 11th (CGPM) meeting (1960) adopted the name « Système International d'Unités » and the international abbreviation « SI ».

Instead of limiting this paper to a few applications in chemical oceanography, it was thought more useful, for better overall use of the SI, to remember its main bases, the notion of unit, the current units with their symbols and the general rules of writing unit symbols. This paper is only a summary that covers most needs.

2. PHYSICAL QUANTITIES AND UNITS

Physical quantities are the basis of experimental sciences. A physical quantity (Q) can be measured by comparing it to another quantity of the same « dimension », chosen as reference and called **unit** (u). Although the value of Q is unique, it can be expressed by different numerical values (q), depending on the unit chosen:

$$Q/u = q$$

or

$$Q = q.u,$$

where « q.u » is the value or the measure of Q.

The SI has defined seven « base quantities » (length, mass, time, electric current intensity, thermodynamic temperature, amount-of-substance and luminous intensity) which are supposed mutually independent. They can be combined to generate « derived quantities ». Two « supplementary quantities » (plane and solid angles) were added. Each quantity of the

system should receive a name and appropriate symbol. The symbols of the base quantities are: *l*, *m*, *t*, *I*, *T*, *n* and I_v (italics recalls that we refer to quantities). Note: do not confuse the symbols of quantities with those of units.

3. SI UNITS, SYMBOLS AND PREFIXES

The structure for units is parallel to that of quantities. The SI is concieved as a « coherent system » since all units of the system can be multiplied or divided to give directly the resulting unit, without needing to introduce coefficients not equal to 1. Units have been given abbreviations, the unit symbols, with precise writing rules. Multiples of the units can be made up with « SI prefixes » belonging to the SI. These multiples of SI units do not belong to the coherent system, but their use is, of course, permitted.

3.1. The seven SI base units

Physical quantity	Unit name	Unit symbol
length	metre	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
amount of substance	mole	mol
luminous intensity	candela	cd

It should be noted that the initials of unit names are not written in capital letters. This is valid for all SI units (exception: degree Celsius).
The currently encountered mistakes when writing the base unit symbols are: capital K for kg, °K instead of K for Kelvin, M or mole instead of mol (no final « e »).

Note on temperature: in addition to the thermodynamic temperature (*T*; unit: K), use is also made of Celsius temperature (*t*; unit: °C), defined by $t = T - 273.15$. Thus 1 °C = 1 K.

Note on amount of substance: the « mole » is a frequently used (but misunderstood) quantity in chemistry, therefore the definition should be remembered.

> « The mole is the amount of a ***system*** which contains as many entities as there are atoms in 0.012 kilogram of carbon-12.
> When the mole is used, ***the elementary entity must be specified*** and may be atoms, molecules, ions, electrons, other particules, or specified groups of such particules. »

The most current mistake is to confuse mole and molecule, although mole concerns any of the entities mentionned in the above definition. All units such as the « gram-atom », « gram-molecule », « gram-equivalent », etc. are obsolete.

3.2. Derived SI units

Derived units are expressed algebraically in terms of base units by mean of mathematical symbols of multiplication and division. Some derived units have been given special names and symbols which, for simplicity, may themselves be used to expressed other derived units.

3.2.1. Examples of derived units without special names

Physical quantity	Unit name	Unit symbol
volume	cubic metre	m^3
density	kilogram per cubic metre	kg/m^3
speed	metre per second	m/s
amount-of-substance concentration	mole per cubic metre	mol/m^3

3.2.2. Examples of derived units with special names and symbols

Physical quantity	SI unit			
	Special name	Special symbol	Expression in terms of other units	Expression in terms of SI base units
frequency	hertz	Hz	-	s^{-1}
force	newton	N	-	$m.kg.s^{-2}$
pressure	pascal	Pa	N/m^2	$m^{-1}.kg.s^{-2}$
energy, work	joule	J	N.m	$m^2.kg.s^{-2}$
power	watt	W	J/s	$m^2.kg.s^{-3}$
electric potential	volt	V	W/A	$m^2.kg.s^{-3}.A^{-1}$
electric resistance	ohm	Ω	V/A	$m^2.kg.s^{-3}.A^{-2}$
conductance	siemens	S	A/V	$m^{-2}.kg^{-1}.s^3.A^2$

3.2.3. Dimensionless derived units

When a derived unit contains the same number of multiplications and divisions for each base unit component this derived unit is « dimensionless ».
For example, the relative density: unit is $(kg.m^{-3})/(kg.m^{-3}) = 1$.

3.3. SI prefixes

Decimal multiples and submultiples of SI units can be formed using SI prefixes with appropriate symbols as follows.

Multiples			Submultiples		
Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^1	deca	da	10^{-1}	deci	d
10^2	hecto	h	10^{-2}	centi	c
10^3	kilo	k	10^{-3}	milli	m
10^6	mega	M	10^{-6}	micro	μ
10^9	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a

3.4. Units outside the SI

Although only SI units should be used, it has been agreed that certain non-SI units, either for their practical importance or from the force of habit, may be used. These are divided into three categories:

- units used with the SI,
- units that may be temporarily used together with SI,
- units to be strongly discouraged.

3.4.1. Units used with the SI

These units, which belong to three physical quantities (time, plane angle or arc, mass), are the following:

- time: minute (symbol: min), hour (symbol: h) and day (symbol: d);
- angle: degree (symbol: °), minute (symbol: ') and second (symbol: ");
- mass: tonne (= 10^3 kg; symbol: t) and unified atomic mass (= 1/12 of the mass of an atom of ^{12}C, with the experimental value of 1.660 57 x 10^{-27} kg; symbol: u).

Note 1: a frequent mistake is to use the angle symbol units « ' » and « " » instead of the time symbol units « min » and « s ».

Note 2: to express time, the units week, month, year and century can be used but exceptionally. They have been given neither precise definition, nor symbol (write in full). ISO attributed to « year » the symbol « a » (neither 'y' or 'yr').

3.4.2. Units that may be temporarily used together with the SI

Two of these units are used for the sea:

- length: nautical mile (= 1852 m exactly; no symbol),
- pressure: bar (= 10^5 Pa exactly; symbol: bar). This unit should be used only to measure pressure differences with manometers.

3.4.3. Units to be strongly discouraged

Some of these units are the following:

- length: micron (= 1 micrometre; symbol: μ); replaced by micrometre (μm);
- volume: litre (= 1 dm^3 exactly; symbol: l or L); see below;
- pressure: atmosphere (= 101 325 Pa exactly; symbol: atm);
- pressure: millimetre of mercury (= 133.322 387 Pa; symbol: mmHg);
- velocity: knot or nautical mile per hour (= 0.514 m/s approximately; no symbol);
- energy: calorie (several definitions of the calorie have been given; symbol: cal).
- content: per mil (‰), per cent (%), part per million (ppm), part per billion (ppb), should be replaced by factor 10 raised at the corresponding power.

Note on the litre: expressing component concentrations in water is indispensable in chemical oceanography. Concentrations used to refer to the legal volume unit, i.e. the litre. The old definition stated that the litre was the volume occupied by 1 kg of water at 4 °C. Subsequent determination found that this volume was 1.000 028 dm^3. Because of this small difference between the litre and the cubic decimetre and of the risks of confusion for highly precise measurements, the 12th CGPM (1964) decided that the terms litre and cubic decimeter would thereafter be synonymous (therefore, 1 l = 1 dm^3 exactly). In addition, the word litre should not be used to express results of high precision measurements of volume.

4. HOW TO WRITE NUMBERS, UNIT SYMBOLS AND VALUES OF QUANTITIES

Wrong writing of unit symbols may generate risks of confusion, in particular when the same letter has been given different meanings.

4.1. Writing of numbers

1) Resolution 7 of the 9th CGPM (1948) specifies: « in the numbers, a comma (French use) or a point (British use) are used to separate the whole and the decimal parts of a number ».

Note on the decimal sign: slightly different versions are proposed for the decimal sign in the papers from Unesco and from Moureau. The French guide mentions that « the point is accepted in texts in English », while the Unesco paper mentions that « the preferred decimal sign is a dot on the line, (but) in French texts, a comma on the line is used ».

For example: 12.7 or 12,7 (as a function of language), never 12·7.

2) When a number is lower than one, a zero should always be placed before the decimal sign.
For example: 0.058 not .058.

3) To facilitate reading, digits may be grouped in threes either side of the decimal sign, but no point or comma should ever be used to separate the groups (except for the decimal sign).
For example: 28 704.561 83.

4.2. Writing of symbols

1) Symbols of units and prefixes are written in roman (upright) type (except Ω, ohm, and μ, micro).

2) Unit symbols are not followed by a fullstop and do not change in the plural.
For example: 5 m but neither 5 m. nor 5 ms.

3) The product of two or more units may be indicated in any of the following ways, for example for newton-metre:

N.m or N·m or N x m or N m (a sign or a space must separate the symbols).

4) For the division of units, an oblique stroke (/), a horizontal line or negative powers may be used.

For example for metre per second: m/s or $\frac{m}{s}$ or $m.s^{-1}$ or $m\,s^{-1}$.

5) When a derived unit contains several divisions the oblique stroke must not be repeated on the same line, unless ambiguity is avoided by parentheses. In complicated cases, negative powers should be used.
For example for production of carbon in the ocean in milligram per square metre and per hour: $(mg/m^2)/h$ or $mg/m^2.h$ or $mg.m^{-2}.h^{-1}$ but not $mg/m^2/h$.

6) Juxtaposition of prefixes is not to be used.
For example: nm (nanometre) but not mμm (millimicrometre).

7) Symbols and unit names should not be combined in derived units.
For example: m/s or metre per second but neither m/second nor metre/second.

8) Note the writing of « °C » (degree Celsius): no space between « ° » and « C ».

4.3. Writing of the values of quantities

The value of a quantity is expressed by the association of a numerical value and a symbol (remember: Q = q.u, section 2).

1) The symbol of unit should be separated from the numerical value by a space (except for angle unit symbols « ° », « ' » and « " »)..
For example: 1 dm^3 but not 1dm^3.

2) When the numerical value is a decimal number, the symbol should not be inserted in the number.
For example: 25.8 m but neither 25 m.8 nor 25 m 8; 18.63° (angle) but not 18° 63.

3) The symbol is invariable, i.e. addition of abbreviations or subscripts to qualify the quantity is not permitted.
For example: do not write 5 m^3S for 5 m^3 at standard conditions.

4) The symbol of a derived unit must be regarded as a single term and should not be split.
For example: the concentration of nitrate is 14 µmol/dm^3,
but not : the concentration is 14 µmol NO_3/dm^3.

5) As the numerical value and the symbol form a consistent association, it is logical that:
- a symbol which is not preceded by a numerical value should be replaced by the name of the unit written in full: for example, « the unit of volume is the cubic metre » (not « ...the m^3 »).
- a symbol should not be used with a number written in full: for example, « two cubic metres » (not « two m^3 »).

5. A FEW APPLICATIONS IN CHEMICAL OCEANOGRAPHY

5.1. Use of the amount-of-substance (mole)

The use of the mole is becoming more and more widespread since it exhibits several advantages:

- direct comparison and computation between the concentrations of several forms of an element is easy: for example, nitrate-N, nitrite-N, ammonia-N and Total-N.
- elemental behaviour can simply be compared to stoechiometric relationships: for example, assimilation ratios C/O/N/P to be compared with the theoretical primary production formula where these element mole ratios are 106/263/16/1.

5.2. Nutrients

For nutrients, concentrations are now rarely expressed in milligram per litre but currently in micromole per litre or more rigorously in micromole per cubic decimetre.
For example, ammonia concentration is 0.83 µmol/dm^3 or 0.83 µmol.dm^{-3} or 0.83 µmol dm^{-3}, or 0.83 µmol/l, or 0.83 µmol/L, or 0.83 µmol.l^{-1}, or 0.83 µmol.L^{-1}, or 0.83 µmol l^{-1}, or 0.83 µmol L^{-1}.
The old unit microgram-atom per litre (µg-at/l) is not to be used.

Note that it is important to specify the reference entity, specially in case of possible ambiguity. For example, the urea molecule contains two nitrogen atoms, therefore it may be necessary to specify whether concentrations are expressed in nitrogen or in urea: 1 µmol/dm^3 of urea is equivalent to 2 µmol/dm^3 of urea-nitrogen (but never split the unit as follows: 1 µmol urea/dm^3).

5.3. Oxygen

For dissolved oxygen (DO), the habit in oceanography was that concentrations referred to the volume of dissolved oxygen at standard temperature and pressure conditions, i.e. DO was expressed in millilitre per litre (ml/l) or cubic centimetre per cubic decimetre (cm^3/dm^3). Now, reference to the mole is more and more frequent. In such case, the reference entity, either atomic oxygen (O) or dioxygen (O_2) should be specified.

5.4. Chlorinity and salinity

According to their definitions, chlorinity and salinity are dimensionless quantities. Chlorinity is the ratio of two masses while salinity is obtained indirectly from chlorinity or from a ratio of conductivity (Practical Salinity).
For chlorinity, the use of the symbol per mil should be replaced by 10^{-3}.
Practical Salinity should be expressed as, for example, S = 35. The use of « PSU » (practical salinity unit), for example 35 PSU, is not correct. Mention of « PSS » (practical salinity scale), for example 35 PSS, in order to specify the measured quantity does not seem to be universally accepted by specialists (F. Millero disapproves of the use of any abbreviation (pers. comm.); in a text, the wording should be, for example, « salt effects were measured at *a salinity of 35* »).

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ANNEX 9

REVIEW OF METHODOLOGY FOR THE DETERMINATION OF TOTAL-N IN SEA WATER

D.S. Kirkwood

(A preliminary version of this review was presented at the QUASIMEME Workshop in Crieff, Perthshire, U.K., in March 1996.)

Introduction

The basis of the most commonly used procedures for the determination of total-N in seawater is the conversion of organic nitrogen (including ammonia) to nitrate by oxidation with alkaline persulphate at ~ 120 °C, followed by colorimetry after reduction to nitrite.

The determination of total-N is therefore best treated as two distinct stages, (a) the oxidation process, and (b) the subsequent determination of nitrate.

It is self-evident that the only laboratories that have a realistic chance of producing good quality total-N data are those that can show that their determination of (nitrate + nitrite), hereinafter referred to as 'Total Oxidised Nitrogen' (TOxN) is under control. As a substantial number of laboratories have now demonstrated that they can consistently achieve appropriate performance targets for TOxN, attention can be turned to the oxidation procedures used by these laboratories in their total-N methods.

In QUASIMEME Round 4 (early 1995), approximately half of the laboratories (28) determined total-N. As this was considered a sufficient number to make a study of this kind worthwhile, laboratories were requested to provide details of their total-N procedures.

Alkaline persulphate oxidation

Koroleff's work, dating from the late 1960s, is a convenient starting point for a review of methodology.

Koroleff wrote chapter 9.8 entitled 'Total and Organic Nitrogen' in Grasshoff's *Methods of Seawater Analysis*, first Edition (1976), hereinafter referred to as Grasshoff-1 (G-1). This chapter refers to earlier work using persulphate, Koroleff (1969, 1973), but his procedure (in Grasshoff-1, 9.8.2 - 9.8.9) became popular, is still in use in some laboratories, and was described as ".....used throughout Scandinavia where it has become a recommended standard method." This method is hereinafter referred to as **KorG-1N**

In KorG-1N, the choice of sample volume is left to the discretion of the analyst, from 5 ml to 20 ml, according to the total-N concentration expected. The volume of reagent is fixed at 10 ml, and, in addition to persulphate, it contains 0.12 mol/l NaOH. When mixed with the sample, the dilution produces anything between 0.08 and 0.04 mol/l NaOH respectively, depending on the sample volume chosen. (The essential details of reagent formulation, *etc.*, for this and other methods discussed below, are summarised in Table 1.)

D'Elia, *et al.*, (1977) proposed a minor modification to KorG-1N; they specified 10 ml of sample and 15 ml of a persulphate reagent containing 0.075 mol/l NaOH. The resultant mixture contains 0.045 mol/l NaOH, and the concentrations of $K_2S_2O_8$ and NaOH are slightly higher than, but similar to those of the most dilute option in KorG-1N.

Nydahl, (1978) presented a well-reasoned case for the use of higher reagent concentrations. He examined the stoichiometry of the reaction, particularly in the analysis of seawater, and pointed out that the NaOH concentration must be at least equivalent to the Mg^{2+} present plus the acidity produced by the decomposition of persulphate. His reagent consisted of 13.5 g/l $K_2S_2O_8$ in 0.15 mol/l NaOH, and he specified 10 ml reagent and 10 ml sample. The resultant mixture contains 0.075 mol/l NaOH; this concentration and that of the persulphate (6.8 g/l) are close to those of the most concentrated option in KorG-1N. Nydahl investigated a large range of N-containing compounds and found similar recoveries at 100 °C and 120 °C as long as extra time is allowed at the lower temperature. According to Nydahl, the heating time required is a function of the autodecomposition of persulphate, 90 minutes at 100 °C, and 15 minutes at 120 °C. Incomplete recovery was obtained from compounds containing N-N or HC=N bonds, and the N=N bond appeared to be totally resistant to oxidation to nitrate.

Solórzano and Sharp (1980), apparently unaware of Nydahl's work, examined the earlier methods (KorG-1N and D'Elia, *et al.*) and found "inadequacies and difficulties with both.....". Their criticism was based on incomplete recovery of urea, which they used as a model compound. They demonstrated that both methods readily recovered urea from freshwater, but recovery from oceanic seawater appeared to depend on the ratio of sample volume to reagent volume. This ratio, they showed, had a bearing on the pH during the reaction (because of the buffering capacity of seawater), and by increasing the pH by using a higher NaOH concentration, they then achieved 100 % recovery. Solórzano and Sharp claimed their investigation showed that pH > 10 was essential, and to ensure sufficient alkalinity, recommended 40 ml sample and 6 ml of a reagent containing 1.5 mol/l NaOH. The resultant mixture contains ~ 0.2 mol/l NaOH, and, when analysing seawater (35 PSS), the reaction remains at pH > 12 throughout. (In this method, the NaOH concentration in the reaction is 2.5 - 5 times that of KorG-1N, and 2.6 times that of Nydahl.)

It seems that Koroleff, pre-1976 was rather less concerned with pH than with the need to ensure an adequate excess of oxidant. In Grasshoff-1 (1976) 9.8.2 - 9.8.9, Koroleff made no mention of pH as such, but stated - "The strength of the hydroxide solution ensures that excess OH^- ions are present after the decomposition of the oxidant."

In the second Edition (1983) of *Methods of Seawater Analysis*, hereinafter Grasshoff-2 (G-2), Koroleff was again the author of the chapter on total and organic nitrogen (9.6), and it is clear that he was aware of the work of D'Elia, *et al.*, (1977), and Nydahl (1978), and Solórzano and Sharp (1980).

- Koroleff referred to the work of D'Elia, *et al.*, thus : "The methodology given in the first edition of this book (KorG-1N) was slightly modified and studied by D'Elia, *et al.*, (1977)."

- Koroleff referred briefly to Nydahl's "...careful investigation of the alkaline oxidation conditions...".

- Koroleff referred to the work of Solórzano and Sharp (1980) thus : "Recently Solórzano and Sharp (1980) found that the recovery of urea from seawater is only 75 % when using a sample volume larger than 10 ml. They suggest that the amount of NaOH be increased to a level well over that needed to precipitate all Mg^{2+} ions in an oceanic sample." The first sentence is potentially misleading, as Koroleff does not make it completely clear that it was *his method*, KorG-1N, that gave the said 75 % recovery. The essential point of Solórzano and Sharp's investigation of KorG-1N is that it was not sample volume, *per se*, that caused recovery problems, but that it was a question of pH, particularly in seawater samples. Full recovery of urea from seawater was obtained only if the final pH was 10 or higher, and they showed that this proviso applied both to KorG-1N and to its minor modification by D'Elia, *et al.*

It appears that Koroleff (1983a) took little or no account of Nydahl's (1978) nor Solórzano and Sharp's (1980) work in his revised method for total-N, (9.6.3 in Grasshoff-2), **KorG-2N**. Once more, a sample size of 5 ml to 20 ml, with 10 ml of oxidising reagent was suggested. This reagent has the same persulphate concentration as in KorG-1N, but NaOH is, surprisingly, lower (0.075 rather than 0.12 mol/l), and a major difference is the inclusion of boric acid, which "gives a starting pH of 9.7 and finishing at 4 - 5." (This is understood to be Koroleff's (1977) 'single' method which he introduced at the Baltic Intercalibration Workshop at Kiel in 1977.) It is not clear whether this starting pH of 9.7 refers to reagent plus 5 ml sample, or reagent plus 20 ml sample, or whether both combinations produce pH 9.7, but in any case 9.7 is below Solórzano and Sharp's critical threshold of pH 10.

Also in Grasshoff-2, in 9.6.4, is Koroleff's (1983b) method for 'simultaneous oxidation of nitrogen and phosphorus compounds by persulphate', hereinafter **KorG-2NP**. (This also was part of his presentation at the Kiel Workshop in 1977.) A sample volume of 50 ml is specified, with 5 ml of "a more concentrated, saturated reagent", which contains persulphate (50 g/l), boric acid (30 g/l), and NaOH (0.36 mol/l). When sample and reagent are mixed, the reagent is diluted (x11), and the reaction mixture contains 0.033 mol/l NaOH.

Subsequent to the Kiel Workshop, **Valderrama** (1981) published a detailed work entitled 'The simultaneous analysis of total nitrogen and total phosphorus in natural waters'. Valderrama's reagent is almost identical to that of KorG-2NP, but there is an essential difference in their procedures. Valderrama specified 30 ml of sample and 4 ml of reagent. When these are mixed, the reagent is diluted (x8.5) and the reaction mixture contains 0.041 mol/l NaOH, *which is 25 % more concentrated than in the 'parent' method, KorG-2NP.*

Valderrama's 1981 paper does not make it clear that his method is that much (25 %) different from KorG-2NP, nor does Koroleff (in Grasshoff-2) point out this difference. In Grasshoff-2 (1983), Koroleff makes no mention of Valderrama under total-N (9.6.3), but under Total-P (9.1.6.1), Koroleff (1983c) refers to Valderrama's work, describing it as ".... a comparison of this new procedure *(apparently referring to that of Koroleff (1977)) (i.e., KorG-2NP)* with former methods....". This suggests that Koroleff was either unaware that Valderrama's method was in any way different from his own KorG-2NP, or that he was aware of the difference but did not consider it significant.

In 1992, in the light of further recovery studies, Valderrama (pers. comm.) improved the efficiency of his 1981 procedure by reducing the sample volume from 30 ml to 25 ml, effectively a further modification of KorG-2NP. In this case the reagent is diluted (x7.25) producing reaction conditions 45 % more concentrated than those of KorG-2NP.

The method listed as **ISO/DIS 11905-1** (1995) takes this modification process a stage further. Its oxidising reagent is the same as for KorG-2NP, but it specifies 50 ml sample and 10 ml reagent. This (x6) dilution produces reaction conditions 83 % more concentrated than those of KorG-2NP. It seems fair to assume that the committee responsible for this method had good reasons for recommending these more concentrated conditions.

Table 1 contains a summary of the details of each of the above *published* methods, and is followed by descriptions of each of the various modifications of these, and other methods used by participating laboratories.

Table 1 Summary of authors' oxidation procedures (chronologically)

published method	volume (ml)		concentrations in reagent			concentrations in mixture		
	sample	reagent	$K_2S_2O_8$	H_3BO_3	NaOH	$K_2S_2O_8$	H_3BO_3	NaOH
KorG-1N -1976	5	10	10	-	0.12	6.7	-	0.080
	20	10	"	-	"	3.3	-	0.040
D'Elia *et al.* 1977	10	15	6.7	-	0.075	4.0	-	0.045
Nydahl 1978	10	10	13.5	-	0.150	6.8	-	0.075
Solórzano & S. 1980	40	6	60	-	1.5	7.8	-	0.196
KorG-2N 1983	5	10	10	6	0.075	6.7	4	0.050
	20	10	"	"	"	3.3	2	0.025
KorG-2NP 1983	50	5	50	30	0.36	4.5	2.7	0.033
Valderrama 1981	30	4	"	"	0.35	5.9	3.5	0.041
" own mod. '92	25	4	"	"	"	6.9	4.1	0.048
ISO/DIS 11905-1 '95	50	10	50	30	0.36	8.3	5.0	0.060

($K_2S_2O_8$ and H_3BO_3 concentrations are in g/l. NaOH is in mol/l.)

Other procedures used by participants in QUASIMEME Round 4 are as follows : - -

1. Modification of KorG-2NP, using 25 ml sample and 5 ml reagent (dil. x6), rather than 50 ml and 5 ml (dil. x11). Reaction mixture is 83 % more concentrated than KorG-2NP. (This method is, in effect, ISO/DIS 11905-1, although this is not stated.) (Lab B).

2. Modification of Solórzano and Sharp, using 50 ml sample and 5 ml reagent (dil. x11), rather than 40 ml and 6 ml (dil. x7.67). Reaction mixture contains 70 % of Solórzano and Sharp's concentrations). (Lab D).

3. Modification of Solórzano and Sharp, using 40 ml sample and 5 ml reagent (dil. x9), rather than 40 ml and 6 ml (dil. x7.67). Reaction mixture contains 85 % of Solórzano and Sharp's concentrations. (Lab F).

4. Modification of KorG-2NP, using 50 ml sample and 8 ml reagent (dil. x7.25), rather than 50 ml and 5 ml (dil. x11). Reaction mixture is 52 % more concentrated than KorG-2NP. (microwave). (Lab L).

5. This method specifies 15 ml sample and 10 ml of reagent consisting of 10 g $K_2S_2O_8$ in NaOH (0.15 mol/l). These details do not conform precisely to any of the methods in this review, and no reference was supplied, but as the reaction mixture contains $K_2S_2O_8$ (4.0 g/l) and NaOH (0.060 mol/l) it resembles that of D'Elia more closely than any other. (Lab M).

6. UV irradiation (2 hours) in quartz tubes using 'Hanovia' 1 Kw Mercury lamp. 20 ml sample with 20 µl of 30 % H_2O_2 . (Lab N).

7. On-line, based on KorG-2N but reaction concentrations are 64 % of the most dilute option in KorG-2N. Heated at 115 °C for 40 minutes. (Lab P).

8. On-line, no details supplied other than "alkaline persulphate.....pH 12,.....95 °C, followed by UV.....and validated against the Koroleff method". (in press). (Lab Q).

9. Modification of Valderrama 1981, using 20 ml sample and 3 ml reagent (dil. x7.67), rather than 30 ml and 4 ml (dil. x8.5). Reaction mixture is 39 % more concentrated than KorG-2NP. Heated by Technicon DD40 Digestor; boiled at atmospheric pressure for 100 minutes, volume restored. (Lab S).

10. UV irradiation (6 hours) in quartz tubes, as described by Armstrong et al., (1966). 50 ml sample with 2 drops of H_2O_2 (Lab U).

11. International Oceanographic Commission (1983) Chemical methods for use in marine environmental monitoring. Manual No. 12. The procedure is identical to that of Valderrama (1981).(Lab V)

12. This method claims to be adapted from Koroleff and Valderrama. It specifies 20 ml sample and 2 ml of reagent having concentrations 2x those of Kor-G2NP. This produces reaction concentrations ~ 10 % higher than those of ISO/DIS 11905-1. Heating is for 1 hour in a 100 °C water bath. (Lab X).

13. Valderrama's own 1992 (unpublished) modification of Valderrama (1981) using 25 ml sample and 4 ml reagent (dil. x7.25), rather than 30 ml and 4 ml (dil. x8.5). Reaction mixture 45 % more concentrated than KorG-2NP, (17 % more concentrated than Valderrama (1981)).(Lab Z)

14. Modification of KorG-2NP, using 40 ml sample and 5 ml reagent (dil. x9), rather than 50 ml and 5 ml (dil. x11). Reaction mixture is 22 % more concentrated than KorG-2NP.(Lab β)

15. KorG-1N, using 20 ml sample and 15 ml reagent. This is equivalent to 13.3 ml sample and 10 ml reagent, giving concentrations intermediate in Koroleff's range. (Lab χ).

(These numbered descriptions are referred to in Tables 3 and 4)

Examination of TOxN and total-N data from QUASIMEME Round 4

Table 2 is an abridged version of Table 6-III in the QUASIMEME Round 4 Report, based on the results of the 28 laboratories which submitted total-N data.

Table 2 lists TOxN and total-N data (for samples QNU32 and QNU33), and **Organic-N** derived by subtracting TOxN from total-N, for each sample.

NOTE :

QNU32 and QNU33 were prepared by spiking the same bulk of low-nutrients seawater at two different concentration levels of nitrate and nitrite. It follows that their Total-N concentrations should differ, *but the natural Organic-N concentration originally present should remain unchanged, and should therefore be identical in both samples.*
(This information was withheld from participants until after the completion of Round 4.)

Table 2 TOxN, total-N, and derived Organic-N concs (µmol/l) from 28 laboratories (Round 4)

Lab.	TOxN		total-N		Organic-N		difference in Organic-N
	QNU32 a_1	QNU33 a_2	QNU32 b_1	QNU33 b_2	QNU32 b_1-a_1	QNU33 b_2-a_2	
*A	*15.31	*14.38	24.00	21.00	*8.69	*6.62	*2.07
B	**15.20**	**14.30**	**23.80**	**22.50**	**8.60**	**8.20**	**0.40**
C	**15.20**	**14.33**	**23.25**	**22.34**	**8.05**	**8.01**	**0.04**
D	**13.90**	**13.00**	**22.50**	**22.00**	**8.60**	**9.00**	**0.40**
E	**15.75**	**14.75**	**22.23**	**21.39**	**6.48**	**6.64**	**0.16**
F	**15.07**	**14.08**	**23.05**	**22.48**	**7.98**	**8.40**	**0.42**
G	15.32	14.16	34.20	24.40	18.88	10.24	8.64
H	15.40	14.40	20.20	23.00	4.80	8.60	3.80
J	**15.20**	**14.50**	**20.00**	**18.50**	**4.80**	**4.00**	**0.80**
K	**14.79**	**14.23**	**24.72**	**23.60**	**9.93**	**9.37**	**0.56**
L	12.10	11.20	12.80	12.40	0.70	1.20	0.50
M	11.00	9.04	38.05	25.30	27.05	16.26	10.79
N	15.80	14.80	19.70	19.90	3.90	5.10	1.20
P	**15.75**	**15.04**	**21.25**	**19.88**	**5.50**	**4.84**	**0.66**
Q	**15.40**	**14.42**	**22.29**	**20.80**	**6.89**	**6.38**	**0.51**
R	**14.80**	**14.01**	**22.06**	**21.10**	**7.26**	**7.09**	**0.17**
S	15.60	14.60	25.00	26.00	9.40	11.40	2.00
*T	*15.31	*14.38	18.56	17.44	*3.25	*3.06	*0.19
U	15.83	14.50	28.64	25.64	12.81	11.14	1.67
V	**16.22**	**15.26**	**21.04**	**19.97**	**4.82**	**4.71**	**0.11**
W	14.66	13.83	26.20	21.70	11.54	7.87	3.67
X	**15.30**	**14.34**	**21.70**	**20.50**	**6.40**	**6.16**	**0.24**
Y	15.65	14.74	23.39	28.65	7.74	13.91	6.17
Z	**14.04**	**14.08**	**23.40**	**23.70**	**9.36**	**9.62**	**0.26**
α	**15.30**	**14.36**	**23.02**	**21.73**	**7.72**	**7.37**	**0.35**
β	**15.31**	**14.24**	**23.70**	**21.90**	**8.39**	**7.66**	**0.73**
χ	**15.40**	**14.40**	**23.00**	**22.20**	**7.60**	**7.80**	**0.20**
δ	14.98	14.98	20.90	19.90	5.92	4.92	1.00

**No TOxN data submitted. Assigned values for TOxN (15.31 & 14.38) used to derive Organic-N.*

As the Organic-N concentrations in samples QNU32 and QNU33 are known to be identical, the laboratories arguably the most likely to produce credible results for Organic-N can be selected by applying two simultaneous criteria.

- A lab's Organic-N results for QNU32 and QNU33 must not differ by > 1.0 µmol/l.
- A lab's Z-scores for TOxN for QNU32 and QNU33 must be < 2.0. (see Round 4 Report).

SIXTEEN laboratories (shown in bold type in Table 2) comply with these criteria.

Table 3 lists the 16 selected laboratories, in descending order of their mean results for Organic-N in samples QNU32 and QNU33, together with brief methodological details and a numerical key to their fuller description.

Table 3 Selected (16) laboratories' results for mean Organic-N (µmol/l) for QNU32 & QNU33, final NaOH conc. (mol/l) in reaction mixture, and method used for total-N (Round 4)

Lab.	mean Organic-N	NaOH conc.	oxidation method	
			description	No.
K	9.65	0.025	KorG-2N (20 sample + 10 reagent)	-
Z	9.49	0.048	Valderrama '92 (KorG-2NP, 45 % more conc.)	13
D	8.80	0.136	Solórzano & Sharp, 30 % less conc.	2
B	8.40	0.060	KorG-2NP, 83 % more conc. (= ISO/DIS 11905-1)	1
F	8.19	0.167	Solórzano & Sharp, 15 % less conc.	3
C	8.03	0.025	KorG-2N (20 sample + 10 reagent)	-
β	8.03	0.040	KorG-2NP, 22 % more conc.	14
χ	7.71	0.051	KorG-1N (20 sample + 15 reagent)	15
α	7.55	0.033	KorG-2NP	-
R	7.18	0.040	KorG-1N (20 sample + 10 reagent)	-
Q	6.64	-	(on-line) alkaline persulphate + UV, (in press)	8
E	6.56	0.033	KorG-2NP	-
X	6.28	0.068	~ 10 % more conc. than ISO/DIS but 100 °C for 1 hour	12
P	5.10	0.018	(on-line) based on KorG-2N, 36 % less conc.	7
V	4.77	0.041	IOC (1983) Manual 12 (Valderrama 1981)	11
J	4.40	0.060	ISO/DIS 11905-1 (KorG-2NP, 83 % more conc.)	-

The individual Organic-N results from the remaining 12 laboratories are listed in alphabetical order in Table 4, together with brief methodological details and a numerical key to their fuller description.

Table 4 Remaining (12) laboratories' results for Organic-N (µmol/l) in QNU32 and QNU33, final NaOH conc. (mol/l) in reaction mixture, and method used for total-N (Round4)

Lab.	Organic-N		NaOH conc.	oxidation method	
	QNU32	QNU33		description	No.
*A	*8.69	*6.62		none supplied	
G	18.88	10.24	0.060	KorG-1N (10 sample + 10 reagent)	-
H	4.80	8.60	0.033	KorG-2NP (microwave)	-
L	0.70	1.20	0.050	KorG-2NP mod. (microwave)	4
M	27.05	16.26	0.060	no reference supplied	5
N	3.90	5.10	none	UV + H_2O_2 (2 hours)	6
S	9.40	11.40	0.046	Valderrama'81 mod. (20 sample + 3 reagent)	9
*T	*3.25	*3.06		none supplied	
U	12.81	11.40	none	UV + H_2O_2 (6 hours)	10
W	11.54	7.87	0.060	KorG-1N (10 sample + 10 reagent)	-
Y	7.74	13.91	0.033	KorG-2NP	-
δ	5.92	4.92	0.060	ISO/DIS 11905-1 (microwave)	-

**No TOxN data submitted. Assigned TOxN values used to derive organic-N. (see Table 2)*

(Subsequent to Round 4, the MAFF-Lowestoft laboratory, using Solórzano and Sharp's (1980) method, produced 9.1 and 9.0 for QNU32 and QNU33, respectively; mean Organic-N 9.05 µmol/l.)

Discussion

In Table 3 there is evidence to suggest that, in general, increasing reagent concentrations in the reagent-sample mixture gives better recovery of organic-N. While this is hardly surprising, some inconsistencies may have resulted from differences in reaction time and/or temperature. No account has been taken of these; analysts generally referred to a nominal 30 minutes at ~ 120 °C.

Given that some long-established users of Koroleff's methods have already decided to move toward more concentrated reagent conditions (Labs B, Z and β), it would seem prudent to follow their example. That said, the low result (4.40) from Lab J using ISO/DIS 11905-1 is surprising, as is the high result (9.65) from Lab K using KorG-2N.

Only two laboratories (Labs P and Q, both in the 16 selected) used on-line oxidation procedures. Results from these laboratories show good precision, presumably because contamination is well controlled, but incomplete recovery looks likely in both cases.

Two slightly different procedures, both based on that of Solórzano and Sharp, performed well despite the use of less concentrated conditions than those originally specified by Solórzano and Sharp. (Labs D and F)

The pursuit of the 'true' concentration of Organic-N in QNU32 and QNU33 has, so far, centred on the results of 16 selected laboratories. While their results suggest that it lies in the range 8.0 - 10.0 µmol/l, the possibility of it being significantly higher must not be discounted.

In this respect, the results of Lab U are particularly interesting. This laboratory's Round 4 TOxN results produced low Z-scores (0.57 and 0.14), so this part of the determination is evidently well under control. Its Organic-N results were 12.81 and 11.14, but as the difference between these exceeded 1.0 µmol/l, this was the reason for its exclusion from the selection process. In an alkaline persulphate context these 'slightly high' results could be readily dismissed as having been caused by moderate contamination problems, or a combination of these with an inappropriate calibration procedure, but, in this case, the reagent was simply six hours of UV irradiation aided by two drops of hydrogen peroxide, (with no significant evaporative losses). From a chemical point of view, this approach is immensely attractive as it involves virtually no reagents (therefore low blanks), and no changes in the major components of the sample matrix (therefore very simple calibration procedure). If UV can reliably produce significantly higher results for total-N than 'the best' alkaline persulphate methods, then it follows that UV should be the definitive technique. In any case, it is surprising that it is not more widely used. It is not new; see Armstrong, *et al.*, (1966).

UV irradiation was also used by Lab N. This laboratory produced excellent results for TOxN but low results for total-N, hence 3.90 and 5.10 for Organic-N. Incomplete recovery of Organic-N seems likely, given that the irradiation time was only 2 hours and that the laboratory admits to not having investigated the recovery characteristics of its procedure.

Some laboratories, with primarily freshwater interests, supplied supporting recovery data for model compounds such as nicotinic acid, urea, glycine and EDTA, but only from freshwater. The reviewed literature indicates that studies in freshwater have very little relevance to seawater of 35 PSS.

Several laboratories indicated that they had investigated recovery *from seawater* using model compounds such as nicotinic acid, urea, glycine and EDTA, and some laboratories use one or more of these compounds as routine controls. While this is to be encouraged as a check on system performance, the limitations of these compounds should be recognised. That is to say, full recovery of any or all of these, when added to seawater, does not guarantee full recovery of all forms of naturally-occurring Organic-N from seawater.

It follows that any practical comparison of methods is incomplete if it fails to include recovery studies of naturally-occurring Organic-N from seawater, (*i.e.*, no addition of model compounds). In this case, for a given seawater sample, if method (*a*) finds more natural Organic-N than method (*b*), then, by definition, (*a*) is the better method.

Finally, a note for present and potential users of ISO/DIS 11905-1. This method has evolved and is now the International Standards Organisation's recommended method for total-N in a variety of types of water (fresh, waste, seawater). Its formulation produces higher reagent concentrations in the reaction mixture than any of Koroleff's precursor versions, and the balance of evidence produced by this review suggests that this should be beneficial. However, in the section on recovery of model compounds is the phrase ".....30 minutes, but some samples may require longer - up to 90 minutes." As the method fails to specify *which* samples require a longer reaction time, logic must surely demand that *all* samples be heated for 90 minutes (particularly in the case of seawater).

Note: Recently (February 1997), the MAFF-Lowestoft laboratory has undertaken trials using the METROHM 705 UV Digester. The digester accommodates 12 x 12 ml silica tubes grouped concentrically around a 500 watt high pressure mercury lamp. (The manufacturers claim that UV photolysis 'eliminates' low to moderate concentrations of Dissolved Organic Matter via reaction with OH radicals. They recommend the technique in the context of the determination of heavy metals by voltammetry, polarography, etc, and their brochure gives examples of its effectiveness.) Using the Metrohm 705 as the sole means of oxidation (no added peroxide) for filtered low-nutrients seawater, has produced promising results for total-N, i.e. good comparability with results obtained by Solórzano and Sharp's procedure. Further work with a view to validating this method for routine use is in progress.

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ANNEX 10

QUALITY ASSURANCE INFORMATION ON MARINE CHEMICAL DATA: TRACE ELEMENTS IN BIOTA, SEDIMENTS, AND SEA WATER

Provisional

1. Participation in intercomparison exercises

-ICES

-QUASIMEME

-Other

Note: It should be possible to specify more than one intercomparison exercise

2. Analyses of reference materials

-name of material

-mean (unit)

-standard deviation (unit)

-number of analyses

-period of time

Note: It should be possible to specify the results of more than one reference material

3. Other information

The detection limit (3 x s.d. of a blind)

The date of sampling and analysis

Relevant cofactors

4. Sampling, pre-treatment, preservation, storage. Sea water.

Theme	Category	Exclusive items/pick list
Sampling	Vessel	-Research vessel-Inflatable raft with engine on -Inflatable raft with engine off -Other
	Technique of collection - by hand	
	Technique of collection - by pumping	-Pump: Peristaltic -Pump: Teflon piston pump -Pump: Other
		-Tubing: Pe/Pp/PVC -Tubing: Silicone - Teflon lined -Tubing: Silicone -Tubing: Other
	Technique of collection - with a sampling bottle	-Sample bottle, type: Go-flow - type -Sample bottle, type: Niskin - type -Sample bottle, type: Other
		-Sample bottle, material: Teflon -Sample bottle, material: Pe/Pp/PVC -Sample bottle, material: Lined with Teflon -Sample bottle, material: Other
		-Sample bottle, acid cleaned: Y/N
		-Type of wire: Stainless steel -Type of wire: Kevlar -Type of wire: Pp -Type of wire: Other
	Subsampling facilities	-On-board clean room -On-board clean bench -Closed system -Other
	Storage bottles	-Material: Pe/Pp -Material: Teflon -Material: Polycarbonate -Material: Borate Silicon Glass (Hg only) -Material: Other
		-Acid cleaned: Y/N
Packaging	In sealed plastic bags	-Y/N
	In the dark	-Y/N
Method of separation of solids	No separation	
	Filtration	-Under pressure -Vacuum -Online -Other
		-Type of membrane: Porosity -Type of membrane: Polycarbonate -Type of membrane: Glass-fiber (Hg only) -Type of membrane: Cellulose acetate -Type of membrane: Teflon -Type of membrane: Other
		-Treatment of membrane: Acid cleaned -Treatment of membrane: High temperature -Treatment of membrane: None -Treatment of membrane: Other

Theme	Category	Exclusive items/pick list
	Centrifugation	(Specify G-force and temperature)
Preservation	Acidification	-Nitric acid -Hydrochloric acid -Other
	Freezing	(Temperature should be specified)
	Lyophilisation	
	Other	

5. Sampling, pre-treatment, preservation, storage. Sediments.

Category	Exclusive items/pick list
Storage	-Frozen (Temperature should be specified) -Freeze dried -Oven dried -Other
Fractionation	-Unfractionated -Fractionated (Fraction should be specified)
Method of fractionation/grain size analysis	(To be supplied by the Marine Sediment Working Group)

6 Sampling, pre-treatment, preservation, storage. Biota

Theme	Category	Exclusive items/pick list
Technique of sampling	Fish	-Sampling device: Trawl-Sampling device: Net -Sampling device: Line -Sampling device: Other
		-Gutted: Alive -Gutted: Dead
	Shellfish	-Sampling device: Handpicking -Sampling device: Dredge -Sampling device: Other
		-Depuration (Y/N, if Y specify time)
	Marine mammals	-Catching: Found dead -Catching: Shooting -Catching: Harpooning -Catching: Knocking -Catching: Other
		-Alive (Y/N, if Y: biopsy taken (Y/N))
	Birds	-Catching: Found dead -Catching: Shooting -Catching: Knocking -Catching: Strawling -Catching: Other (If shooting, specify weapon (shotgun/rifle/other) and bullet material (lead, stainless steel, other)
	Copepoda	-Catching: Type of net
	Seaweed	-Catching: Type of sampling device
Storage	Prior to dissection/subsampling or preservation	-Y/N (If Y, specify time and temperature)
Early dissection/subsampling	Organs/tissue sampled prior to preservation of whole animal	-Y/N (If Y, specify organs/tissue)
Packaging	Material	-Glass -Aluminium -Plastic (specify type: Pp/Pe/PVC/Teflon) -Other
	Cleaning of packaging material	-Y/N (If Y, specify solvent)
Equipment for dissection/subsampling organ sampling	Material	-Stainless steel -Glass -Ceramics -Plastic (specify type: Pp/Pe/PVC/Teflon) -Other
	Cleaning of dissection/subsampling equipment	-Y/N (If Y, specify solvent)
Cleaning of subsample	Cleaning of subsample (tissue/organ) prior to homogenisation	-Y/N (If Y, specify solvent)
Homogenisation		-None -Ultra-Turrax -Worning-blender -Grinding -Other
Subsampling after homogenization		Y/N
Preservation prior to analysis		-Freezing (time, temperature) -Lyophilisation (time, temperature) -Drying (time, temperature) -Other -None
Lipid analysis		(List of methods to be supplied by the organics subgroup

7. Analytical methods. Overall categories (QUASIMEME system)

Chelating Agent for aqueous extraction
Solvent for aqueous extraction
Buffer for aqueous extraction
Chromatographic separation
Standard preparation
Sample digestion (sea water)
Sample treatment procedure
Preconcentration Techniques
Sample preservation
Standard procedure
Electrochemical Detection
Detection system AAS-FLAME
Detection system AAS-ETA
Detection system Other Techniques

ANNEX 11

DISSOLVED OXYGEN IN SEA WATER: DETERMINATION AND QUALITY ASSURANCE

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1. INTRODUCTION

Dissolved oxygen (DO), a parameter of primery interest in water quality investigation, is measured in almost every laboratory dealing with environmental studies and monitoring. This paper reviews the context of DO determination, including aquatic importance, main procedures and quality assurance (QA) rules.
Although QA in analytical chemistry covers all aspects that concur to give confidence in an analysis result (including an adequately equipped laboratory, well trained analysts, good laboratory practice), this paper focuses only on specific analytical points that are important in the procedure and on good technical practices for producing accurate DO data.
The work on DO done by the Chemical Oceanography Subgroup of ICES-MCWG is also remembered and the conclusions of DO intercomparison exercises are reviewed.

2. DISSOLVED OXYGEN IN THE AQUATIC MEDIUM

It is postulated that QA is greatly enhanced when analysts know the implications of the determinations they perform for the study of aquatic mediums.
Dissolved oxygen is the common term for dissolved « dioxygen », which means that the corresponding determination will be restricted to the concentration of molecular O_2 exclusively, and no other oxygen form present in any inorganic or organic combination. This molecular form governs all oxic biological processes, i.e. most terrestrial life.
DO concentration in water results from several physical, chemical and biological processes:

- exchange at the air-water interface (gain or loss),
- diffusion and mixing within the water body,
- photo-oxidation (loss),
- chemical oxidation (loss),
- respiration of aquatic organisms, including mineralisation (loss),
- nitrification (loss),
- photosynthesis (gain).

If only physical processes are involved, DO concentration is governed by the laws of solubility, i.e. it is function of atmospheric pressure, water temperature and salinity. The corresponding equilibrium concentration (solubility) is generally called *saturation*. It is an essential reference for interpretation of DO data. As an example, DO saturation under 1 atmosphere and at 20 °C is 6.4 ml l^{-1} in pure water and 5.1 ml l^{-1} in seawater at the salinity of 35. Precise saturation data, tables and mathematical functions were established (Carpenter, 1966; Murray and Riley, 1969; Weiss, 1970) and adopted by the international community (UNESCO, 1973). However, Weiss (1981) drew attention to an error in the international tables in which the values are lower by 0.10 %. Later, the Joint Panel of Oceanographic Tables and Standards recommended that the oxygen saturation formula of Benson and Krause (1984), which incorporated improved solubility measurements, be adopted and tables updated (UNESCO, 1986). However, no official document has been published yet.

It must be quite clear that as far as purely physical processes are involved, DO concentrations will always tend to reach saturation. This has several implications. Firstly, when pressure or temperature, for instance, change, exchange of DO with the atmosphere will take place until a new equilibrium concentration is reached. As physical characteristics generally change slowly or little, they rarely induce significant divergences from saturation. Secondly, and consequently, large differences with saturation prove that biological activity is taking place (chemical and photo-chemical processes remain of minor importance). Thirdly, purely physical action such as shaking and bubbling (waves, ship propeller mixing, etc.) always modifies DO concentrations towards saturation, whether water was previously under- or over-saturated: apparent over-saturation obtained after a physical action must be attributed to micro-bubbles, not to truly dissolved oxygen.
Very low DO concentrations are lethal for superior animals, specially fishes. According to Train (1979), a DO concentration of 5 mg l^{-1} (3.5 ml l^{-1}) seems to be the minimum for a well-rounded population of fishes in fresh water. Low concentrations are mostly generated by degradation of organic matter (for example in case of eutrophication) or intense nitrification (mainly in estuaries). When a medium becomes anoxic, only micro-organisms can live and chemical conditions lead to particular processes (some metals can be trapped while others are dissolved). Such conditions can be encountered temporarily in estuaries, or permanently in the bottom water layer of semi-enclosed seas and basins with a threshold (e.g. Baltic Sea, Black Sea).

3. METHODS FOR THE DETERMINATION OF DISSOLVED OXYGEN

Two main types of methods are communly used for the determination of dissolved oxygen: chemical methods and sensors. Chemical methods are used to treat discrete water samples in order to lead to volumetric titration as the final step. Sensors are particularly interesting for in situ measurements (but some can be used for discrete samples).

3.1. Chemical DO determination with particular reference to the « Winkler method »

Chemical determination of DO must be performed on discrete samples, and therefore it requires adequate sampling procedure (see below).Very few chemical methods have been developped for DO measurement. For seawater, the so-called « Winkler method », which is now more than one century old (Winkler, 1888), seems universally used.
In this method, Mn II and hydroxide ions (together with iodide) are added to the sample. Manganese hydroxide precipitates and reacts with oxygen dissolved in the sample. Mn II is thus oxidized into Mn III and Mn IV. This first step must be performed as soon as the sample is taken. The fixing reaction takes some time, but once the oxygen is fixed the sample is stable, and the second step of the Winkler determination can be postponed. After the reaction is complete, acid is added to dissolve the precipitate. Iodide is then oxydized by Mn III/IV into iodine which can be titrated by thiosulfate. Finally, 4 moles of thiosulphate correspond to 1 mole of O_2 initially present in the water aliquot.
The Winkler method was carefully re-examined for its accurate application to seawater (Carritt and Carpenter, 1966; Carpenter, 1965) and it still remains today the reference method for calibrating oxygen sensors. Carpenter's (1965) version of the Winkler method was soon adopted by the Baltic oceanographers (Carlberg, 1972) and recently for the WOCE programme (Culberson, 1991). Unfortunately, Strickland and Parsons (1972) did not update the last edition of their manual, hence depriving many users of more accurate DO data.

3.2. DO sensors and probes

DO sensors have been developped since the introduction by Clark (1956) of the membrane-covered DO electrode. It offers several advantages: simplicity, few interferences from other solutes, rapid and in situ measurements, the possibility of continuous measurements for real-time investigations. The sensors consist of a cathode and an anode immersed in an electrolyte separated by an O_2-permeable membrane from the medium in which DO has to be measured. The sensor exploits the reduction of O_2 at the cathode: the resulting current is measured and expressed in its DO equivalent. In polarographic sensors, a constant voltage is applied between a suitable reference electrode and the noble metal cathode and the electrolyte participate in the overall reaction. In galvanic sensors, the anode is made of a relatively basic metal and the cathode of noble metal, thus the generated voltage is sufficient for the reduction of O_2; the electrolyte does not participate in the reaction (Lee and Tsao, 1979). Most oceanographic probes seem to be of the polarographic type. One of the main uses of in-situ probes in oceanography is for continuous vertical profiles.

4. QUALITY ASSURANCE

The following sentences of Carritt and Carpenter (1966) should be kept in mind: « to an uninitiated person, the Winkler procedure is likely to be deceptively simple, ... However, changes in procedure that may appear to be insignificant to the nonchemist may actually produce significant differences in the results ». At many stages, such as sampling or subsampling in particular, quality assessment and traceability are difficult to establish, and therefore QA relies almost entirely on application of good practice rules. Consequently, this section focuses on those technical points that are important for accurate DO measurements. However, it does not intend to replace original publications or handbooks in which detailed descriptions of the protocol are given.

4.1. MCWG works relevant to dissolved oxygen

Problems concerning DO are regularly dealt with in the MCWG. Within the last years, the following topics were examined:

- 1988: determination of DO at low concentration,
- 1989: problems with the determination of DO
- 1990: design of an intercomparison exercise for DO in Baltic waters,
- 1990: high precision measurements of DO,
- 1991: results of the Visby intercomparison exercise (preliminary data),
- 1992: results of the Visby intercomparison exercise,
- 1993: the WOCE protocol for DO determination,
- 1993: the WOCE intercomparison for DO.

Information from the corresponding documents or conclusions of the group will be referred to in the following sections.

4.2. Sampling and handling

This section is relevant to discrete samples and consequently to the « Winkler » determination essentially. The whole sampling/subsampling protocol is reviewed, since most points are somewhat rigid, and the few test results or comments available on that essential part of the protocol are given. Operations described in this section are normally undertaken onboard a ship (« deck work »).

4.2.1. Sampling from water mass

General sampling rules stand for dissolved oxygen. Conventional plastic or glass sampling devices are suitable, but metallic bottles should not be used if samples are trapped in the bottles for long periods, for instance for deep sampling (Riley et al., 1975; Worthington, 1982).

Note:

- The results of the Visby intercomparison lead to conclude that there were no significant differences due to sampling equipments (ICES, 1991, 1992).

4.2.2. Sample bottle

Only glass vials with rounded or tapered ground-glass stoppers meet the requirements for subsequent Winkler determination for several reasons. First, glass is both inert towards oxygen and not permeable to this gas, contrary to plastics. Second, the ground-glass stopper is the only closing system which permits rejection of water of the bottle neck in contact with air, without trapping air bubbles (caution: no grease on the ground-glass joint!). Vials of 50-150 ml capacity are generally convenient.

Note:

- If the whole bottle procedure is used (strongly recommended, see below), vials must be colorless and calibrated; stoppers and vials must be identified since they are not interchangeable.

4.2.3. Filling the sample bottle

As for all gases and highly reactive substances, DO samples should be the first (or one of the first) sample to be drawn from the hydrocast bottle. As exchange between the sample and air must be avoided, there is no better way to fill the sample bottle than to use a flexible, transparent plastic tube fitted to the hydrocast bottle tap and plunging down to the bottom of the sample bottle. After slow filling (avoiding bubbling and turbulence), sufficient overflow must be ensured: 2 to 3 times the content of the bottle is recommended, but, obviously, saturated waters require less overflow than those far from saturation.

Note:

- The tube used to transfer the water from the hydrocast bottle to the sample bottle should be stored in water prior its use for the first time in order to reduce the risk of trapping air bubbles inside the tube (WOCE intercalibration, ICES, 1993).
- The Visby intercomparison exercise showed that no significant difference could be attributed to sampling staff (ICES, 1991, 1992).

At this stage, either oxygen can be measured using an oxygen sensor or reagents must be added.

4.2.4. Adding the reagents

When the bottle is filled to the brim, the reagents are immediately added (without intermediate stoppering), well below the water surface, by mean of dispensers or automatic pipettes with a new tip for each pipetting (see Reagents in section 4.3.). The stopper is then placed, care being taken not to trap bubbles, and the sample shaken vigorously to disperse the precipitate (shaking has to be repeated when the precipitate has partly settled).

Note:

- Classical pipettes do not meet the requirements for QA: i) dipped successively in samples and in a reagent, they are sources of contamination, ii) they are particularly difficult to handle in rough seas.
- Grasshoff (1962) showed that reaction time was ~ 1 min with continous shaking.
- Diffusion of oxygen from air into the sample, between end of subsampling and adding the reagents, is not too critical: Grasshoff (1962) showed that a water sample only 25 % saturated reached no more than 26 % saturated when left open 10 min.

At this stage, samples are left some time, in order to allow the precipitate to settle to one third of the vial volume; during this time oxygen is completely fixed. Then determination can proceed.

4.2.5. Storage of the samples

Storage of the fixed samples can be considered (up to three days), provided temperature of the bottles is maintained almost constant and the ground does not become dry, in which case air will contaminate the sample (Grasshoff, 1962).

Note:

- For prolonged storage or if the temperature is likely to vary after oxygen is fixed, Riley et al. (1975) suggested keeping the sample bottles under water.
- The acidified sample (= iodine solution) must not be stored (Grasshoff, 1962; Riley et al., 1975).

4.3. The « Winkler » method

This section describes problems in managing the fixed samples. This can be done onboard or at the shore-laboratory (« bench work »). According to Carpenter (1965), the sources of error in the Winkler method are the following:

1. air oxidation of iodide,
2. volatilization of iodine,
3. oxygen contributed by the reagents,
4. iodate contamination of the iodide solution,
5. consumption or production of iodide by reagent contaminants,
6. difference between titration end point and the equivalence point.

Consequently, some conditions and critical steps in the procedure must be carefully controlled (Carritt and Carpenter, 1966), these are:

1. the acid concentration,
2. the iodide concentration,
3. the blank determination,
4. the transfer of iodine solutions,
5. the cleanliness of sample bottles (titration flask).

4.3.1. Reagents

The composition and volume of the reagents optimized by Carpenter (1965) fulfil the following criteria:

- final pH of ~ 2 to minimize air oxidation of iodide and < 2.7 for quick solubilisation of the precipitate and reaction of iodide with manganese,
- formation of the triiodide complex (high iodide concentration) to minimize iodine volatilization.

The main reagents are accordingly:

1) $MnCl_2,4H_2O$ (3 mol l^{-1}),
2) NaOH (8 mol l^{-1}) + NaI (4 mol l^{-1}),
3) H_2SO_4 (5 mol l^{-1}).

The same volume of the three reagents is added in the sample, i.e. 1 ml for a sample of 130-140 ml.

Note:

- For solubility reasons, sodium iodide must be used, instead of potassium iodide, to reach a concentration of 4 mol l^{-1} of iodide in reagent 2.
- For proper pH control, Carpenter (1965b) stated that errors in the volumes of reagents 2 (alkaline) and 3 (acid) should not exceed 5 %; dispensers must therefore be well calibrated.
- The reagents contain some dissolved oxygen which must be subtracted from the final result. Murray et al. (1968) determined the oxygen content of the reagents precisely: a total amount of 0.0017 ml of O_2 for 1 ml of each of the reagents 1 and 2. For samples of ~ 130 ml, this would correspond to O_2 results in excess by 0.013 ml l^{-1}.

4.3.2. Whole bottle titration

As iodine volatilization is one of the main source of inaccuracy, transfer of an aliquot of the acidified sample in another vessel for titration must strongly be discouraged. This leads to the development of whole bottle titration (Carpenter, 1965b; Carritt and Carpenter, 1966). With stopper inserted, sample bottles are calibrated « to contain » by weighing and the whole volume is titrated in the bottle itself. If necessary, some room can be made in the bottle, for addition of the titrating solution, by removal of a known volume of solution with a pipette.

Note:

- Loss by transference is stated to be 1-2 % by Riley (1975), and ~0.5 % was found by Aminot (1988) when using Carpenter's reagents. Strickland and Parsons' reagents generate a loss of ~1.6 % (Aminot, 1988). Variability is also generally increased.
- After titration, bottles must be carefully cleaned with tap and distilled water to remove all traces of Mn ions.

4.3.3. Manual titration (starch indicator)

Once the sample is acidified, the titration of iodine has to be undertaken without delay, for iodine can both volatilize and photo-oxidize. For this reason, most of the thiosulphate is added rapidly while gently stirring until the solution reaches a straw yellow colour. Then the starch indicator is added and the titration is continued slowly until the complete disappearance of the blue colour.

Note:

- Starch should not be added from the beginning of the titration since a strong complex forms with I_2.
- The starch solution is unstable and should be renewed frequently.

4.3.4. Automated titration

Electrochemical or spectrophotometric end-point detection is now widespread, specially when the iodine titration is performed using an automated titrator. The titrator must ensure sufficient time between final additions of the thiosulphate to enable the complete mixing of the solution and thus to avoid overrunning the end-point.

4.3.5. Calibration

Routine DO determination cannot be calibrated directly with O_2 standards. A iodide standard is prepared by oxidation of iodide with iodate. A precise volume of the potassium iodate standard (usually 0.01 N) is introduced in a clean sample bottle and distilled water (not seawater) is added to complete the bottle as in the case of a sample. Then, while stirring, the acid reagent 3 is added, followed by the alkaline-iodine reagent 2 then reagent 1. The liberated iodine is immediately titrated with the thiosulphate solution as for the sample.

Note:

- In his protocol, Carpenter (1965b) adds no manganese (reagent 1), and mentions that bottles should be carefully rinsed to avoid presence of Mn ions. Other authors (Grasshoff, 1983; WOCE manual) specify to add reagent 1 too, since it is added for the blank determination. It must be clear that Mn must be absent during the hydroxyde addition and that all hydroxide must have been neutralised by reagent 3 (including traces on the flask wall) before Mn is added.
- Although, several oxidizing compounds have been proposed for calibration, potassium iodate is recommended for it is available commercially with a high purity, it is stable up to 180 °C (no risk of decomposition on drying as for biiodate) and it reacts rapidly with iodide; dichromate is not to be used since it leads to less reliable data (Riley et al., 1975).
- The thiosulphate solution deteriorates slowly and must be calibrated every day.
- The concentration of the thiosulphate solution should be adapted to the burette used, in order that the delivered volume can be measured with sufficient accuracy.

4.3.6. Blanks

Either positive or negative blanks may be found for the reagents, therefore procedure must be able to measure both kinds. The general procedure consists of titrating iodine liberated by a small, precise volume of iodate standard (typically 1 ml), following exactly the calibration protocol, then adding a second identical amount of iodate and titrate again. The second volume minus the first volume of thiosulphate represents the blank. Remarks for calibration stand for the blank determination.

4.3.7. Expected performance

The DO measurements using the Winkler method as outlined by Carpenter (1965) are expected to have an accuracy of 0.1 %. Standard deviations of 0.004 to 0.015 ml l^{-1} (CV of 0.06 to 0.3 %) are reported in ten papers, by either manual or automated titration, using starch, photometric, amperometric or potentiometric end-point detection (Graneli and Graneli, 1991).

4.3.8. High precision DO determinations

For the highest accuracy and precision measurements, a lot of minor corrections in volumetry and weighing have to be taken into account. This is out of the scope of this paper. Analysts interested in these corrections can find their description in the WOCE manual (Culberson, 1991).

4.3.9. Problems in areas with anoxic waters

This problem was considered at the MCWG (ICES, 1989). Sometimes, samples contain hydrogen sulfide in very low concentrations. Such samples may yield erroneous positive values for oxygen. In case the presence of sulfide is suspected, several options can be considered:

- collect one sample for sulfide and another for oxygen; if positive for sulfide discard the other;
- accept the possibility that low oxygen and sulfide concentrations coexist in mixing zones, but view the oxygen data with reservation;
- add Winkler reagents as usual, let precipitate settle and, just before titration, replace an aliquot of the supernatant with an exact amount of iodate solution; titrate and calculate potential sulfide concentration according to Fonselius (1983).

4.4. Sensor measurements

In the MCWG (ICES, 1988, 1989, 1993), attention was paid to particular aspects of the use of sensors: calibration of the sensors and problems encountered in areas with anoxic waters.

4.4.1. General maintenance

Accurate measurement using sensors requires first of all strict respect of the constructor's operating instructions. In particular, the membrane and the electrolyte have to be renewed regularly. Diffusion of oxygen through the membrane is temperature and pressure sensitive, consequently response time is too. Between stations, the membrane should be kept damp and clean, specially free of oil contamination.

4.4.2. Calibration of sensors

Sensors should preferably be used in conjunction with conductivity-temperature-depth (CTD) devices in order to evaluate oxygen profiles from an oceanographic viewpoint (stratification, ...) and simultaneously acquire information for the determination of saturation rate.
For calibrating the sensors, laboratory work does not appear successful at yielding useful field calibration parameters (WOCE manual from Millard, 1991 and ICES, 1993). Instead, discrete oxygen samples are collected at different depths for traditional Winkler determination. The results of repeated calibrations in this way will show how many samples are needed per profile and whether each profile should be sampled (ICES, 1989).

Note:

- The WOCE manual suggests that down-profile CTD oxygen data are merged with corresponding up-profile discrete DO samples (at corresponding pressure levels). As DO sensors are flow sensitive, down-profile data are indeed more reliable.
- With minor criticisms, the procedure of the WOCE manual can be recommended for CTD oxygen calibration (ICES, 1993).

4.4.3. Problems in areas with anoxic waters

Specific problems are raised in areas with anoxic waters (ICES, 1989). Indeed, hydrogen sulfide can pass through the membrane and modify the response of the sensor to oxygen. Therefore, it has to be established:

1) whether or not the sensor can recover from exposure to sulfide-bearing water;
2) what time is required to produce meaningful oxygen data after exposure to sulfide;
3) if the sensor does not recover rapidly, it must be protected (or not immersed at all) in anoxic water.

4.5. Associated determinands: temperature and salinity

Interpretation of DO data requires calculation of the percentage of saturation of oxygen in the studied water. For this, corresponding temperature and salinity of the water need to be available. It is interesting to determine the precision needed for these two parameters in order not to introduce errors and misinterpret percentages of saturation.
Within the ranges of temperature 0-35 °C and of salinity 0-40, changes (hence errors) in saturation values are the following:

$\Delta DO_{SATUR.}$ = 0.05 ml l^{-1} (t = 35, S = 40) to 0.28 ml l^{-1} (t = 0, S = 0) *for* $\Delta t = 1$ °C,

$\Delta DO_{SATUR.}$ = 0.02 ml l^{-1} (t = 35, S = 40) to 0.07 ml l^{-1} (t = 0, S = 0) *for* $\Delta S = 1$.

Assuming that it is possible to be accurate within 0.01-0.03 ml l^{-1} for reasonable routine determination of DO, it follows that the temperature shoud be known within ± 0.05-0.1 °C and salinity ± 0.1-0.2.

4.6. Learning from intercomparison exercises and conclusion

Many oxygen intercomparisons have taken place since the Winkler method was re-examined by Carpenter (1965). The main conclusion reported by Carritt and Carpenter (1966) from two exercises involving up to 11 institutes was that the accuracy of ± 0.05 ml l^{-1} often stated for DO data was actually the precision achievable during certain standardization procedures. Recent exercises were undertaken under the auspices of the WOCE Hydrographic Programme (onboard the R/V Akademik Vernadsky) and of HELCOM (in Visby). Five « groups » (= laboratories) were involved in the WOCE exercise; four of them produced oxygen values in the range of 3-5 ml l^{-1} which were consistent within ± 1 %, although WOCE requirements were ± 0.5 %. Intra-group precision was generally in the range 0.1-0.4 %. As for the HELCOM exercise, although each laboratory produced consistent data, inter-laboratory differences were significant (up to 7 %).
Intercomparison exercises show that biases are generally of the systematic kind and that calibration errors seem to cause most of them.
In addition to a strict application of the procedure, analysts should replicate samples at regular intervals to assess their own repeatability. Good repeatability on samples, that is in agreement with what can be expected from a correct protocol, is the first point that must be achieved. Then, as accuracy strongly depends on right calibration, high repeatability in titrating iodate standards must also be achieved, i.e. several standards must be titrated with each series of samples. Poor standard repeatability denotes some failure in the calibration process and its cause must be determined (it may be due to impossibility for the analyst to handle correctly reverse addition of reagents 2 and 1, in which case reagent 1 (Mn solution) should not be added).

5 DO UNITS

DO is usually expressed in the unit « milligram per litre » in fresh water, while oceanographers are accustomed to use « millilitre per litre », at standard pressure and temperature conditions (1 atmosphere, 0 °C). International tables use the irreproachable SI unit « cubic centimetre per cubic decimetre ». Noting that « litre » is just another name for « cubic decimetre » (1 l = 1 dm^3, exactly), 1 ml l^{-1} = 1 cm^3 dm^{-3}. Conversion of units may lead to erroneous data, therefore conversion factors are given:

concentration in	*when multiplied by*	*is converted into*
millilitre per litre	1.429	milligram per litre
milligram per litre	0.700	millilitre per litre
millilitre per litre	0.0893	millimole O per litre
millimole O per litre	11.20	millilitre per litre

The conversion of theamount of DO (mass, volume or mole) per litre into the amount per mass (kilogram) of seawater requires determining seawater density from temperature and salinity (and possibly pressure for deep-sea in situ values) using international tables.

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ANNEX 12

TOC, DOC, AND POC IN CHEMICAL OCEANOGRAPHY

Literature review

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REVIEW

The interest in organic carbon in the marine environment appears to have been elevated during recent years. In particular, the controversy about the actual levels of DOC in the oceans, a result of the later withdrawn data presented by Sugimura and Suzuki (1988), has encouraged a healthy discussion on both the analytical methods and the measured amounts of organic carbon in the oceans. After Sugimura and Suzuki presented their new method (high temperature catalytic oxidation, HTCO) for the determination of DOC in the oceans, and claimed they found 2-3 times higher levels than using the old analytical methods, research has been going on all around the world to try to confirm or dismiss these results. We now know that the original findings were wrong (Suzuki, 1993), and that the HTCO method produces results that are very similar to, though probably slightly higher than, earlier results.

A literature survey shows that rather many papers on the topic of organic carbon have been published recently. A closer examination of the articles also shows that we still have a limited knowledge of both the nature of the organic carbon and the actual concentrations of the different fractions found in the oceans. Our knowledge is also very limited about the sinks and sources in the oceans, as well as the availability of the organic carbon and nitrogen to biological processes (Allard et al., 1994; Barber, 1968; Benner et al., 1992; Coble et al., 1990; Dhargalkar and Verlencar, 1992; Gearing et al., 1994; Hedges, 1992; Hedges et al., 1992; Henneke and de Lange, 1990; Hulth et al., 1995; Ittekott, 1988; Kieber et al., 1989; Kieber et al., 1990; Kristensen and Blackburn, 1987; Meyers-Schulte and Hedges, 1986; Mopper et al., 1991; Mopper and Stahovec, 1986; Pecherzewski, 1980; Saliot et al., 1984; Skoog et al., subm.; Tan and Strain, 1983; Williams and Druffel, 1987; Woodwell et al., 1978; Zepp, 1988).

The by far dominating resaon for measuring organic carbon has been to study the global carbon cycle (Craig et al., 1994; Druffel et al., 1992; Gordon and Cranford,

1985; Hedges, 1992; Meyers-Schulte and Hedges, 1986; Mopper et al., 1991; Mopper and Stahovec, 1986; Woodwell et al., 1978). Part of the anthropogenic carbon dioxide released into the atmosphere disappears, and the removal mechanism has not been found (Paillard et al., 1993; Sarmiento, 1991; Siegenthaler and Sarmiento, 1993). The pool of organic carbon in the sea has approximately the same size as the pool of atmospheric CO_2. Dissolved CO_2 is transformed to organic material by the photosynthetic plants that live in oceanic surface water. The export of biogenic carbon from the surface layer is responsible for maintaining the vertical gradient of CO_2 over the sea atmosphere interface, and thus for a part of the regulation of the atmospheric CO_2 level. The transport of carbon both as POC and DOC within the oceans can be of significant size (Burdige and Homstead, 1994; Craig et al., 1994; Wassmann, 1990). Some papers also treat the availability of both the carbon and nitrogen contained in the organic material to primary production and other biological processes (Carlsson and Granéli, 1993; Geller, 1986; Hung et al., 1980; Lara et al., 1993; Lindell et al., 1995; Ogura, 1969; Postma and Rommets, 1984; Woodwell et al., 1978)

Attempts have been made to use TOC and DOC as water mass tracers for mixing in large basins. TOC was succesfully used for studying mixing in the Baltic (Wedborg et al., 1994; Wedborg et al, ms). In an investigation in the Weddell Sea, Antarctica, it was shown that humic substances, which make up 10-30% of the DOC, could be used as a tracer for water mass age, while DOC could not be used for the same purpose (Skoog and Wedborg, ms). In other investigations, however, DOC has showed a conservative behaviour (Mantoura and Woodward, 1983).

A number of investigations treat complexation between metals and organic compounds. This is an interesting topic for many reasons, the most obvious one being that complexation of metals to other compounds strongly affects their role as micronutrients or toxins (Anderson and Morel, 1982; Haraldsson et al., 1991; Haraldsson et al., 1993). Only a small fraction of the total metals contained in the oceans appears to be directly available to organisms. Certain fractions of DOC (notably humic substances), with a strong tendency towards binding metals, are believed to play an important role in the transport of metals within the oceans (Gu et al., 1995; Sholkowitz et al., 1978; Tipping, 1981).

CONCLUSIONS

Organic carbon in the oceans is mainly measured because it plays a very important role in the global carbon cycle, with implications on for example global warming through the elevated atmospheric carbon dioxide levels. The usefulness of TOC and DOC for oceanographic purposes is very limited, and indeed very few succesful atttempts to use these parameters as tracers for ocean mixing processes have been reported. It is indeed even hard to find papers describing any kind of correlation between organic carbon and other chemical or biological parameters. The main reasons are the problems of measuring TOC/DOC accurately in seawater and, more

importantly, that they are insufficiently characterized parameters with strongly varying composition and behaviour between different sea areas.

Important aspects of TOC/DOC, apart from the global carbon cycle, are their role in the complexation of metals within the oceans and their potential role as sources of carbon and nitrogen in primary production.

The working group cannot see any reason to recommend generally that organic carbon should be included in monitoring programmes. Data on organic carbon is only useful if monitoring programmes are targeted to ask specific questions.

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ANNEX 13

ACTION LIST

G. Audunson	Prepare a note/report to the next MCWG meeting about the outcome of the Icelandic study on the influence of parameters like fish size, liver size and fat content in the liver on the trace metal concentration.
S. Berman, G.Asmund, B.Pedersen and D. Wells	Finalise the report on 7/TM/SW taking the comments by MCWG 1997 into consideration. Distribute the final copy to all participants.
	Send a letter to prospective NUTS 6 participants to advise them to participate in the new QUASIMEME Laboratory Testing Scheme.
M. Krysell	Make the comments on the ICES/HELCOM paper on Quality Assurance of Chemical Measurement in the Baltic Sea available for the ICES/HELCOM Steering Group.
J.R. Larsen (coordinator), D.Wells, J. Klungsøyr, S. Carlberg, and G. Asmund	Work intersessionally on the preparation of an ICES data collection system covering not only analytical information but also sampling, sample handling and storage information.
J.-F. Chiffoleau and A. Gudjonson	Send information on Hg in biota to M. Leermakers.
R. Law, G. Asmund, B. Pedersen, M. Lebeuf, and K. Stange	Complete the speciation paper on mercury and send a copy to ICES for submission to ACME as soon as possible.
M. Leermakers	
G. Asmund	Act intersessionally as chairman of Trace Metal Subgroup and for MCWG 1998
J. Klungsøyr	Act as chairman of the Organics Subgroup for MCWG 1998 and in the intersessional period.
S. Carlberg	Act as chairman of the Chemical OceanographicSubgroup for MCWG 1998 and in the intersessional period.
A van der Zande	Approach his colleagues in Rijkswaterstaat regarding the paper on organotin compounds presented at MCWG, to ask if they would be willing to prepare an updated version incorporating information on usage in other countries for MCWG 1998. If so, then he will contact subgroup members for national information.
J. Klungsøyr and R. Law	Complete the draft guidelines for the determination of PAHs in biota and sediments within 1-2 weeks of the meeting. The draft will be circulated to subgroup members and nominees of MSWG for comment, and given to Ms Kari Stange for discussion at WGEAMS 1997. All comments received to be incorporated and a final copy to be sent to ICES for submission to ACME by 1st April 1997.
Jacob de Boer	Send a copy of review notes on toxaphene to ICES for submission to ACME by 1st April 1997.
R. Law	Send a copy of review notes on Irgarol 1051 to ICES for submission to ACME by 1st April 1997.
D. Wells (coordinator) S. Berman, E. McGovern, and M. Lebeuf	Update the list of contaminants which can be monitored on a routine basis in advance of MCWG 1998 (see 8.1)
J.Rene Larsen	Present a plenary lecture on the new structuring of the ICES database and its capabilities at the MCWG 1998.
D. Wells	Coordinate the second phase of the joint study on PCBs in fish-eating mammals
A.Bignert	Present a plenary lecture concerning the Swedish seabird monitoring programme utilising guillemot eggs at MCWG 1998.

All Organic Subgroup members	Send information on national monitoring programmes involving seabird eggs to Professor Bo Jansson intersessionally, for discussion at MCWG 1998.
Participating laboratories	Send data on TCPM and TCPMe to Dr Jacob de Boer during 1997. TCPM and TCPMe exercise.
J. de Boer	Summarise the TCPM & TCPMe data to be discussed at MCWG 1998.
G. Rimkus	Prepare a review note on synthetic musk compounds in the marine environment for MCWG 1998.
D.Wells	Coordinate a plenary presentation describing progress within the QUASIMEME and QUASH programmes for MCWG 1998.
A van der Zande	Present information on the problems and limitations in the analysis of dissolved concentrations of highly hydrophobic compounds, and bioconcentration in mussels from the mussel watch monitoring programme at MCWG 1998.
A Abarnou	Present information on modelling PCB bioaccumulation in the Seine estuary at MCWG 1998.
K. Nagel	Report on progress in the application of high temperature techniques for het determination of total nitrogen in sea water at the MCWG 1998.
O.Vagn Olsen	Prepare a discussion paper on statistical tools to demonstrate the reliability of old nutrient data.
M. Krysell	Review a paper on particulate organic carbon (POC) in anoxic water.
M Krysell (and others)	Demonstrate one or more screening softwares for chemical data to be entered into data bases at the MCWG 1998.
A. Amonot	Review a paper on quality assurance aspects in the determination of chlorophyll in sea water.
Chemical OceanpgraphicSubgroup	Collate and review information on the experience of the use of automated insitu systems for observation of chemical variables.
J. Olafsson:	Present a plenary lecture on 'Impact and Fluxes of materials carried with a glacial outburst flood caused by volcanisu, Skeida Nov, 1996' at the MCWG 1998.
M.Krysell:	Present a plenary lecture on 'The impact of Rhine overflow water on the Skagerrack and the Kattegatt.' at the MCWG 1998.

ANNEX 14

RECOMMENDATIONS

Recommendation 1

MCWG recommends that the final report should be published in the ICES Cooperative Research Report series.

Recommendation 2

MCWG agrees that in view of the QUASIMEME initiative in this area there is no need for an ICES interlaboratory study on organotins.

Recommendation 3

MCWG recommends that the review paper on Irgarol 1051 should be finalized and forwarded for review to ACME, with a view to its inclusion in their report.

Recommendation 4

MCWG recommends that the review paper by B. Jansson on HCBs, should be included as an annex to the MCWG 1997 report (Annex 6) and that it should be considered by ACME as an example of the complexity of behavior of even a single persistent organic pollutant in the marine environment.

Recommendation 5

MCWG recommends that the review paper on toxaphene by J. de Boer should be finalized and forwarded for review to ACME, with a view to its inclusion in their report.

Recommendation 6

MCWG recommends that toxaphene should be considered for future routine monitoring programs, once the present analytical difficulties have been overcome. Steps are being taken to overcome these problems.

Recommendation 7

MCWG recommends that the review note paper on bioaccumulation and biomagnification of PCBs in the food chain by A. Abarnou should be forwarded to ACME after a minor revision and included as an annex to the ACME report.

Recommendation 8

MCWG recommends that the praxis with user defined (free text) fields for the reporting of quality assurance information to the ICES Environmental Data Bank. in principle should be replaced by a system where the data supplier chooses from a list of defined options.

Recommendation 9

MCWG recommends that the paper on mercury speciation by M. Leermaker after minor revisions and after it had been reviewed by G. Asmund and G. Audunsson, should be forwarded to ACME for information and appended to their report,

Recommendation 10

MCWG (B. Pedersen, Chairman) should accept the offer made by the SMHI in cooperation with the University of Stockholm, to host the next meeting in Sweden. This meeting should be held from 2-6 March 1998 to carry out the following tasks:

a) review the outcome of the Icelandic study on the influence of parameters like fish size, liver size and fat content in the liver on the trace metal concentration;

b) review the note on a new ICES data collector system covering not only analytical information but also sampling, sample handling and storage information;

c) review the updated paper on organotin;

d) review the updated list of contaminants which can be monitored on a routine basis;

e) review the progress of the second phase of the joint study on PCBs in fish-eating mammals;

f) review the progress on the work done intersessionally on variance components in seabird egg analysis and the use of seabird eggs in national monitoring programs;

g) review the progress in the collaborative study on TCPM and TCPMe;.

h) review the note on synthetic musk compounds in the marine environment;

i) review information on the problems and limitations in the analysis of dissolved concentrations of highly hydrophobic compounds, and bioconcentration in mussels from the Dutch mussel watch monitoring programs;

j) review information on modeling PCB bioaccumulation in the Seine estuary;

k) review a note on progress in the application of high temperature techniques for the determination of total nitrogen in sea water, a discussion paper on statistical tools to demonstrate the reliability of old nutrient data, a paper on particulate organic carbon (POC) in anoxic water and a paper on quality assurance aspects in the determination of chlorophyll in sea water;

l) review information on the fate of nutrients in estuaries and on the experience of the use of automated *in situ* Chemical Oceanographic systems for observation of chemical variables.