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REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Brussels, 18 - 22 March 1991

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EXECUTIVE SUMMARY

The ICES Marine Chemistry Working Group met in Brussels during March 18 to March 22, 1991. The meeting was hosted by Prof. R. Wollast, and attended by 33 people.

This summary is confined to the tasks allotted to the Marine Chemistry Working Group by ACMP, and to major items raised by the Group itself.

The **baseline study of trace metals in seawater** has been finalized. The editorial comments of the reviewers have been taken into consideration. Dr Balls agreed to incorporate the changes into a final version for submission to ACMP in 1991. Material of this document will be used to prepare a paper for the open literature. The trace metal group has the opinion, that the data are not yet fully explored, and a more profound study is appropriate, particularly with respect to the metal-salinity relationships. A number of members agreed to work on the data intersessionally.

The **report on the second phase of the intercomparison exercise for CBs** has been finalised. The Group acknowledged the considerable amount of work invested in this exercise, in particular by the coordinator Dr J. de Boer. The preparation of calibration solutions was not under control by the majority of laboratories. Some commercial solutions were shown to be inaccurate. The results on the seal blubber point to insufficient chromatographic separation as an important cause of poor performance. The sediment extract gave rise to problems owing to the low concentrations, however, the concentrations are representative for North Sea sediments. The results for the sediment extract were disappointing. It is concluded that joint studies (e.g., monitoring in NSTF/JMG context) of CB's in sediments for a number of laboratories are impracticable for the time being. Poor separation, incorrect calibration and insufficient sensitivity were (again) identified as problems. Laboratories were classified into three groups according to the overall quality of their results. Advice has been given to each group for continuation or improvement of their performance.

he discussion of the report led to the formulation of criteria which laboratories would have to adhere to in order to be allowed to participate in future exercises. These entail among others the use of columns with minimum lengths of 50 m and internal diameters of 0.25 mm or (preferably) less. The quality of commercial standards has to be checked against solutions prepared from weighed solid standards. Results obtained without the use of internal standards will no longer be accepted. It is up to the laboratories which internal standards they apply. It is recommended that laboratories which did not respond at all in step 2 be excluded from further participation.

The design of future stages has been discussed; the experience gained has led to improved strategies.
Many laboratories have to modify their methodology in order to improve. Therefore, the Group considered it not appropriate to distribute new samples in the short term. Instead, a new stage has been introduced into the programme, designated as step 3a, which gives laboratories time to make these modifications. Specifications for the validation of methods have been prepared, making use of existing certified and laboratory reference materials. Each laboratory has to provide, in a harmonised manner, data on accuracy (trueness) and precision by the end of this year. The results of this exercise will be taken into account when plans for step 3b are finalised during the MCWG meeting next year.

The resources, in particular manpower, required to continue the CB intercomparison exercise are very large. The work can no longer continue on a voluntary basis. The MCWG recommends that the coordinator be financially compensated. The costs are estimated to be 40,000 DKK for step 3a and 250,000 DKK for step 3b. The planned step 3a will not proceed if no financial support is given.

The report on the second step will be submitted to ACMP, and is recommended for publication in the Cooperative Research Report series.

The **report on the first stage of the 4th round hydrocarbon intercomparison exercise** has been finalized. In this stage standard solutions have been studied. The results indicate that intralaboratory precision is acceptable, but that the bias is disappointing. The causes have been discussed. The report will be submitted submitted to ACMP, and is recommended for publication in the Cooperative Research Report series.

The design of the second stage of the intercomparison exercise was discussed. A cleaned sediment extract will be distributed together with a standard solution. Laboratories will be requested to maintain control charts during the PAH analyses, and to submit these data too.

The document on **quality assurance of sampling of sea water for the measurement of trace metals** has been discussed. Modifications have been proposed. The modified document is to be submitted to ACMP.

Guidelines for the conduct of intercomparison exercises have been discussed. Dr J. van der Meer (WGSATM) took part in the deliberations. The adoption of a single statistical methodology for application to all intercomparison exercises poses problems, as the choice of the most appropriate methods to be employed will depend on the quantity and type of data involved in each case. A first draft of the guidelines has been prepared and is included in this report as Annex 4. Intersessionally further consideration will be given to this problem.

ACMP requested the Marine Chemistry Working Group to '**report on quality assurance protocols, for the analyses of contaminants in water, tissue and sediment**, that would allow groups concerned with the assessment of data and the preparation of regional assessments to undertake their tasks in the light of quantifiable evidence as to the quality of data available to them.' The Group felt that considerable work has been done in the past, and that the protocols requested were available. The implementation of these protocols and guidelines should be a priority. The conclusions of the Group together with some guidance are set out in a paper given in Annex 3 of this report.

The North Sea Task Force has requested ICES to prepare a **note on the occurrence and concentration of nonylphenol in the marine environment**. This request has been passed on to the Marine Chemistry Working Group. A note has been prepared. It is given in Annex 5 of this report.

The **guidelines for the sampling of seawater for the measurement of nutrients** have been finalised. The paper prepared by the MCWG last year has been combined with a paper prepared intersessionally by D. Kirkwood for the UK delegation to the NSTF. This paper is included as Annex 9 of this report. The MCWG recommends that the paper of D. Kirkwood, 'Practical notes on the determination of nutrients in seawater', be revised with the aim of having it published in the ICES TIMES series.

Intersessional work on nutrient studies has been reviewed. An intercomparison study (NORSAP) has been organised by Dr S. Kirkwood and Aminot (NORSAP) in the context of the monitoring programme in the Irish Sea. Much benefit was taken from the previous experience of the ICES NUTS 4 intercomparison. Considerable improvement was observed. Dr F,øyn presented the SKAGEX intercalibration experiment.

Participants analyzed samples along a transect. Systematic errors were apparent, mainly due to calibration errors. The need for a reference material for nutrients is clearly demonstrated by both the NORSAP and SKAGEX experience.

The HELCOM/ICES intercomparison exercise for the determination of dissolved oxygen was discussed. The statistics need to be repeated. A preliminary assessment of the data indicate, that no significant differences occur between sampling bottles, and operators. There was no significant difference between reagents supplied by the participants or the convener. Most laboratories exhibit consistent high or low values, but the differences were not substantial.

Plans for an **assessment of the effects of sampling and storage on nutrient measurements** have been discussed. A "standard intercomparison study" cannot be formulated for the sampling and storage of nutrients. The Group took notice of on-going or planned intersessional activities on storage. The outcome of these experiments will provide direction to future work. It was decided to try to assemble as much information as possible for discussion at the MCWG meeting next year. All members of the MCWG have been requested to provide information on past, on-going and planned activities to a central coordinator, Dr Kirkwood.

In response to a request of the ACMP, the MCWG recommends that **nutrient intercomparison exercises** be organised with a frequency of once every four years. This implies that NUTS5 and NUTS6 will be scheduled in, respectively, 1993 and 1997. The MCWG recommends that D. Kirkwood and A. Aminot are requested to organize NUTS5 in 1993. In addition, it is recommended that NUTS5 be open for participation by manufacturers of equipment.

Seven **overview papers** were considered by the Marine Chemistry Working Group. The papers on chromium in seawater, octachlorostyrene and linear alkylbenzenesulphonates will be submitted to ACMP. The paper on chlorinated waste water discharges to the marine environment will be sent to the WGBEC, and can be submitted to ACMP if the WGBEC responds positively in a short term. Papers on nickel, atrazine and brominated flame retardants have been discussed and will be amended intersessionally.

The overviews gave rise to considerable discussion. The 'official' guidelines for the preparation of overviews are outdated. A new model has informally been established last year. The MCWG recommends that these guidelines be formally accepted. For some contaminants, however, overviews prepared along these lines become too large a task.

It is recommended that the ACMP assess the amount of work involved in the preparation of overviews, and where appropriate confines the scope of overviews so that an acceptable workload is requested from the authors. The requests put forward by ACMP should specifically outline the scope of the paper.

Difficulties are experienced in finding authors and in assessing the papers. These problems are caused to a large extent by the rather vague fate of the overview papers. Authors are reluctant to spend considerable time preparing papers for ACMP when there is little or no recognition, and the names are removed from the paper. The MCWG recommends that it should be an ACMP policy that overviews are published in the open literature. This implies that the overview should meet standards which are generally accepted in scientific practice. It should be up to the author to decide in which journal the paper will be published. The MCWG recommends, however, that ICES offer the possibility to publish the paper in its own journal. The route can be: acceptance by the MCWG (if relevant in cooperation with other working groups, e.g. the WGBEC) and recommendation for publication to the ACMP, the approval by the ACMP for publication in the ICES Journal of Marine Science.

The **allocation of tasks by the ACMP to ICES working groups** gave rise to discussion. An example is provided by work on nutrients. The MCWG has built up a considerable expertise in the field of chemical oceanography, and has been particularly active in matters related to the quality of data in relation to the information needed (e.g., monitoring). It was pointed out that the ICES Shelf Seas Oceanography Working Group was assessing trends in nutrients, and was involved in the optimization of the NSTF MMP. Such tasks require the contribution of chemical oceanographers, and thus of the MCWG. Papers of the WG on Shelf Seas Oceanography on these subjects should be considered by the MCWG in a comparable manner as the arrangement between the MCWG and WGBEC regarding sections on toxicological aspects in overview papers.

Work on environmental matters in the marine environment requires increasingly a multidisciplinary approach. For ICES this implies that particular attention has to be paid to the flow of information between working groups, and to the cooperation between them. The MCWG recommends that the ACMP set up an operational programme in order to encourage and establish multidisciplinary projects. This programme can entail a close involvement of WG chairmen by distributing tasks for working groups among them for comments and the identification of areas of mutual concern.

The Group discussed **the mode of operation within the Marine Chemistry Working Group**. It is appreciated that the advisory role of MCWG is important, and that requests from agencies will form a substantial portion of the MCWG agenda. However, the MCWG has a considerable potential as a platform to set up cooperative research projects, to highlight contrasting views on marine research, and to discuss and identify important developments in marine research. This research does not necessarily have to be restricted to marine pollution. More contacts between the three MCWG subgroups for "cross-fertilisation" is necessary. Some initiatives have been taken to make advancements in this direction.

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1. Opening of the Meeting

The chairman, Dr W. Cofino, opened the meeting at 9.45 hrs on March 18, 1991 and welcomed the participants.

Prof. Dr R. Wollast of the Université Libre de Bruxelles, then welcomed the participants and introduced Dr M. Loijens, a coworker who took care of a major part of the organization of this meeting.

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

2. Adoption of the Agenda

The Working Group reviewed the draft and annotated agenda, which had been prepared and distributed by the Chairman before the meeting. The adopted agenda is attached as Annex 1 and the list of participants as Annex 2.

As usual, most of the tasks would be dealt with by the respective sub-groups prior to being discussed in plenary. Sub-group sessions would begin in the afternoon of the first day, and would be completed by the end of the fourth day. Each morning a short plenary session would be held. The reports from each sub-group would be discussed in plenary on Friday, March 22. The reports would include any recommendations and action lists for the forthcoming intersessional period.

An *ad hoc* sub-group would meet on March 19 to discuss the problem of establishing guidelines for the conduct of intercomparison exercises. Working group members who have been involved in the coordination of intercomparison exercises for trace metals, organics and nutrients would participate. In addition, Dr J. van der Meer of the ICES WGSATM would take part in the discussions. This meeting would be chaired by Dr Cofino.

The sessional chairman for the sub-groups on organics and chemical oceanography would be, respectively, D. Wells and S. Carlberg. The trace metal sub-group had to elect a new chairman. The remaining members and visitors were grouped as follows:

Chemical Oceanography:
A. Aminot, M. Baeteman-Cools, L. Føyn, D.S. Kirkwood, K. Makela, E. Nixon, G. Weichart.

Organics:
A. Abarnou, J. de Boer, J. Biscaya, J. Boon, S. Einarsson, H. Haahti, J. Klunsøyr, R. Law, T. Nunes, P. Roose, F. Smedes, J. Tronczynski.

Trace Metals
D. de Armas, P. Balls, S. Berman, V. Besada Montenegro, L. Brügmann, J. Olafsson, B. Pedersen, S. Westerlund, P.A. Yeats, S. Wilson.

3. Report of the 78th Statutory Meeting

The Chairman informed the Group that all of the tasks requested at the Statutory Meeting for attention by MCWG had been incorporated in the draft agenda.

4. Report of related activities

4.1. Joint Monitoring Group of OSPARCOM

No note concerning JMG matters was available at the meeting; requests of JMG have been included in the draft agenda.

4.2. Intergovernmental Oceanographic Commission (IOC)

No note concerning IOC activities was available at the meeting, nor was an IOC representative present. Dr Berman drew attention to a recommendation of GEMSI on the production of reference materials.

4.3. ICES Working Groups

The Chairman called attention to a resolution adopted at the 78th Statutory Meeting, which entails that the Working Group on Biological Effects of Contaminants (WGBEC) would review the "biological effects sections of contaminant overviews prepared by the MCWG".

Dr Addison, Chairman of the WGBEC, had requested to obtain MCWG overview papers for consideration at the WGBEC meeting in Copenhagen in the beginning of March. This request had been passed on to MCWG members, and a number of papers were available at the WGBEC meeting. A proper mechanism for communication between WGBEC and MCWG has to be established. Dr Wells brought forward the view that a cooperation between MCWG and WGBEC members in the preparation of overviews would constitute the most efficient approach. The Group agreed with this point of view.

Mr Carlberg, Chairman of the WGEAMS, had provided the MCWG for consideration two papers on the monitoring of trace metals using benthic algae. At the meeting, he provided in addition a document which combined these papers. The papers were to be discussed in the Trace Metal Sub-group.

4.4. EC-BCR QA pilot project "Quasimeme"

Dr Wells presented an overview summarizing the present situation. A proposal describing the design of the project and an estimate of the costs has recently been forwarded to the BCR. In addition, a QA manual has been prepared, giving guidelines for the collection, storage and analysis of samples and for the management of Marine Pollution Monitoring Programmes at the laboratory level. The project can be divided into three parts:

1. The establishment of a management programme, having a holistic approach to quality assurance in marine monitoring.

2. The establishment of an operational programme for the improvement of measurements of mandatory contaminants through a series of learning/training exercises, through a continuous programme of laboratory self assessment, and through a feedback programme to assess the comparability of information.

3. The establishment of a communication programme, for the dissemination of experience and information and the mutual encouragement of participating laboratories, and the establishment of a link between the laboratories, the Steering Group of the project, and the Commissions, for the purposes of quality assurance.

The proposed pilot programme will move towards establishing a Quality Assurance Programme for the Marine Monitoring Programmes of the Oslo and Paris Commissions and the North Sea Task Force. It is hoped that the EC will give a favourable reply, and that the project will start in 1992.

Mr Smedes remarked that the proposal does not seem to provide for the exchange of technicians. The Group agreed with Mr Smedes that provisions to let technicians work in expert laboratories is a good approach for quality improvement. Dr Wells replied that it is the intention to identify regional coordinators, and that arrangements can be made on a regional basis.

The pilot project is completely run by the Commission of European Communities for the North Sea Task Force and for OSPARCOM. No formal relationship between the project and the ICES MCWG is present.

4.5. Other activities

The Chairman stated that no matters had been raised by members under this agenda item.

5. Reports on projects and activities in member countries

The Chairman informed the Group that no matters had been raised by members under this agenda item.

6. Requests from ACMP and other regulatory agencies

The Chairman informed the Group, that all requests had been incorporated in the agenda. Special attention was paid to the request "to report on quality assurance protocols for the analyses of contaminants in water, tissue and sediment, that would allow groups concerned with the assessment of data and preparation of regional assessments to undertake their tasks in the light of quantifiable evidence as to the quality of the data available to them." ACMP requested additionally to state the need for QA procedures which have to be implemented, to identify the type of QA data needed by assessment groups to evaluate the data properly, to provide guidance on how monitoring data should be judged against these QA data, and to provide guidance on how to assess the quality of data if only some information arising from quality assurance procedures is available.

The Group noted that considerable work has been done in this field, and that it would not be appropriate to produce the documents requested at the meeting. It was agreed to produce a short note, identifying papers in which most of the information requested could be found, and highlighting some important issues. A paper was prepared during the meeting by Drs Pedersen, Berman and Cofino, and approved by the Group. The paper is given in Annex 3.

7. Sub-group activities and discussions

7.1. Trace Metal Sub-group

7.1.1. Election of Chairperson

Dr Yeats was elected chairman and Dr Balls agreed to act as rapporteur.

7.1.2. The report on the results of the Baseline Study of Trace Metals in Coastal and Shelf Sea Waters

This document was presented for final review together with reviews solicited by ACMP. All of the non-editorial comments of the reviewers were discussed by the group and changes made where considered appropriate. Editorial changes had been incorporated previously by Simon Wilson. Members of the sub-group suggested many other changes; these were discussed and a draft of such changes was prepared and made available to the group for acceptance. Major points raised were:

a. Tables containing concentration data from individual laboratories should be incorporated into an annex at the end of the report.

b. The box- and whisker-plots should be modified so as to eliminate negative values on the y axis. In addition, metal/salinity plots should be modified so that only one symbol is used on each (Simon Wilson to complete).

c. Comment should be made on those data which appear anomalously high, e.g., Cu in NORC and Hg in IRS and KATT.

d. In the conclusions, typical baseline concentrations for individual metals should be inicated. Clarification is also required on the significance of metal/salinity relationships.

e. Comment f in the final section gives the incorrect impression that the exercise had not been a success, this needs to be rewritten.

Dr Balls agreed to incorporate all changes into a final version for submission to ACMP.

7.1.3. The overview on chromium.

A modified version of the overview on chromium was reviewed by the sub-group. It was felt that the overview on sea water was now of a good standard, although the English still needed some attention. Other aspects of the overview, i.e., sediments, biota and toxicity were inadequate.

In order to maintain progress with this piece of work, it was recommended that the overview should be sent to ACMP as a review of chromium in sea water only. The paper will be returned to Dr Schmidt with suggestions for improvement in the English. Dr Yeats will contact Dr Addison (Chairman WGBEC) for guidance as to progress with biota and toxicological aspects.

7.1.4. The QA document on the sampling of seawater for the measurement of trace metals

The sub-group received a discussion document on this subject from Drs Cofino, Berman and Yeats. Although intended to focus on QA aspects of sampling, this paper contained much information which the group felt was unnecessary for the purpose. A number of changes were therefore suggested to shorten the paper and present a clearer message. This involved changing the title to include "trace metal" and "seawater", and to remove references to the description and validation of analytical methodology. The authors agreed to revise the paper and submit it to ACMP.

7.1.5. The overview on nickel

The first draft of an overview on nickel in the marine environment was received from Mr Jones. The group felt that there were some major shortcomings with the paper, notably:

a. None of the recent data concerning the oceanic behaviour of nickel is included and only a small amount of new estuarine information is present. More recent data would give a different picture of the distribution and behaviour of nickel.

b. No quantification of inputs (e.g. rivers, industries) and no mass balance calculations are included.

c. Inadequate reference is made to removal mechanisms such as biological uptake and incorporation into sediment.

The sub-group felt that the paper should be returned to the author and that individual members should provide him with additional information to assist with the preparation of an improved version. This information would include recent information on seawater (Yeats), particle-water interactions (Balls), anoxic seawater (Westerlund) and organo-nickel species (Brügmann).

A more general discussion on overviews followed: this resulted in the following recommendations:

1) Overviews should be submitted to the MCWG chairman a few months before the meeting. The chairman would then arrange for review by a suitable expert prior to the meeting.

2) ACMP finds a mechanism whereby overviews can be published in the ICES Journal of Marine Science.

7.1.6. The QA protocols and assessments

The request for protocols was discussed by the sub-group. The principal outcome was the identification of the conflicting pressures between established rigorous QA protocols and the need for assessment when QA is inadequate or absent. A short note entitled "QA Protocols and Assessment" was prepared for discussion in plenary.

The request by ICES for experts to assist with the assessment of data was also discussed. Dr Pedersen agreed to help with assessment of metals in biota and Dr Brügmann with those involving sediments.

7.1.7. Any other business

7.1.7.1. Advice on the use of benthic algae for contaminant monitoring

This paper was received for consideration from the chairman of WGEAMS, in view of possible publication in the ICES TIMES series. None of the members of the group felt well qualified to review the paper, however two general comments were made:

a. A more extensive literature review is required together with an indication of the success of this particular technique in monitoring, typical concentrations, and the suite of elements for which the method appears to be applicable. Items in section 7 should be included in this part.

b. Insufficient information is given to enable the reader to use the document as a guide to the technique. In particular more details of the method are required including QA and the use of reference materials.

Since the group had no qualified reviewers, the paper should go to external review.

7.1.7.2. Initiatives

Three potential areas of future work were identified during the discussions of the sub-group:

1) Preparation of a paper for publication in the open literature based on the baseline study (agenda item 7.1.2.).

2) The QA document on sampling (agenda item 7.1.4.) includes a description of three approaches which could be taken to address this problem. Dr Berman expressed an interest in commencing work on a reference sampling method (kit). In order to undertake such an exercise, assistance is required from an organisation able to provide ship time. Both Dr Yeats and Dr Olafsson indicated a willingness to cooperate.

3) The estuarine data collected during the baseline study (7.1.2) has not been fully explored. Balls, Brügmann, Pedersen, Westerlund and Yeats agreed to initiate an interpretation of these data; de Armas will determine if one of his colleagues is interested in participating. During the intersessional period, with the help of Simon Wilson, these people will collect the available data and prepare metal/salinity plots for each metal in each estuary. These will be discussed at the next meeting.

7.2 Organic Sub-group

7.2.1 Report on the second phase of the intercomparison exercise for CBs, and make recommendations for phase 3 of this exercise

J. de Boer presented document 1991/7.2.1, the Draft Report on the ICES/IOC/OSPARCOM Intercomparison Exercise on the Analysis of Chlorobiphenyl Congeners in Marine Media - Second Step. During the first step of this exercise, two main problem areas were identified: linearity of the ECD detector and separation of CBs. There was an encouraging agreement in the results, with coefficients of variation of 1.11-1.12. However, this should not be taken too optimistically since the matrix for the analysis was only a standard solution.

The second step of the exercise required:

- the analysis of a standard solution;
- the analysis of a cleaned seal blubber extract; and
- the analysis of a cleaned marine sediment extract.

The aims were to check the ability of participants to prepare their own CB calibration solutions and to compare the results of the participants on the analysis of CBs in both cleaned extracts. An extra test was included, for laboratories which were submitted outlier results in step one and for new laboratories, who indicated their interest in joining this exercise after the first step was finished. This extra test was a short version of the first step. Participants were asked to optimize their instruments, to prepare linearity graphs of the ECD detector and to analyze a simple CB solution using a calibration solution supplied.

Approximately 700 ampoules were prepared for the exercise. The seal blubber extract was prepared by the Swedish Environmental Protection Agency, Solna, Sweden from a seal sample supplied by the Icelandic Fisheries Laboratories. The sediment extract was prepared by the Rijkswaterstaat, Tidal Waters Division, in Groningen, The Netherlands. The ampoules for both extracts were filled, prepared and sent to the participants by The Netherlands Institute for Fishery Investigations (RIVO), IJmuiden, The Netherlands. Before being sent to participants, the ampoules were tested for homogeneity at the RIVO.

The ampoules were dispatched during the last week of August 1990, together with the guidelines. The deadline for results was set as 1 December 1991, however, a large number of laboratories informed RIVO that they would have some delays in submitting their results. The delay showed that people usually tend to start too late, and that the analysis is critical and difficult for the majority of the laboratories. The acceptance period was then extended to 8 January 1991.

The results were evaluated by J. de Boer and L. Reutergårdh. The statistical evaluation of all the data was performed by J. van der Meer (Netherlands Institute for Sea Research, Texel) on behalf of the ICES WG on Statistical Aspects of Trend Monitoring (WGSATM) (J. van der Meer presented an overview of the statistical methods used for this exercise later during the MCWG meeting (see section 7.4 of this report)).

In the report the following problems areas were highlighted:

The standard deviations for the reproducibility of the analysis of the unknown CB solution for all laboratories excluding outliers were 1.16-1.17 for CBs 52, 101, 118, 138, 153 and 180. CBs 31, 105, 118 and 156 showed considerably higher SRs. The mean results are within 10 % of the target values, except for CB 28 (+13 %) and CB 52 (+12 %). The main conclusion was that the preparation of calibration solutions is not under control by the majority of the laboratories. A number of reasons were again identified: bad weighing practice, poor control of the temperature in the weighing room, incorrect storage and dilution of calibration solutions. A number of participants used commercially available calibration solutions, which were shown to be inaccurate.

The standard deviations (SRs) for the seal blubber results were 1.20-1.33 excluding the outliers for CBs 52, 101, 118, 138, 153 and 180. Higher SRs were obtained for CB105: 1.38 and CB156: 1.62. Statistical results for CB28 and CB31 were not given because too few results were submitted for these CBs. A large variation was found for these CBs, possibly due to coelution with other components. In addition to the errors made in the calibration, there was again insufficient chromatographic separation which is an important cause of the poor performance. CB105 elutes close to CB132 and CB153, and CB156 coelutes with CB171 and close to CB202 on a SE54 column.

The main conclusions were that the analysis of an uncleaned seal blubber extract can be taken a step forward if the columns used had a minimum length of 50 m with an internal diameter of 0.25 mm or less (e.g. preferably 0.20 mm). Chromatograms, demonstrating the effect of the increase of the column diameter, were shown. It was stressed that the use of appropriate columns is essential to improve the separation. A good quality of CB analysis certainly makes high demands on equipment and qualified personnel.

J. de Boer stated that the sediment was selected in a way that the extract would be representative of sediment samples usually taken in several areas for programmes like the JMP, which are often not highly contaminated. He pointed out that it would not be appropriate to have a highly cotaminated sediment sample for the intercomparison exercise with a chance of better results, when the real samples usually have much lower concentrations.

The results without the outliers gave SRs between 1.31 (CB153) and 1.56 (CB52). No statistical data could be given for CBs 28, 31, 105 and 156, because too few complete data sets were available, and the quality of these data sets was very poor. The analysis of these CBs must be judged as impossible for the majority of the participants.

The high SRs for the remaining CBs were caused by poor separation and incorrect calibration. Sensitivity was another major problem for most laboratories (the samples had to be concentrated prior to analysis), which often resulted in high blanks and a noisy background. Also negative peaks were observed regularly, indicating the presence of electron donating compounds in the chromatographic system. This may indicate that additional clean-up was required.

J. de Boer reported that there was a very poor response for the extra test in this exercise. It is recommended that laboratories which applied to participate for this extra test or for the second step exercise and did not respond at all should be excluded from further participation. Thirteen laboratories participated in this test and SRs between 1.18 (CB28) and 2.80 (CB118) were obtained for a group of 9 laboratories (without outliers). The separation of CB118 from CB 149 was difficult for most of these laboratories, although in most cases the separation was obtained on at least one column.

Based on the two applied statistical criteria: deviation from the mean performance and deviation from the target values or mean values, and on the chromatographic performance, the participating laboratories were classified according to the overall quality level of their results. Three groups were identified:

Group 1 (13 laboratories): in general reliable results for the three solutions. All results within 20 % of the target or mean values with the exception of a maximum of 3 results. Acceptable chromatographic performance and calibration.

Group 2 (28 laboratories): several deviating results. Several deficiencies in the calibration procedure and/or the chromatographic system.

Group 3 (15 laboratories): statistical outliers for different solutions. Poor chromatography and/or difficulties with calibration.

The Group 1 laboratories are advised to maintain the present quality level and to try to improve where possible, especially for CBs 105 and 156. Group 2 are advised to correct the deficiencies which appear from this exercise by installing the appropriate chromatographic columns, reconsidering the calibration procedures, and following further suggestions given in the report. Group 3 laboratories are advised to reconsider totally their calibration procedures, chromatographic conditions and optimisation of their instruments.

The main conclusions and recommendations of the report were:

- to repeat the analysis of the unknown CB solution in the next step of the exercise, and also in further steps. Participants using commercial solutions for calibrations should be excluded.

- for the seal blubber, to recommend that the laboratories use columns of a minimum of 50 m, and reduce the i.d. (0.20-0.25 mm), in order to improve separation. Enough time must be given to participants for the installation of the appropriate columns. Advice on weighing procedures should be included in the next guidelines.

- for the sediments, to wait until progress is obtained from the repetition of the standard solution and seal blubber extract step.

The Chairman thanked J. de Boer for his presentation and for the extremely hard work undertaken in this stage 2 of the exercise.

The Sub-group discussed the report under the following headings:

1. Review of intecomparison exercise report
    (i) Additional information
    (ii) Additional graphical representation

2. Specify target accuracy/precision (long- *versus* short-term)

3. Confirm or modify recommendations

4. The way forward (regardless of cost at present)
    (i) for laboratories under statistical control
    (ii) for laboratories who require improvement in specific areas
    (iii) for laboratories who demonstrated they do not wish to improve.

1. The sediment extract matrix was discussed at length, in relation to sampling strategy of sediments for analysis of organic contaminants and the difficulties of the analysis of extracts, since concentrations are often very close to detection limits (the WGMS views in this aspect were also pointed out in this context).

The WG recommended that the ranking of laboratories should be made separately for the unknown CB solution, the seal blubber and sediment extract.

With respect to point (ii), it was agreed to include 3 principal component analysis graphs in the report.

2. Based on earlier, similar exercises within the Community Bureau of Reference (BCR) it was concluded that at present the overall reproducibility coefficients of variation would be no better than 30 % for real samples. It was agreed that this should serve as an initial target value for this CB intercomparison exercise.

3. As a result of the separation problems, it was recommended that participants using columns less than 50 m long and with internal diameters of >0.25 mm should be excluded from future exercises. The use of smaller diameters is strongly recommended.

he Sub-group's conclusion on item d was to suggest that laboratories should check commercial calibration solutions (when used), and their quality should be confirmed against solutions prepared from weighed solid standards. It was also recommended that participants be supplied with guidelines about the preparation and storage of standards.

Some laboratories reported problems with their internal standards. In future exercises the laboratories will have to choose their own internal standards. It was agreed that results obtained without the use of internal standards should no longer be accepted. A recommended list of internal standards will be included in the final report.

4. The plans for the future work on the CB intercomparison exercise were extensively discussed. The ICES WGMS, the NSTF and the Oslo and Paris Commissions emphasise the need for quality control on the analysis of CBs in sediments. However, this exercise shows that joint studies on CBs in sediments are impracticable for the time being, except for laboratories in Group I.

The following action is recommended to give participants time to install new columns and to improve their equipment and calibration procedures:

Participants are advised to reconsider their method and improve where possible, to buy a certified reference material (fish oil or sediment), to analyze this material 6 times on CB 153 and CB 156 with a frequency of 1 analysis per week, and to design control charts for both CBs and return these charts to the coordinators. This action, designated as step 3a of the exercise, is scheduled to be ready before the next MCWG meeting (evaluation in January 1992).

Depending on the results of this test, the following is designed for step 3b:

- repeat of the analysis of a standard solution;
- analysis of a cleaned and an uncleaned seal blubber extract; and
- analysis of a sediment extract, possibly cleaned and uncleaned.

Step 3b is scheduled for 1992 (evaluation in January 1993).

Financing organisations must be well aware of the cost of this exercise:

- for step 3a: about 40,000 DKK (10,000 DKK for materials and administrative costs, 30,000 DKK for manpower).
- for step 3b: about 250,000 DKK (70,000 DKK for materials, administrative costs, and coordinators meeting, and 180,000 DKK for manpower).

The MCWG recommends that this sum of money be made available for these exercises. If not, then the exercises will certainly not be carried out since no volunteers are available to carry out these programmes without any compensation for their time spent.

It was agreed that, at present stage, none of the laboratories, except those which did not submit results at all for the second stage, will be excluded from the further stages of the CBs intercomparison exercise.

On behalf of the WG, Dr. Wells thanked again J. de Boer for the work carried out in the coordination and preparation of this exercise.

7.2.2. Report on the first stage of the 4th round hydrocarbon intercomparison exercise

R. Law gave a short introduction of the report to the members of the sub-group and apologised that because the report had been completed only one week before this meeting, it had not been possible to circulate it for members to study in advance. The first stage of the exercise consisted of two phases. In the first phase, standards were dissolved in acetonitrile for both GC and HPLC methods. In the second phase, standards were prepared in hexane for GC methods and in acetonitrile for HPLC methods. Also flame-sealed ampoules were used in the second phase instead of crimp-top vials.

The results of the exercise showed that although the analyses of many laboratories were precise (good repeatability), the overall agreement among laboratories indicated significant bias. This was somewhat disappointing considering that only standard solutions were being analyzed.

Since the exercise only involved standard solutions, the results did not reflect the state of the art for real samples. Realistic concentrations of PAH would be 10-100 times lower for sediments, and in biota the concentrations would be perhaps 1000 times lower.

The bias from the declared concentrations was often higher than 20% and in the second phase more so than in the first one. In the second phase for benzo[*ghi*]perylene there was a consistent bias of 30% for all participants using HPLC. Analysis of both standards by GC-FID has shown an error in standard solution H1 for the compound. The bias for all other compounds was randomly distributed among the laboratories and compounds. A difference was observed between the GC and the HPLC methods using Canonical Discriminant Analysis for the second phase which was independent of the standard concentrations. This was further investigated by cross-analysis of the standard solutions. The Tidal Waters Division (The Netherlands) offered to analyze the hexane standard also by HPLC. It had also analyzed the NIST SRM 1647 together with the samples and promised to submit those data also.

General comments were made by members of the sub-group. Improved graphical presentation of the results of each laboratory was requested. Raw data should be included as an annex to the report. Examples of the visual plots of the statistical treatment would be included with some explanatory text. The causes of the large biases seen in this intercomparison were discussed. Incorrect calibration could have caused the bias, but it should have been similar in the first phase as well as in the second. In most cases the biases seemed completely random. The targets for this intercomparison were considered further. After discussion, the group agreed that the repeatability should be better than 10%, with a long-term variability around 10%. For the bias a maximum of 20% was a target with the present state-of-the-art, but a lower figure is desirable. As long as the exercise involves only standards, these figures seem high, but as the exercise extends to the analysis of samples these targets would be more realistic.

It was agreed that, as for CBs, the target value for interlaboratory variability for samples will be 30%. A further section concerning the sources of PAHs and their impact on the methods of analysis was requested, emphasising the implications for HPLC and GC-FID methods of the presence of alkylated PAHs from oil. This exercise is only concerned at present with a selection of 10 unbranched PAHs, which may be sufficient for some monitoring purposes.

Stage 2 of the intercomparison exercise

In the second stage, a cleaned sediment extract will be distributed together with a standard solution. After some discussion it was agreed to perform a clean-up suitable for GC-FID, assuming that such an extract will be suitable for all other techniques also. Laboratories will be asked to maintain control charts during the analyses of PAHs and to submit data on the analysis of reference materials.

The sub-group agreed that, after modification, the report should be submitted to ACMP for eventual publication in the Cooperative Research Report series.

7.2.3. Preparation of a note on the occurrence and concentrations of nonylphenol in the marine environment

In response to a request for information from the NSTF, five papers concerning nonylphenols and nonylphenolethoxylates were considered by the group. A note on the occurrence and concentrations of nonylphenol in the marine environment was prepared on the basis of this material, and then modified in the light of comments from the sub-group members. The final copy is included in this report as Annex 5.

7.2.4. The overview on octachlorostyrene

Drs Klungsøyr and Law presented an overview on octachlorostyrene. The sub-group agreed that the overview was well-written along the guidelines for overviews of ICES. Some suggestions were put forward:

- J. de Boer will send some papers to the authors containing data from The Netherlands.
- Octachlorostyrene (OCS) is produced during combustion processes in the presence of a chlorine source. As such, it is part of a whole suite of compounds that can be formed under the same conditions, such as lower chlorinated styrenes, hexachlorobenzene, chlorinated naphthalenes and chlorinated dibenzodioxins and dibenzofurans.
- It would be advantageous to include more information on the analytical methodology could be included in the manuscript, including suitable references.
- A statement on the necessity for monitoring OCS in specific areas of the marine environment was requested.
- Attention was drawn to a commercially available OCS standard (Promochem).

The authors were thanked for their excellent presentation. Since the manuscript has already been to the ICES WGBEC for comment, the sub-group recommends that the paper be sent to ACMP as soon as possible.

7.2.5. The overview on chlorinated sewage effluents

Dr Abarnou presented the paper 'Chlorinated Water Discharge to the Marine Environment: Chemistry and Environmental Impact. An Overview' which he had prepared with a colleague, Dr L. Miossec. This overview is a summary of an extensive French report of IFREMER which appeared in 1990. Again, the sub-group agreed that this overview was very clear and well written. Below, the suggestions have been summarized:

- A table of contents could be added at the beginning of the manuscript.
- The meaning of the units used is sometimes ambiguous, e.g. mg/l: Is this the concentration of added chlorine or is it the concentration in the receiving water?
- More information on the identity of the emerging halogenated organics would be very useful from a toxicological point of view.

Since the paper contains a considerable amount of toxicological data, Dr Abarnou will send the paper to the chairman of the WGBEC, Dr R.F. Addison. If the comments of the WGBEC are received before 15 May, they can be included in the version of the manuscript which will go ACMP for information. The paper will be submitted for publication in the journal "The Science of the Total Environment".

7.2.6. The overview on linear alkylbenzenesulphonates (LAS) and alkylphenolethoxylates (APE)

Dr Abarnou presented the paper 'Presence and Behaviour in Aquatic Environment of Linear Alkylbenzenesulphonates (LAS) and Alkylphenol Ethoxylates (APE). A Review.', which has been prepared by a co-worker, Dr G. Thoumelin (IFREMER, Brest). This paper will be submitted for publication and will be sent to ACMP for information.

7.2.7. The overview on atrazine

Dr Tronczynski presented the paper 'An Overview of Atrazine in the Estuarine Environment'. The original request had been for an overview on simazine as well but the title was changed because of lack of information on the subject. The group requested the inclusion of physical and chemical properties of atrazine as well as potential harmfulness. It was decided that the paper will be circulated to the members of the sub-group as well as to members of the WGBEC for comments later on this year.

7.2.8. The overview on brominated flame retardants

The overview, Brominated Flame Retardants Occurrence and Toxicity, was presented by two of the authors J.P. Boon and J. de Boer. In the following discussion, the authors informed that a section on the analytical chemistry of the components would be added. The overview will be sent to the Working Group on Biological Effects of Contaminants for comments.

7.2.9. The document on QA protocols and assessments

The document, QA Protocols and Assessments, was discussed by the group. There was general agreement regarding the contents of the document. There was a discussion on how to deal with cases such as when laboratories do not send in QA data and the underlying reasons for this.

7.2.10. Assistance for NSTF QSR assessments

In connection with the 1991/2 assessments of data for the NSTF QSR, it was requested that the Organic Sub-group identify 3 persons willing to take a role in these assessments, in relation to QA aspects. As a minimum, this would involve reviewing assessment reports of other groups, however, more direct participation in the assessment activities was desirable.

7.2.11. Any other business

The following subjects for discussion during the 1992 MCWG meeting were suggested:

1) planar CBs :
   a. results of Swedish intercomparison exercise
   b. analytical methods
   c. levels in marine organisms.

2) the role of dissolved organic matter in the behaviour of contaminants in the marine ecosystem, and implications for the measurement chemical and physical parameters;

3) extraction techniques for metal species (organo-metallics); and

4) sampling of sea water for trace organic analysis.

L. Reutergårdh will be requested to provide information on item 1a. J. de Boer was asked to prepare a short note on item 1) and F. Smedes and J. Tronczynski were asked to prepare a short note on item 2).

J. de Boer informed the group about levels of planar CBs and toxaphene in North Sea fish. The contribution of planar CBs to the total amount of TCDD equivalents in North Sea fish, especially of CB126, is estimated to be an order of magnitude higher than the contribution of dibenzodioxins and dibenzofurans.

Due to analytical difficulties, until now only little information is available about toxaphene in the marine environment. Because of the relatively low ECD response, levels of toxaphene may have been under-estimated in the past. Recent data show that, after PCBs, toxaphene levels in marine fish are the highest of all other organic contaminants.

J. Tronczynski gave information about a solid phase sampling device, which can be used for the extraction of organic contaminants from sea water. First experiments are planned in the Seine Bay, in summer 1992.

F. Smedes presented a method for dealing with non-linear calibration curves. Further calculation on the data of the second step of the CB intercomparison exercise showed the influence of the calibration errors on the results of solution B.

7.3. The Chemical Oceanography Sub-group

The Chairman opened the session and invited the members to submit modifications or additions to the agenda. It was agreed to include in the agenda a discussion on the ISO norm about nitrite determination, that will be adopted as a European standard. A. Aminot agreed to act as rapporteur.

7.3.1. Guidelines for sampling sea water for the measurement of nutrients

The Chairman reminded that in 1990 the sub-group was asked to prepare such guidelines without having the form or the extent of the document specified. A draft was written by Matti Perttilä and amended by Stig Carlberg according to suggestions from the sub-group. Then, the paper was submitted to ACMP, which produced a revised version for the Working Group on Nutrients (NUT) of PARCOM. During the same time, Don Kirkwood was approached by the Chairman of ACMP to produce a paper on analytical guidelines.

The sub-group decided to combine the two documents in the light of the responsibility of the NUT to arrange the monitoring of nutrients, i.a., under the North Sea Task Force Monitoring Master Plan.

Following this clarification of the context, the two papers were reviewed in order to include more details on the parameters to be measured, on the sampling depths, on strategy (transects instead of just single stations), on frequency, etc.

The group took advantage of the presence of Monique Baeteman to discuss the combined document. Some discussion took place concerning the parameters to be determined. It was agreed to divide the parameters into two groups only: "nutrients" and "supporting parameters" in order to avoid the usual distinction between "mandatory" and "voluntary" parameters. The text of the Guidelines gives adequate explanations about the meaning of "supporting parameters". To be fully consistent with the list of parameters, the Guidelines have been limited in their purpose, to geographical distribution and to trend studies.

The rest of the document was reviewed and it was decided that it needed some text improvements. These will be made by Don Kirkwood and Stig Carlberg within the next two weeks. The revised text is included in this report as Annex 9. The group agreed to request Don Kirkwood to revise the text of the "Practical notes" with the aim of having it published in the TIMES series.

7.3.2. Intersessional work on nutrient studies

Don Kirkwood presented information on the NORSAP intercomparison exercise on nutrients. This exercise was part of a monitoring programme on the Irish Sea. Most participants were not familiar with the low levels encountered in sea water and took part in a three-step intercalibration programme. Additional laboratories were invited to participate.

This exercise took much benefit from the previous experience of the ICES intercomparison exercise. During the course of the programme, two meetings allowed people to discuss with experts about analytical problems and D. Kirkwood organised a visit to some laboratories in order to help them overcome technical difficulties.

Starting with rather bad results, laboratories have considerably improved their results which for nitrate are now close to those of the core group identified in the ICES NUTS 4th intercomparison exercise. For phosphate, however, the agreement was less satisfactory, but subsequent modifications to techniques produced the necessary level of improvement.

Concerning the ICES NUTS 4th intercomparison exercise, S. Carlberg informed the members that the publication is now going ahead and that every participant will receive a free copy of the report.

Lars Føyn presented the the results of the SKAGEX intercalibration experiment. He pointed out the greater difficulties of working at sea rather than in the laboratory. The sub-group took note that, in the exercise, all the participants analyzed not only intercalibration samples from a single station but rather from a transect in the Skagerrak. In most cases, differences in the results were consistent and due to systematic errors, mainly in calibration. Consequently, correction factors may be calculated for almost each vessel data set. The exercise is an intercalibration in the sense that data can be adjusted to a common reference. However, from this point, progress must be made in order to improve analytical performance. Since the adjustment of data is only based on statistical computation and not on reference material results, the final distribution pattern will be consistent but it will not necessarily represent the true concentrations of nutrients.

The need for reference material appears clearly from the results of such programmes that involve many laboratories/ships/countries. The European Programme on Quality Assurance initiated by BCR and NSTF (QUASIMEME) should give an answer to these problems since the production of a low-cost nutrient reference material is one of its objectives.

Stig Carlberg gave a description of the HELCOM/ICES intercomparison exercise for the determination of dissolved oxygen, involving different laboratories with their own reagents and their own sampling devices.

The sub-group received constructive advice from Shier Berman about the use of statistics to treat analytical data from the oxygen intercomparison.

The statistics will be redone following the advice given by Shier Berman, but at present some conclusions can already be presented:

- Test 1 on the comparison of sampling bottles: no significant difference between the sampling bottles used.

- Test 2 on the comparison of sampling persons: no significant difference between operators on part 2H (high level of oxygen); statistics have to be repeated on part 2L in order to draw conclusions, but the risk is that the test will be inconclusive.
- Test 3 (H/L) on the comparison of reagents and procedures: no significant difference in the results whether people used their own reagents or the convener's reagents.

Most of the laboratories are consistent in producing high or low values, although in most cases the differences were not substantial. However, calibration errors alone seemed to have caused discrepancies of up to 7%.

7.3.3. The effects of sampling and storage on nutrient measurements

Attention was paid to sampling procedure in order to try to formulate plans for the assessment of its effects on nutrient measurements with the aim of intercomparison studies. It was concluded that (1) ships cannot be compared, (2) hydrowires cause no problems for nutrients, and (3) sampling bottles can produce a "tailing effect", depending on the difference in diameter between the opening and the body of the sampling bottle (this effect might generate a distortion of profiles in areas with strong vertical gradients).

It was agreed that usual intercomparison studies, that can be undertaken for the determination of parameters, cannot be applied to sampling and storage. The usual control of the quality based on the use of reference materials does not seem applicable to sampling and storage.The sub-group decided that it was premature to arrange an intercomparison exercise on storage.

The Group was in a position where it can look forward to the results of some on-going or planned intersessional activities on the storage of sea water samples for nutrient measurements:

- on Baltic waters, three methods of storage are to be compared (deep freezing, mercuric chloride and sulphuric acid) on waters of various salinities and at two seasons (productive and non-productive);
- on southern North Sea waters, the effect of different concentrations of mercuric chloride is checked at different times of the year;
- in Norway, studies are being performed on the use of chloroform;
- in Ireland, the effect of filtering is being studied;
- in Aberdeen, comparative experiments are being performed about filtration or not, freezing or not, in deep and surface waters using plastic and glass bottles. Also, the use of chloroform as a preservative for phosphate is being investigated; and
- in addition, the unpublished results of other institutes on freezing could probably be made available.

The outcome of these experiments will provide direction to future work. It was decided to try to assemble as much information as possible for discussion at the MCWG meeting next year.

7.3.4. Schedule for regular intercomparison exercises for nutrients

In view of the timescale of each exercise and of the time required for the organizers to do the work, a frequency of every 4 years appeared reasonable (instead of 2 years, given as an example at the last meeting of MCWG). Taking 1989 as the starting point, the next exercises will thus be performed in 1993 and 1997.

The group recommends that the Institutes involved in the organisation and preparation of the last exercise (1989) should be approached by ICES to organise also the forthcoming two exercises. It is recommended that the next exercise should also be open to manufacturers of relevant equipment.

In addition, it is noted that when several ships are involved in a joint project, they should participate in an intercomparison specially developed for the purpose of the project.

7.3.5. The document on QA protocols and assessments

The sub-group reviewed the paper on QA Protocols and Assessments and noted that for nutrients there are few RMs available today but that the situation will improve.

7.3.6. The enforcement of standard methods

The sub-group perceives a growing problem due to the arbitrary imposition of standard methods in situations such as marine environmental monitoring, where the use of one particular method may prejudice the performance of another being used in close proximity. For example, the proposed standard ISO 6777-1984 uses phosphoric acid in the determination of nitrite and this poses a serious contamination risk to the determination of phosphate at marine concentration. This standard is now likely to be adopted by CEN (Comité Europêen de Normalisation) of the EC as a mandatory method for all water quality studies. It was recommended that ICES, through its General Secretary, should notify the EC of this problem.

7.4. Guidelines for the conduct and evaluation of intercomparison exercises

The MCWG has been given the task to prepare guidelines for the conduct of intercomparison exercises. A special meeting was arranged, with participation of members from all three sub-groups. Dr J. van der Meer, from the Netherlands Institute for Sea Research and a member of the WGSATM, was invited to attend the meeting, and had accepted this invitation. The meeting was chaired by Dr Cofino. An agenda was provided, together with a draft outline for guidelines.

It is recognized, that intercomparison exercises can have different objectives. Among these were the assessment of the "state of the art", intercomparison studies as part of a programme to improve analytical capability, and laboratory proficiency testing. Common to all these objectives is that the exercises should provide feedback to the laboratories about their performance, and to the community of users of data (e.g. the monitoring agencies) about between-laboratory variance. The objective of the guidelines is to ensure that the design, execution and evaluation of the exercise are performed in a valid manner so that proper inferences are made, and that the presentation of information is lucid for both the laboratories and monitoring agencies.A draft of the guidelines was discussed and commented. This document is provided in Annex 3.

The group acknowledged the need for a profound statistical competence in the project team which conducted the exercise. Statistical methodology, however, gave rise to considerable discussion. In past exercises, various approaches have been adopted. The series of exercises conducted by the National Research Council of Canada employed a simple, straightforward approach. The data were subjected to a t-test, to consider if the set forms a normal population. Data are successively rejected until this condition is fulfilled. Then, the consensus value and the relative standard deviation are calculated. This approach assumes a normal distribution of the results, which may not be the case. It is the experience from trace metal investigations, however, that non-normal distributions are predominantly caused by positively biased results, which can be attributed to contamination. A normal distribution is to be expected for a group of well-performing laboratories. The procedure applied by the NRCC effectively rejects biased laboratories until a normal distribution is approximately obtained.

The ICES 4th nutrient intercomparison exercise employed robust (distribution independent) statistics. This type of statistics is being applied increasingly in intercomparison exercises, and also has been proposed in a ISO/IUPAC/AOAC paper on the harmonisation of laboratory proficiency testing. The data of this intercomparison exercise have also been analyzed with more sophisticated statistical techniques, but the presentation of the results was not transparent for non-statisticians.

The statistical evaluation of the CB intercomparison constitutes a third approach. Dr J. van der Meer gave a stimulating presentation. The standard ISO 5725 was introduced. This standard employs an additive model, i.e. $y_{ij} = \mu + \alpha_{ij} + e_{ij}$[1], gives procedures for the identification of outliers, and for the calculation of repeatability and reproducibility. The group noted that the ISO 5725 standard is designed for method evaluations, in which all participants adhere strictly to one protocol, and not for laboratory proficiency tests. The use of the concept of reproducibility is in principle only valid for well-defined individual methods. It was understood, however, how the concept was employed.

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[1] y_{ij} : result of laboratory j for sample i
μ : estimated true concentration for sample
e_{ij} : error of laboratory j for sample i (normal)
α_{ij} : bias of laboratory j for sample i
η_{ij} : error of laboratory j for sample i (log-normal)

Dr van der Meer explained that ISO 5725 also requires a normal distribution of the results, and stated that in practice e often skewed distributions are encountered. It is his experience that a log normal distribution better represents intercomparison results. This complies with the application of a multiplicative model in the statistical analysis, i.e. $y_{ij} = \mu_i * \alpha_{ij} * \eta_{ij}^2$. It is interesting that the multiplicative model renders a lower (= more favourable) value for the reproducibility than an additive model. This may imply that up to now the inference of the results of intercomparisons for the variability in environmental data is somewhat pessimistic (additive model: with a between-laboratory relative standard deviation of 40% one has to anticipate that differences of a factor of 9 may be due to bad interlaboratory comparability, versus a factor of approximately 6 predicted on the basis of a multiplicative model).
Dr van der Meer proceeded with a discussion of multivariate models. He stated, that the CB-data call for such a treatment, and that a univariate approach was not valid because the CB-results are not independent. Dr van der Meer then presented the outcome of statistical techniques (such as principal component analysis). Inconsistencies of laboratories pointing to analytical problems could be identified. The power and potentials of these techniques became very clear, and were valued highly by the Group. However, no agreement was present about the statement that a multivariate approach was a necessary requirement to analyze the data. A comparison was drawn with the evaluation of the intercomparison exercise on trace metals in biological tissue. Here, using one and the same digest, several determinations of trace metals are performed. There is no fundamental difference with the analysis of CBs. The majority of the group felt that the techniques presented represent an important diagnostic tool. In many cases, for instance "routine" laboratory proficiency testing, less sophisticated techniques will be adequate.

The Chairman then stated that a standard approach for the presentation of the results of intercomparison exercises would be of value, as it facilitates the understanding of the results by laboratories and users of data alike. He proposed to try to identify a set of "intercomparison performance characteristics" (e.g. number of participants, number of data submitted, number of data rejected, target or consensus value, relative standard deviation or reproducibility) and a harmonised method to obtain these. The coordinators of intercomparison exercises would then be free to present, in addition to this standard approach, results from more advanced techniques. Some objections were made against this proposal. It was felt that the statistical method should be chosen taking the data into consideration. An assessment of the distribution is an important aspect in this context: bimodal or normal distributions require different approaches. Unfortunately, time ran out during the discussion. Drs Berman and Cofino agreed to try to develop such a standard presentation. The Chairman thanked the participants for the contributions and, in particular, Dr van der Meer for his very stimulating contribution.

A first draft of the guidelines was discussed and approved. This paper is included as Annex 4 in this report.

8. Plenary discussions of the sub-group reports

The Chairman proposed not to discuss the reports of the individual sub-groups in great detail, but to focus on important issues and to consider the action list and the recommendations. In addition, he proposed to allocate time to discuss the mode of operation of the MCWG. This proposal was accepted.

The recommendations drafted by the sub-groups were adopted by the whole working group, apart from some aspects on overviews. Discussions on the topics of overview papers and of the allocation of tasks to working groups by the ACMP resulted in two additional recommendations.

(Potential) authors should have clear guidelines for the preparation of overviews so that they can assess the amount of work expected when they accept to make one, and can prepare these overviews accordingly. The 'official' guidelines for the preparation of overview papers are somewhat outdated. This has been appraised by the MCWG last year. In 1989, the chairman of the Group discussed this matter with the chairman of the ACMP. It was concluded that the preferred model for an overview covers the issues:

> natural occurrence, production and uses, physico-chemical properties, routes into the environment, methods of analysis, levels in the environment, fate in the environment, bioaccumulation, effects on marine biota and man, and conclusions as to present and future environmental significance.

This year, the usefulness of the model itself was questioned. For instance, in the field of organic contaminants, the overviews requested on some topics, octachlorostyrene, represent a manageable amount of work because the field is relatively young. However, for trace metals a considerable amount of information is present in literature, eg., chromium in the marine environment, so that an overview along the lines given above is a considerable task.

It is recommended that the informally established model be accepted by the ACMP. In addition, it is recommended that the ACMP assess the amount of work involved with the preparation of overviews and, where appropriate, confine the scope of overviews so that an acceptable workload is requested from the authors. The requests put forward by ACMP should specifically outline the scope of the paper.

The amount of work which is put into the preparation of overview papers is substantial. The papers, however, are not formally published. This has two problems:

1. It is becoming more difficult to find authors; the tendency is that the MCWG receives papers which are written for other purposes, or have been/will be submitted to journals.

2. The criteria against which to judge the papers are difficult to establish. It is difficult (not to say impossible) to apply the standards employed by scientific journals. In addition, some members consider it difficult to criticise close colleagues and to have them put a lot of additional effort into a paper with a rather vague fate.

The MCWG recommends that it should be an ICES policy that overviews are published in the literature. This implies that the overview should meet standards which are generally accepted in scientific practice. It should be up to the author to decide in which journal the paper will be published. The MCWG recommends, however, that ICES offers the possibility to publish the paper in its own journal. The route can be: acceptance by the MCWG (if relevant, in cooperation with other working groups, e.g., the WGBEC) and recommendation for publication to the ACMP, the approval by the ACMP for publication in the ICES Journal of Marine Science.

The Group noted further that overviews should be distributed for consideration prior to the meeting. The sub-group chairmen are given the task to stimulate people to prepare the overviews in time and to distribute them one month before the meeting commences.

The allocation of tasks by the ACMP to ICES working groups gave rise to discussion. An example is provided by work on nutrients. The MCWG has built up a considerable expertise in the field of chemical oceanography, and has been particularly active in matters related to the quality of data in relation to the information needed (e.g., monitoring). It was brought forward that the ICES Shelf Seas Oceanography Working Group was assessing trends in nutrients, and was involved in the optimization of the NSTF MMP. Such tasks require the contribution of chemical oceanographers, and thus of the MCWG. Papers of the WG on Shelf Seas Oceanography on these subjects should be considered by the MCWG in a comparable manner as the arrangement between the MCWG and WGBEC regarding sections on toxicological aspects in overview papers.

Work on marine environmental topics requires increasingly a multidisciplinary approach. For ICES this implies that particular attention has to be paid to the flow of information between working groups, and to the cooperation between them.

The MCWG recommends that the ACMP set up an operational programme in order to encourage and establish multidisciplinary projects. This programme can entail a close involvement of WG chairmen by the timely distribution of tasks for working groups among them for comments and the identification of areas of mutual concern.

The mode of operation of the MCWG was discussed. It was concluded that the division into three sub-groups was efficient, but that the three sub-groups tend to operate quite independently. In addition, in the past years discussions in the group were dominated by quality assurance items and by the discussion of overviews; "marine science was lacking".

It is appreciated that the advisory role of MCWG is important, and that requests from agencies will form a substantial portion of the MCWG agenda. However, the MCWG has a considerable potential as a platform to set up cooperative research projects, to confront different views on marine research, and to discuss and identify important developments in marine research. This research does not necessarily have to be restricted to marine pollution. More contacts between the three sub-groups for "cross-fertilisation" is necessary.

As a result of the discussions, J. Tronczynski and P. Yeats agreed to try to produce a position paper about the interaction between DOC and contaminants.

An overview of the papers discussed at this meeting is given in Annex 8.

9. Any other business

No matters were raised under this agenda item.

10. Recommendations and action list

The action list and recommendations are given in Annexes 6 and 7, respectively..

11. Date and venue of next meeting

MCWG discussed the venue and time of the next meeting. Dr de Armas offered to host the meeting. MCWG thanked Dr de Armas and recommends that the meeting be held in Tenerife in February, 1992.

12. Closure of the meeting

Prof. Dr R. Wollast, Dr M. Loijens and members of their staff joined the closing session of the Working Group. On behalf of MCWG, the Chairman thanked them for their warm hospitality and all substantial efforts and services they provided.

The Chairman thanked the members for their hard work, and closed the meeting at 16.30 hrs on 22 March 1991.

ANNEX 1

ICES MARINE CHEMISTRY WORKING GROUP
BRUSSELS, 18-22 MARCH 1991

AGENDA

1. Opening

2. Adoption of the agenda

3. Report of the 78th ICES Statutory Meeting

4. Reports on related activities
    - 4.1. Joint Monitoring Group of OSPARCOM
    - 4.2. Intergovernmental Oceanographic Commission (IOC)
    - 4.3. ICES Working Groups
    - 4.4. EC-BCR QA pilot project "QUASIMEME"
    - 4.5. Other activities

5. Reports on projects and activities in member countries

6. Requests from ACMP and regulatory agencies

7. Sub-group activities and discussions
    - 7.1. Trace metal sub-group
        - 7.1.1. Election of chairperson
        - 7.1.2. Finalise the report on the results of the Baseline Study of Trace Metals in Coastal and Shelf Sea Waters
        - 7.1.3. Finalise the overview on Cr
        - 7.1.4. Finalise the QA document on the sampling of seawater for the measurement of trace metals
        - 7.1.5. Review the overview on Ni
        - 7.1.6. ACMP request for protocols
        - 7.1.7. Any other business (AOB)
    - 7.2. Organic sub-group
        - 7.2.1. Finalise report on the second phase of the intercomparison exercise for CBs, and make recommendations for phase 3 of this exercise
        - 7.2.2. Finalise report on the first phase of the intercomparison exercise for PAHs, and make recommendations for the second phase
        - 7.2.3. Prepare a note on the occurrence and concentrations of nonylphenol in the marine environment
        - 7.2.4. Review the overview on octachlorostyrene
        - 7.2.5. Review the overview on chlorinated sewage effluents

        - 7.2.6. Review the overview on linear alkylbenzenesulphonates (LAS) and alkylphenolethoxylates (APE)
        - 7.2.7. Review the overview on atrazine
        - 7.2.8. Review the overview on PBDE and PBBs
        - 7.2.9. ACMP request for protocols
        - 7.2.10. AOB
    - 7.3 Chemical Oceanography Sub-group
        - 7.3.1. Finalise guidelines for the sampling of seawater for the measurement of nutrients
        - 7.3.2. Report on intersessional work on nutrient studies, including the outcome of the Visby intercomparison exercise for dissolved oxygen and nutrients and the level of intercomparability achieved in the SKAGEX studies
        - 7.3.3 Formulate plans for the assessment of the effects of sampling and storage on nutrient measurements (intercomparison study)
        - 7.3.4. Propose a schedule for regular intercomparison exercises for nutrients in seawater
        - 7.3.5. ACMP request for protocols
        - 7.3.6. AOB
    - 7.4. *Ad hoc* group on Intercomparison Exercises
        - 7.4.1. Prepare a paper outlining guidelines for the conduct of intercomparison exercises

8. Plenary discussion of sub-group work
9. AOB
10. Recommendations and action list
11. Date and venue of next meeting
12. Closure of meeting

ANNEX 2

ICES MARINE CHEMISTRY WORKING GROUP
BRUSSELS, 18-22 MARCH 1991

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ANNEX 3

ICES MARINE CHEMISTRY WORKING GROUP
BRUSSELS, 18-22 MARCH 1991

QA PROTOCOLS AND ASSESSMENTS

The importance of quality assurance (QA) in marine monitoring is clearly illustrated in reports of assessments conducted in the past (e.g. the ICES/HELCOM/OSPARCOM Evaluation of the Baseline Study of Contaminants in Fish and Shellfish, 1985). Measures are required on the level of the monitoring agencies (e.g. NSTF, JMG), and of the laboratories submitting data.

In the past decade, the MCWG paid considerable attention to analytical problems and expanded the concepts of quality assurance to encompass the design, execution and evaluation of monitoring programmes. Approaches developed by the MCWG have been proposed to, and to a significant extent adopted in, the NSTF monitoring programmes, and form in addition the basis of the proposed EC Quasimeme project (Report of the joint NSTF/JMG Workshop on Marine Monitoring Programmes in the North Sea and North East Atlantic, London, 1989). Monitoring laboratories are increasingly applying the principles of good laboratory practice. Guidelines for the development and implementation of quality systems in laboratories are now readily available (TIMES6, ISO25, EN45001).

The MCWG sees no need to devise any new protocols. Considering technical aspects, sufficient information is available in the literature and in ICES publications, notably in reports of intercomparison exercises. The report of the NSTF/JMG Workshop on Marine Monitoring Programmes presents an adequate approach to manage quality in marine monitoring. Attention should be devoted to the implementation of these concepts.

QA data required for a proper assessment are mentioned in the NSTF/JMG document. They involve:

- data to assess accuracy (CRMs);
- data on statistical control (control charts, etc.);
- data from intercomparison exercises, conducted for quality control by the monitoring agency.

It has also to be noted that specific designs of sampling programmes may render information which forms a basis to assess the quality of data.

It is obvious that the data reporting formats to ICES need to require additional information related to the QA programme of each laboratory. It is recommended that the following information be submitted:

a. Control chart information for all reported materials and analytes;
b. Reference material used in each as control samples;
c. The mean and standard deviation derived from each control chart for each sample material for each analyte; also the number of replicates used to calculate the respective means and standard deviations;
d. Any comment the laboratory may wish to make regarding particular material and/or analyte problems; and
e. Sampling QA protocols.

If information has been given and it is apparent that the laboratory has the analytical process under control, the results should be assumed to be reliable.

If only some of the QA information was submitted, the reliability of the results must be questioned. The assessors must then rely on other information, such as was necessary to do in the tedious assessments of the 1985 baseline study of contaminants in fish and shellfish (ICES Cooperative Research Report No. 151) and the Baseline Study of the Trace Metals in Seawater (in preparation). These should include for example:

a. Area input and characteristics;
b. Pertinent literature data for the area;
c. Participation in an intercomparison exercise (some of these are now quite dated); and

d. Environmental processes (e.g., salinity *vs* TM concentration for sea water).

All data must be available to the assessors long before they meet jointly to write their report; the final session ought to entail a collation of work done in advance.

In summary, data produced by a laboratory with acceptable QA procedures are assumed to be reliable unless there are extraneous circumstances which may lead to their ultimate rejection. On the other hand, good excuse must be found in order to accept data which do not have adequate QA support. Also, it is recognized that the present QA protocols apply mainly to the analytical measurement procedures. The assessors must consider problems which could arise from inadequate control of sampling methodologies and additional variability arising from sampling and storage procedures.

ANNEX 4

ICES MARINE CHEMISTRY WORKING GROUP
BRUSSELS, 18-22 MARCH 1991

AN ANNOTATED OUTLINE OF GUIDELINES FOR THE CONDUCT OF INTERCOMPARISON EXERCISES

1. Introduction

Intercomparison exercises are coordinated by different laboratories for any of a range of parameters, compartments and objectives. An intercomparison exercise may be organized between a small group of laboratories in order to study particular methodological problems (a research-type objective), but may also be held as a means to qualify laboratories (e.g. acceptance of data in monitoring programmes).

These guidelines do not describe a rigid structure for the conduct of intercomparison exercises. They are primarily aimed at proficiency testing, for instance schemes which are employed to qualify laboratories with respect to the acceptance of data. The objectives of these guidelines is to ensure that the design, execution and evaluation of the exercise is performed in a valid manner so that proper inferences are made, and that the presentation of information is lucid for both the laboratories and the community of users of laboratory data (e.g., monitoring agencies). The contents are, however, in principle generally valid.

2. Assessment and description of objectives

It is necessary that a clear understanding regarding the objectives of the intercomparison exercise exists between the parent organisation, the coordinators and the participants. The coordinators have to (1) assess the stated and implied needs to conduct the exercise, (2) describe the objectives fully, and (3)ascertain that the objectives have the approval of the parent organisation.

3. Communication with the participants

A proper scheme for communication with the participants should be established. When laboratories are invited to participate in an exercise, information has to be provided on the following subjects:

- the objectives of the exercise;
- the way the results of the exercise will be used;
- the identification of the laboratories (are laboratories coded or can the results be traced back to the individual laboratories);
- the availability of the report for non-participants;
- the time schedule for the whole process;
- the input which is expected of the laboratory; and
- measures which will be taken if a laboratory subscribes but does not send in data.

Proper information regarding the nature of the samples should be provided, e.g. the origin, the way of processing the material, a crude estimate of the concentration range and so on. The ISO standard specifying information which is to be included for certified reference materials can be taken as a guideline (ISO Guide 31: Contents of certificates of reference materials). Protocols describing what has to be done with the samples are to be provided, as well as clear forms for reporting the data.

The participants ought to be notified of any delay in the programme, and should receive a report describing the results of the exercise.

4. Design of the exercise

4.1. Project team

A project team has to be established. A profound statistical competence is necessary. This input can be provided by a chemist with long experience in this field, or by a statistician who is a coworker in the coordinating laboratory. Alternatively, a member of the ICES WGSATM can be identified.

4.2. Selection of samples

In principle, the concentration levels of the parameters of interest and the characteristics of the samples should be as representative as possible of "daily practice". It is recommended to include different samples with different concentration levels or sample characteristics in the exercise.

4.3. The preparation and distribution of samples

The preparation and distribution of the samples should be performed in such a manner that the integrity is maintained. It should be assured that the samples are sufficiently homogeneous and stable. Assessment of stability should also take the conditions during transport into account. In international exercises, samples may be inspected by custom officers, resulting in a loss of integrity. Therefore, sealing of the samples is required, so that any manipulations with samples by custom officers will be noted.

4.4. Statistical considerations

The statistical model to evaluate the data should be chosen in advance. The model may be employed to determine the number and different types of samples, and the number of replicates which are to be determined.

No statistical model is prescribed. However, it is recommended to apply internationally accepted models (e.g. for method evaluation ISO 5725; for laboratory proficiency tests international standards are presently being discussed).

4.5. Selection of participants

Criteria for the acceptance of participants should be formulated.

4.6. Target for accuracy

Where appropriate, an estimate of the true concentration ("the target concentration") for accuracy assessment should be established. For some contaminants/matrices this can be done by selecting a number of expert laboratories. These laboratories should provide evidence with respect to accuracy (e.g. CRM data) and statistical control (control charts). Target concentrations can be established when the data of the expert laboratories come close to each other within the body of the data.

5. Statistical evaluation

A print-out of the data submitted should be sent to the participants for control of correct input before the statistical analysis is conducted. The statistical evaluation should include at least:

- the consensus concentration; and
- a parameter describing the range of the data (relative standard deviation, reproducibility).

6. Presentation of the information

The outcome of the exercise should be presented in a transparent manner. Where possible, graphical illustrations are to be used (e.g. plots of bias *versus* repeatability , Youden plots). Criteria for the rejection of data and for the qualification of laboratories (if relevant) have to be stated clearly. Rejected data should be marked. In an annex, all data reported by the laboratories should be included.

ANNEX 5

ICES MARINE CHEMISTRY WORKING GROUP
BRUSSELS, 18-22 MARCH 1991

A SHORT NOTE ON THE OCCURRENCE OF NONYLPHENOLS IN THE MARINE ENVIRONMENT

MCWG 1991/7.2.3/6

This note has been prepared in response to a request from the North Sea Task Force concerning the finding of nonylphenols in the feathers of 18 dead seabirds in the FRG.

Although vast amounts of anionic, cationic and non-ionic surfactants are released into estuarine and marine systems as a result of domestic and industrial use, there is little information available concerning concentrations in near shore waters. One clearly defined route for surfactant entry to the marine environment is via sewage. Giger and coworkers have shown that nonylphenols (NPs) arise from the breakdown of nonylphenol polyethoxylates (NPEs) in anaerobically digested sewage sludges. Another possible source is from operational discharges from chemical product tankers, although currently we have no information on patterns of transport for NP or NPE. Such discharges are controlled under the provisions of MARPOL 73/78.

The chemical composition of NPE, with one lipophilic and one hydrophilic part, implies that NPE have surface tension properties and may accumulate at interfaces (e.g., air/water and water/biological membranes) and could interact with other compounds and influence their toxicity, or result in physical effects such as a reduction in the water resistance of the feathers of seabirds. NPs are both more persistent and more toxic than NPEs. The concentrations of NPEs in the natural environment has been little studied until now, and most measurements have been made in fresh water.

In the marine environment concentrations of NPE_n ($0 < n < 13$) varying between 0.5 and 4.5 $\mu g/l$ were determined in the waters of the Venice lagoon. This is subjected to inputs of domestic and industrial origin. The heaviest concentrations were recorded near the Porto Marghera industrial zone; this confirms the principally industrial use of NPE. In the same zone, collective concentrations of NPE_1 and NPE_2 in sediment (0 to 5 cm) varied between 18 and 129 ng/g (dry weight), with an average value of 49 ng/g; concentrations in superficial sediment (0.01 to 0.05 mm) are higher, as they vary from 0.2 to 13.7 $\mu g/g$ dry weight, average value 2.2 $\mu g/g$ (35). Finally, levels of 0.25 ± 0.15 $\mu g/g$ dry weight were determined in macrophytic algae, principally *Ulva rigida*; these values suggest that, in eutrophic marine waters of shallow depth, macrophytic algae play an important role in the dynamic behaviour of NPE in sediment. Also in the marine environment, there is evidence of very rapid dilution of NP after discharge of anaerobically stabilised sludge in the external part of the Thames estuary. Immediately after discharge, the NP level at one metre depth was 9.5 $\mu g/l_{-1}$; after 30 minutes it was no longer detectable (0.5 $\mu g/l^{-1}$). This can be explained by the fact that important renewal of waters at the chosen site causes rapid and substantial dilution of sludge.

Concentration of NPE in coastal waters off Barcelona, Spain were measured, 0.85 $\mu g/l^{-1}$ were found in the dissolved phase and NPEs were not detected in the particulate phase. The concentration of NPE in sediment was found to be 6.6 $\mu g/g^{-1}$.

Bioconcentration factors for NP in mussels up to 3400 have been reported. The lethal toxicity of NP to mussels occurs at concentrations around 100 times higher than those seen in coastal waters, with a "no effect" concentration of 110 $\mu g/l^{-1}$. Sublethal effects appear at concentrations above 60 $\mu g/l^{-1}$.

Concentrations of nonylphenols have been measured on two occasions in the estuary of the River Mersey and Liverpool Bay. The Mersey has been regarded historically as an impacted riverine system and receives inputs from a variety of industrial processes and raw and primary-treated sewages. Samples of water were collected during two cruises in 1989 and 1990 and concentrations of nonylphenols, coprostanol and a variety of other potential organic contaminants were measured.

It was clear from the few data obtained that the levels of nonylphenols in the water samples were closely related to the concentration of coprostanol, confirming that the source of input was sewage discharge. Further from sources of sewage input, the concentrations attenuated to values below the detection limit (≤ 0.05 $\mu g/l^{-1}$). Despite semi-continuous inputs of sewage sludge to the Liverpool Bay disposal ground, no increase in either coprostanol or nonylphenol concentrations was measured close to the point of dumping activity.

Since the study area described was felt to represent a worst case scenario it appears likely that measurable concentrations of nonylphenols would be encountered only in coastal areas.

ANNEX 6

ICES MARINE CHEMISTRY WORKING GROUP
BRUSSELS, 18-22 MARCH 1991

ACTION LIST

All members:

To submit before the 1992 MCWG meeting results of intersessional (or past) experiments and studies related to sampling and storage of seawater samples for the determination of nutrients to D. Kirkwood (coordinator).

To distribute overviews timely (i.e. 2 months) before MCWG meetings so that people can prepare themselves.

Sub-group chairmen:

To stimulate sub-group members which have agreed to prepare overviews to distribute these in a timely manner.

Trace Metal Sub-group:

P. Balls: Incorporate final revisions to baseline report and submit to ACMP.

P. Balls, L. Brügmann, B. Pedersen, S. Westerlund, P. Yeats: Begin interpretation of estuarine data in the ICES data bank.

S. Berman: Begin work on development of reference sampling method.

S. Berman, W. Cofino: Try to develop standard method for the evaluation and/or presentation of intercalibration results.

W. Cofino, P. Yeats: Make final revision to QA document in sampling and submit to ACMP.

P. Yeats: Provide editorial comments on Cr overview to Schmidt and coordinate provision of input on biota and toxicology to Cr overview with R. Addison (chairman of WGBEC).

P. Yeats, P. Balls, S. Westerlund, L. Brügmann: Provide references on Ni to B. Jones.

J. Tronczynski, P. Yeats, P. Balls: Prepare a position paper on the interaction between DOC and contaminants.

Organic Sub-group:

J. de Boer: Prepare a note about stage 3a of the CB intercomparison exercise.

R. Law: Prepare a preliminary report on the 2nd stage of the PAH intercomparison exercise.

J. Tronczynski: Finalise the overview on atrazine.

J. Boon/J. de Boer: Finalise the overview on PBBs and PBDEs.

J. Troncsynski/F. Smedes: Prepare a short paper about the role of dossolved organic matter on the transport of contaminants.

L. Reutergårdh: Prepare a note on the results of the Swedish intercomparison exercise on planar CBs.

J. Tronczynski, P. Yeats, P. Balls: Prepare a position paper on the interaction between DOC and contaminants.

Chemical Oceanography Sub-group:

S. Carlberg:	Contact the General Secretary of ICES to arrange that ICES expresses its concern to the secretariat of CEN TC 230 and to CEC DG 11 over the fact that methods are being adopted as mandatory European standards, despite the fact that these methods in several cases are unsuited for marine chemistry and marine environmental monitoring.

ANNEX 7

ICES MARINE CHEMISTRY WORKING GROUP
BRUSSELS, 18-22 MARCH 1991

LIST OF RECOMMENDATIONS

Recommendation 1

The MCWG recommends that the final reports on the following be published in the ICES Cooperative Research Report Series:

- The Report on the Baseline Study of Trace Metals in Sea Water;
- The Report on the second step of the CB intercomparison exercise.

Recommendation 2

The Marine Chemistry Working Group recommends that during 1991 the action dealing with quality control of CBs will be carried out as stage 3a of the CB intercomparison exercise, coordinated by J. de Boer with statistical advice of J. van der Meer of the ICES WG on Statistical Aspects of Trend Monitoring.

The MCWG acknowledges that the organisation of these exercises requires so many resources and manpower that it cannot be continued on a voluntary basis. The MCWG recommends that ICES finances step 3a for 40,000 DKK, and that ICES allocates 250,000 DKr to fund step 3b of the exercise, which is planned for 1992.

In addition, the MCWG recommends that the CB intercomparison exercise will be further conducted through the Quasimeme pilot project in Quality Assurance should this project take place.

Recommendation 3

The Marine Chemistry Working Group recommends that laboratories who accepted to take part in the second step of the CB intercomparison exercise, but did not submit any results afterwards, are not invited for any further steps of this exercise. The Marine Chemistry Working Group recommends that these laboratories be informed about this, through a letter from the chairman of ACMP.

Recommendation 4

The MCWG recommends that the second phase of the PAH intercomparison exercise be organised in 1991 and be coordinated by R. Law. It is also recommended that the meeting of participants in the PAH intercomparison exercise scheduled for 1991 should now take place prior to the 1992 meeting of MCWG.

Recommendation 5

The MCWG recommends that the ICES fifth and sixth nutrient intercomparison exercises (NUTS5/NUTS6) are conducted in 1993 and 1997, respectively. It is recommended that D. Kirkwood (MAFF Fisheries Laboratory, Lowestoft) and A. Aminot (IFREMER, France) are requested to organise the NUTS5 exercise in 1993. This exercise ought to be open for participation by manufacturers of equipment for (automatic) nutrient determinations.

Recommendation 6

The MCWG considered a number of overview papers. It recommends:

- that the overview paper on Chromium in the Marine Environment be published by ICES as an overview on Chromium in Seawater, as an annex to the ACMP report;
- that the overview paper on Octachlorostyrene be published by ICES as an annex to the ACMP report;
- that the revised QA document on sampling be published by ICES as an annex to the ACMP report.

The overview on chlorinated discharges into the marine environment is being forwarded to ACMP for information, as it will be published in the open literature.

The MCWG recommends that the ACMP adopts the revised model for the preparation of overviews established informally in 1990 and, in addition, that the ACMP specifies in the future the scope of overviews in such a manner that a reasonable workload is requested.

The MCWG expresses its concern about the difficulties in finding authors for papers and in assessing them. These problems are caused to a large extent by the rather vague fate of the paper. In addition, authors are reluctant to spend considerable time preparing papers for ACMP when there is little or no recognition, and the names are removed from the paper. The MCWG recommends that ACMP establishes a policy that overviews are published in the open literature, implying that they should meet standards which are generally accepted in scientific practice. The MCWG recommends that ICES offers the possibility to publish the paper rapidly after approval by ACMP in its own journal.

Recommendation 7

The Marine Chemistry Working Group recommends that the manuscript "Practical notes on the determination of nutrients in seawater" by D. Kirkwood be published in the TIMES series after revisions.

Recommendation 8

The Marine Chemistry Working Group recommends that ICES expresses its concern to the secretariat of CEN TC 230 (water quality) and to CEC DG 11 over the fact that methods are being adopted as mandatory European standards for all water quality studies, despite the fact that these methods in several cases are unsuited for marine chemistry and marine environmental monitoring.

Recommendation 9

The Marine Chemistry Working Group recommends that the ACMP sets up an operational programme in order to encourage and establish multidisciplinary projects between Working Groups. This programme can entail a close involvement of WG chairmen by the timely distribution of tasks for working groups among them for comments and for the identification of areas of mutual (inter-group) concern.

Recommendation 10

The MCWG recommends that the Working Group should accept the offer made by Prof. D. de Armas to host the next meeting of MCWG in Tenerife. This meeting should be held for five days (or six if additional tasks are allocated to MCWG) in February 1992 to carry out the following tasks:

- to review the progress in the evaluation of estuarine data held in the ICES data bank;
- to review the progress on the reference sampling method for trace metals in seawater;
- to review the progress on the development of standard methods for the evaluation of intercomparison exercises and for the presentation of results thereof;
- to review the results of stage 3a of the CB intercomparison exercise;
- to review the results of the second stage of the PAH intercomparison exercise;
- to review the overviews on atrazine and on PBBs and PBDEs;
- to review the results of the Swedish intercomparison exercise on planar CBs;
- to review the information on experiments and studies related to sampling and storage of seawater samples for the determination of nutrients;
- to make plans for step 3b of the CB intercomparison exercise;
- to consider any other matters raised by ACMP.

ANNEX 8

ICES MARINE CHEMISTRY WORKING GROUP
BRUSSELS, MARCH 18-23, 1991

OVERVIEW OF PAPERS

Agenda item	Code	Subject
3.	MCWG 1991/3/1	1990 Council resolutions related to environmental issues.
4.3	MCWG 1991/4.3/1	'How to use bladder wrack (Fucus vesiculosus) as a bio-indicator for metal pollution'. S. Söderlund, M. Pedersén (WGEAMS 1990/10/1)
	MCWG 1991/4.3/2	'Methods for collecting benthic algae for contaminant monitoring', N. Green, M. Munk Hansen, CM 1989/E:13 (WGSATM).
4.4	MCWG 1991/4.4/1	Information note on the EC-BCR QA pilot project "Quasimeme".
7.1	MCWG 1991/7.1.2./1	'A review of measurements of trace metals in coastal and shelf sea waters; collected by ICES and JMG laboratories during 1985-1987, by Ad Hoc group of ICES Marine Chemistry Working Group.
	MCWG 1991/7.1.3./1	An overview of chromium in the marine environment (Dr D. Schmidt).
	MCWG 1991/7.1.4./1	Quality assurance of sampling and analysis of trace metals in seawater.
	MCWG 1991/7.1.5./1	Nickel in the marine environment: an overview.
	MCWG 1991/7.1.6./1	QA protocols and assessment
	MCWG 1991/7.1.7./1	Advice for the use of benthic algae for contaminant monitoring
7.2	MCWG 1991/7.2.1./1	Report of ICES/IOC/OSPARCOM intercomparison exercise on the analysis of chlorobiphenyl congeners in marine media - second step.
	MCWG 1991/7.2.2./1	Report of ICES Fourth Round Hydrocarbon Intercomparison Programme: Assessment of Stage 1.
	MCWG 1991/7.2.3./1	"Bioaccumulation of 4-Nonylphenol in Marine Animals- A Re-evaluation", R. Ekelund, Å. Bergman, Å. Granmo, M. Breggren, Environmental Pollution 64 (1990) 107-120

	MCWG 1991/7.2.3./2	"Lethal and Sublethal Toxicity of 4-Nonylphenol to the Common Mussel (*Mytilus Edilus* L.)", Å. Granmo, R. Ekelund, K. Magnusson, M. Breggren, Environmental Pollution 59 (1989) 115-127
	MCWG 1991/7.2.3./3	Information paper on seminar on nonylphenols in Sweden.
	MCWG 1991/7.2.3./6	A short note on the occurence of nonylphenols in the marine environment (annex 5 of this report).
	MCWG 1991/7.2.4./1	Overview on octachlorostyrene, Dr R. Law, Dr J. Klungsøyr
	MCWG 1991/7.2.5./1	Paper: Chlorinated discharges into the marine environment: chemistry and environmental impact- an overview, Dr A. Abarnou and Dr L. Miossec.
	MCWG 1991/7.2.6./1	Paper: Presence and behaviour in the aquatic environment of linear alkylbenzenesulfonates (LAS) and alkylphenolethoxylates (APE)., Dr G. Thoumelin.
	MCWG 1991/7.2.7./1	Overview on atrazine, Dr J. Tronczynski
	MCWG 1991/7.2.8./1	Overview on PBDE and PBB's, in preparation by J. de Boer and J.Boon
7.3	MCWG 1991/7.3.1./1	ANNEX 4 (1990 ACMP Report): Basic Guidance for the sampling and analysis of nutrients in seawater (G. Topping).
	MCWG 1991/7.3.1./2	Practical notes on the determination of nutrients in seawater, D.S. Kirkwood.
	MCWG 1991/7.3.2./1	SKAGEX 1990: Preliminary results from the nutrient intercalibration, by L. Føyn (ICES C.M. 1990/C:44).
	MCWG 1991/7.3.2./2	Northern Seas Action Programme (NORSAP) nutrients intercalibration exercise (1990), by D. Kirkwood and A. Aminot.
	MCWG 1991/7.3.2/3	Preliminary draft of the ICES (first) intercomparison exercise for the determination of dissolved oxygen and hydrogen sulphide in Baltic Sea water, by S. Carlberg, K. Fyrberg, J. Valderrama and B. Yhlen.
	MCWG 1991/7.3.3./1	On the stability of nutrient salts in solution, by D. Kirkwood.
7.4		An annotated outline of guidelines for the conduct of intercomparison exercises (annex 4 of this report).

ANNEX 9

BASIC GUIDANCE FOR SAMPLING AND THE DETERMINATION OF NUTRIENTS IN SEA WATER

1. Sampling Strategy

The measurement of nutrients in sea water is carried out for, inter alia, the following reasons:

1) to study the geographical distribution of nutrient concentrations in specific estuarine and coastal waters which are directly influenced by anthropogenic inputs, i.e., via rivers, pipeline discharges, sea dumping and atmospheric inputs (this is equivalent to purpose c) of the JMP);
2) to monitor the changes in the above concentrations with time in order to assess whether there is an increasing or decreasing trend as a result of changes in inputs (this is equivalent to purpose d) of the JMP);
3) to study the relationship between nutrient concentrations and the production and species composition of phytoplankton:
4) for the classification of water masses in oceanographic studies.

(For the Paris Commission's interests, these guidelines will be confined to 1) and 2) above).

2. Station network

The selection of sampling points must be based on sufficient knowledge of the hydrographic characteristics of the sea area and the location and magnitude of the various inputs containing nutrients. Since winter levels of inorganic nutrients in sea water can vary from year to year, it is important to ensure that national reference stations are selected which are not directly affected by anthropogenic nutrient sources. Further reference stations can in many cases be selected in the vicinity of institutes. This procedure should also ensure a high sampling frequency.

Taking into account the oceanographic characteristics of the North Sea as well as the conditions in the Skagerrak and Kattegat areas it is important to note that in most cases the coastal regions have to be studied by means of transects (perpendicular to) the coastline. If this advice is not adhered to it will be very difficult to describe the oceanographic conditions and the nutrient situation in the coastal areas.

Generally, in coastal areas transects are already well established for oceanographic purposes and these should be used and, if necessary, complemented with further stations to reach off-shore areas. In the off-shore areas well established oceanographic standard stations should be utilised since they will also offer results from previous studies as background information.

On each sampling occasion, a sufficient number of water samples has to be collected along the salinity gradient (transect), created by the mixing of river water with the offshore water, thus allowing the construction of a graph of salinity versus nutrient concentrations.

As described below, a continuous profiler for the measurement of temperature and salinity is most useful to allow the investigator to identify this salinity gradient. In the absence of either a salinity probe or on-board measurement of salinity, it will be necessary to design a grid of stations to cover the area where the gradient is likely to be located.

3. Parameters

3.1 Nutrients: Ammonium (NH_4), nitrite (NO_2), nitrate (NO_3), silicate (SiO_4), orthophosphate (PO_4), total phosphorus and total nitrogen (for discussion and definition of terms, see Grasshoff et al, Chapter 9 (ref 1)).

3.2 Supporting parameters: temperature, salinity, dissolved oxygen, suspended solids/Secchi-depth/turbidity, chlorophyll-a and algal cell number. Algal composition (species, their abundance and distribution), primary production.

Institutes will have different capabilities and capacity to carry out this list of parameters and probably very few institutes will be able to carry out all. Rather than dividing the parameters into mandatory and voluntary groups it is here stressed that rather than doing many determinations of the nutrients only it is extremely important to include supporting parameters (particularly temperature and salinity) in order to describe the oceanographic situation. It is also essential to include supporting biological parameters so it can be decided whether data are suitable for time trend monitoring, i.e. that the sampling actually has been carried out when biological production has been at a minimum level.

4. Sampling depths

ICES standard sampling depths for the North Sea and the Skagerrak and Kattegat areas should be used as below. Additional depths (indicated in brackets) may prove useful, particularly for sampling during periods of high productivity.

(all depths are in metres)

North Sea and Skagerrak	Kattegat
0	0
(5)	(5)
10	10
(15)	(15)
20	20
30	30
(40)	(40)
50	50
75	60
100	70
125	80
150	90
200	100
250	125
300	150
400	
500	
600	
700	

5. Sampling frequency

In the case of 1) above the sampling frequency will depend on the number of situations with different regional distribution that is to be studied and described. The number of samplings per situation will depend on the actual dynamics concerning water exchange, biological activity etc.

In the case of 2), sampling should be carried out during the "winter" period. This requirement is based on the fact that during spring, summer and autumn the surface waters (0-50 m) will become progressively depleted of inorganic nitrogen (NO_3, NO_2 and NH_4) following removal by phytoplankton. As a consequence, it is difficult to assess the impact of anthropogenic inputs on coastal and estuarine waters. Therefore, the sampling period cannot be specified in terms of months or dates for the whole convention area; the period is dependent on regional and interannual differences. It is of great importance to understand that the sampling period preferred for time trend monitoring of surface and shallow waters should be characterised by a minimum in primary production and a corresponding high level of remineralised nutrients. Consequently, sampling for time trend monitoring should be carried out as frequently as resources allow during the rather short winter period. In most cases it will be possible to decide only after the sampling, with the assistance of the supporting parameters, whether the data are free from the influence of biological activity and therefore suitable for time trend studies.

6. Sampling Equipment

There is a variety of sampling bottles which can be used for the collection of nutrient samples. All of these samplers are either deployed on a rosette or clamped to a hydrowire, lowered to the prescribed depth and then 'triggered' electrically or by means of a weight which slides on the hydrowire. However, the use of a rosette sampler combined with a profiling probe for measurement of temperature and salinity (CTD profiler) is preferred since it offers a better and more precise control by ensuring that sampling is done at the correct depths. Some investigators, working in estuaries and coastal areas, have collected sea water samples by pumping water through a flexible plastic hose which is deployed over the side of the ship. This system facilitates very fine structured sampling along a profile.

The sampling equipment, the ship and on-board activities can be a source of contamination during the collection of samples. Cooling water and waste water from toilets are significant sources of organic nitrogen, ammonia and phosphate. Sampling should be done in such a way that discharges from these ship's sources are avoided. When samplers are not in use, they should be kept closed, and when handling them one should avoid touching the inside of the sampler since contact with the hands may lead to contamination. (See also section 10.5).

7. Pre-treatment of Samples

It is self-evident that visible flora and fauna, and other suspended material, should be removed from the sample or at least be prevented from taking part in the analytical chemistry.

7.1 Filtration

The filtration process is a potential source of serious contamination. Where sample size permits, a 1-litre Buchner or similar apparatus, preferably plastic, is recommended, and ample rinsing of the filter with the sample, and of the receiving flask with the filtrate.

Glass fibre (GF/C) discs of around 50 mm diameter having an effective pore size of around 1 µm are widely used, but these may contribute measurable silicate contamination at excessively slow filtration rates (< 100 ml/min).

A more thorough filtration can be achieved using polycarbonate membranes if preferred.

7.2 Centrifugation

To avoid the potential contaminating influence of filtration, Kerouel and Aminot (ref. 2) have described a system whereby the sample is centrifuged, then, without transferring supernatant to a second container, the original bottle is presented directly to continuous-flow analysis (CFA) using a modified commercial sampler. Where facilities are available for centrifugation immediately after sampling, this approach clearly has some advantages.

8. Sub-sampling

Glass sample bottles should be used for the storage of sea water intended for the determination of salinity, nitrate and phosphate; plastic bottles should be used for silicate samples. It should be noted, however, that nutrients may be lost due to absorption to the walls of plastic bottles.

9. Storage of samples

Because, in general, seawater samples remain biologically active after sampling, the subsequent analysis should preferably be carried out on board the research vessel as soon as possible after the collection of the samples. Modern automated methods allow the nutrient analysis to proceed on board even in relatively bad weather conditions, so that storage over periods of time longer than a few hours is seldom necessary. Nutrient samples can usually be relatively safely stored for several hours in a cool and dark place (i.e. refrigerator).

Although several institutes have established procedures under which they can preserve and store samples for selected nutrients for a limited time, there is at present no procedure which can be recommended for general use, i.e. for all nutrients in all sea areas at all times of the year. Therefore, analysis at sea is to be preferred and is strongly recommended for nutrients. If this is not feasible for logistic reasons, each institute must verify storage procedures before they are used routinely.

Sub-samples for total nutrients (total phosphorus and total nitrogen) should be transferred directly to autoclavable vials (glass or polyethylene). Since the whole vial undergoes the complete digestion procedure, no preservatives are needed. However, as the atmosphere is a source of contamination for nitrogen compounds, it is recommended that autoclaving (digestion) should take place immediately after sampling, as the stability of the samples is increased after the oxidation step. (Valderrama, ref 3).

10. Analysis

To recommend that there should be a Standard Method for each determinand in a nutrients context, is unrealistic, impractical and unnecessary. Technical and instrumental constraints can make it impossible to produce a faithful copy of a method using equipment B if the method was originally designed around the characteristics of equipment A. However, what can be and should be standardised is the underlying chemistry on which the methods are based.

Because the requirements of individual workers are so varied, it is difficult to formulate consistently positive advice that will apply in all situations, nevertheless, a comprehensive list of 'don'ts' should prove useful particularly if accompanied by explanations why not.

10.1 Analytical Techniques - General

Some nutrients have been measured for several decades by manual colorimetric techniques but the introduction of segmented continuous-flow analysis (CFA) brought about an upsurge of activity in marine chemistry in the 1960s as a result of the increase in sample handling capacity.

The main advantage of automated techniques over manual techniques is not so much their speed of operation but their ability to handle large numbers of samples, treating each in an exactly similar manner within strictly prescribed and maintained operating conditions.

Despite such advantages, a substantial minority of marine laboratories continue to use manual techniques (e.g. in a recent Nutrients Intercomparison Exercise (ref 4), organised by the International Council for the Exploration of the Sea, 28 out of 68 laboratories indicated that they used manual techniques for phosphate) although economic constraints probably play a considerable part in this choice, as good quality CFA instrumentation is expensive.

However, it is also evident from the ICES exercise that possession of CFA does not necessarily guarantee good quality results; it is quite clear that in inexperienced hands, CFA can do much more damage than the equivalent manual techniques. This is particularly likely in cases where a customer has been supplied with a complete package including a computerised data-system which is capable of producing very precise-looking numbers, irrespective of the quality of the analytical chemistry. Apparent precision is often mistaken for high accuracy.

Flow-injection (unsegmented) techniques are superseding segmented CFA techniques for some determinations, but as these generally have to trade off sensitivity in order to increase the speed of analysis, flow-injection analysis (FIA) is not readily applicable to methods where lack of colorimetric sensitivity is the major problem.

These notes dwell on the problems encountered when using segmented CFA as it is anticipated that this technique will continue to be widely used for several more years, and particularly in its latest form, micro continuous-flow analysis.

Equipment suppliers generally understate the difficulties of seawater analysis to prospective customers, quite probably unknowingly, because they usually lack personal hands-on experience of, for example, the determination of phosphate in seawater at sub-micromole per litre concentrations, but, by far the major problem is that many users are insufficiently critical of their results and particularly of the manner by which they are obtained.

Much of the current effort devoted to measuring nutrients in seawater is in a trend monitoring context where high accuracy and precision are vital to the detection of trends, given that year-to-year changes of less than 5% may well be real and meaningful.

Accurate and precise measurement of seawater concentrations necessarily means operating CFA instrumentation sometimes uncomfortably near to the limits of its performance capabilities, where unforeseen problems have to be expected, but it is nevertheless possible if all of the known variables are controlled and optimised. As an example consider the determination of phosphate.

10.2.1 Example - PHOSPHATE

Phosphate at natural levels in seawater, is not the most difficult nutrient determination by CFA, nor is it the easiest, but it is a good example which can be used to demonstrate the various problems that can be encountered.

Given that the molar Absorptivity of the phosphoantimonylmolybdate complex at 880 nm is 22,700 $l\ mol^{-1}cm^{-1}$, a 50 mm path-length cell containing sample with added reagents should produce an Absorbance of 0.113. (This value is not attained in practice in CFA, because the light-beam's field of view does not consist solely of the internal diameter of the flow-cell).

Spectrophotometric detectability being typically 0.001 A, the measurement of sub-micromolar phosphate concentrations with a precision of ± 0.01 µmol/l is about the best that can be expected, but it becomes quite impossible if the system in question involves any appreciable dilution of the sample (by reagents or anything else).

Measurement in the 0-1.0 µmol/l concentration range generally requires substantial amplification of the basic electrical signal, and this reveals an important optical effect which can contribute substantial bias if not taken into account.

This problem, first described by Atlas *et al.* (ref 5), pertains only to CFA (not to manual techniques using conventional cuvettes) and is related to the geometry of individual flow-cells, and consequent refraction of the light-beam, (see below).

10.2.2 Flow cells and the Inter-Sample Wash

In the interests of good hydraulic characteristics, CFA flow-cells require to have rounded ends and low dead-volume, but this produces refractive effects that masquerade as Absorbance signals. (These effects do not occur in the corresponding manual techniques where the optical surfaces of the cuvettes are aligned at precisely 90 ° to the incident light-beam.)

These signals are unrelated to determinand concentrations, and they can be demonstrated both in the presence and absence of reagents. They are the results of gross changes in the refractive index of the flow-cell contents such as occur when saline samples are separated by a distilled or demineralised water wash.

The disruptive effect of these signals ranges from slight, in good quality flow-cells, to catastrophic in those with unfavourable internal geometry, and, in the latter case, the use of artificial or natural low-nutrients seawater as an inter-sample wash is the normal recourse. (Use of a 9.7 % ethanol solution in water (ref 6), and other similar formulations of equivalent refractive index, has been described but such devices have not gained widespread acceptance.)

Some manufacturers, aware of this problem, advise the use of 'artificial seawater' as an inter-sample wash. While this overcomes the effects of refraction, it is unlikely to be the complete simple answer to the problem, because the background concentrations of nutrients have to be considered and possibly compensated for.

10.2.3 Artificial Seawater (ASW) as the Inter-Sample Wash

A typical formulation for ASW is 31.0 g NaCl and 10.0 g $MgSO_4.7H_20$ per litre in distilled or demineralised water, but even assuming the water supply is of adequate purity (e.g. with respect to phosphate and nitrate) the analyst's problems are by no means over.

Consider typical supplier's specifications for good quality (analytical reagent grade) sodium chloride and magnesium sulphate.

	Maximum concentration limits for specified impurities.	
	Phosphate (as PO_4)	N compounds (as N)
Sodium chloride	0.0005	0.0005
Magnesium sulphate	0.001	0.002

Multiple zeros after the decimal point are intended to impress, but the units of concentrations are 'per-cent', and these represent potential impurity levels that are far from satisfactory.

Consider for example, the case where both phosphate and nitrate are present in these two salts at only one tenth of their respective maximum concentration limits, and the N is exclusively nitrate.

There is still a serious problem; phosphate will be 0.27 and nitrate 2.5 µmol/1.

Both of these concentrations will exert appreciable bias on a system set up for typical seawater concentrations if the resultant baseline is simply *defined* as zero-concentration.

This does not preclude the use of ASW, but its users not only need to find ways of measuring its nutrient concentrations before use, they need also to ensure that these concentrations remain constant during use.

10.2.4 'Pure' Water as the Inter-Sample Wash

There is no totally satisfactory substitute for a 'zero-nutrients' inter-sample wash which can also serve as a concentration reference. This is more readily achieved using 'pure' water rather than ASW or some alternative preparation.

i. Demineralised Water (DMIN)

The demineralisation process is one of ion-exchange and its effectiveness is monitored in terms of electrical conductivity or resistivity. Modern small scale purification systems specially designed for laboratory use generally employ reverse osmosis prior to ion exchange and such systems can produce water close to the theoretical resistivity of 18.15 megohms/cm at 25 °C, highly suitable for most purposes in nutrients work (ref 7).

ii. Distilled Water (DW)

Users must beware of making assumptions about the purity of distilled water. The distilled product is likely to be purer than the feedstock, but its suitability for nutrients work has to be demonstrated, not assumed. This warning applies equally to double-distilled water.

Irrespective of the method of purification, a useful safeguard is a small replaceable mixed ion-exchange resin cartridge placed in the pumped supply line immediately upstream of the auto-sampler's wash-point.

A suitable device can be readily made using the body of a 20 ml disposable syringe filled with a self-indicating resin such as Duolite MB6113 from BDH.

10.2.5 Sensitivity

Equipment suppliers' methods are generally compromises and may claim, for example, to be 'suitable for the concentration range 0-4 µmol/1' but a typical supplier's configuration is usually substantially different from that which would extract the maximum sensitivity from the measurement system, a condition required for working exclusively in the 0-1 µmol/1 concentration range.

Users should not hesitate to alter manufacturers' manifolds in a *systematic* manner where the application demands.

10.2.6 Chemistry

Every phosphate method that uses molybdate, sulphuric acid, potassium antimonyl tartrate, and ascorbic acid as reducing agent, whether manual or automated, is almost certainly descended from Murphy and Riley's (ref 8) manual technique and their's must be the nearest there is to a method that can claim to be 'standard'.

A recent re-investigation of the original Murphy and Riley technique by Pai, Yang and Riley (ref 9), describes a comprehensive study of the effects of variation of acidity and molybdate concentration.

The acid/molybdenum ratio was shown to be crucial, influencing not only the form of the final reduced complex but also playing a vital role in the control of the reaction kinetics.

The message is clear; the underlying chemistry of the original manual method should not be tampered with.

Nevertheless, the ICES Intercomparison Exercise (which included a survey of phosphate methodology) shows that workers and equipment suppliers alike, are capable of making apparently arbitrary changes to their own and to each others' methods, sufficient to cause substantial divergence from the parent methods on which they claim to be based.

Conclusions drawn from chemical interference studies on the original method may be rendered invalid by such changes.

10.3 Calibration

A linear relationship between Absorbance and determinand concentration (i.e. compliance with the Beer-Lambert law) must be demonstrated, not assumed.

It is generally prudent to assume that seawater matrix salts may exert some influence on the kinetics of colour-forming reactions, and for this reason, working calibration solutions (those actually presented to the analyser) are normally produced by 'spiking' low-nutrients seawater (LNSW) with standard solutions of nutrient salts.

By diluting for example, a 1 ml aliquot of a standard solution to 200 ml using LNSW as diluent, the salinity of the product is close enough to that of the diluent to ensure that their refraction effects will be indistinguishable. (Modern liquid handling devices can dispense a 1 ml aliquot with highly acceptable accuracy and precision, but they should be checked gravimetrically from time to time to ensure they meet performance specifications.)

Low-nutrients seawater can be conveniently produced by collecting a bulk sample in late spring after the main plankton bloom. If stored in a polyethylene carboy in daylight and at room temperature, it will continue to deplete naturally and after a few weeks the supernatant should be siphoned off carefully, without filtration, into containers of more convenient size for laboratory use. There is no need for filtration if these operations are carried out carefully. LNSW with nitrate <0.1 µmol/l and phosphate <0.02 µmol/l is readily obtained. (A residual silicate concentration of ~1 µmol/l can be expected.)

10.4.1 Stability of Standard Solutions

When using LNSW as a base-water for the preparation of working calibration solutions, it is important to appreciate that with or without filtration LNSW must be assumed to contain micro-organisms, consequently when it has been spiked with a mixture of nutrients the depletion process is liable to resume.

Working calibration solutions are best prepared immediately before their intended use; they may be stored in darkness for short periods but should not be trusted for more than one or two hours.

Concentrated primary standard solutions of single nutrient salts (hundreds of milligrammes per litre) can be assumed to have an indefinite shelf-life if stored in darkness and protected against evaporation.

Solutions of intermediate concentration containing mixtures of nutrients can be protected indefinitely against depletion by biological action by the addition of mercuric chloride at 20 µg/ml.

Chloroform has also been recommended in this context, but it suffers the disadvantage that it may be lost by evaporation, especially from plastic containers, in which case depletion may then commence if micro-organisms are present. (In effect, chloroform is seen as an anaesthetic whereas mercury is a permanent poison).

Storage of such solutions under refrigeration is widely practised but workers should ensure that they are brought to room temperature before use, otherwise systematic volumetric errors will be introduced.

10.4.2 Stability of Samples

As a general rule, samples should not be exposed unnecessarily to any source of light. Analysis within minutes of sampling must remain the preferred and definitive procedure, but where this is not possible, methods of preservation and storage must be considered.

There is ample literature on this subject and the one thing that authors are agreed on is that there is no single universally applicable preservation/storage regime that will satisfy all requirements.

For example, storage in glass is unacceptable if silicate is a consideration, while some workers claim that phosphate is removed from the sample by adsorption on to container walls (particularly polyethylene).

Some literature claims appear to be openly contradictory but a large part of the apparent confusion is almost certain to be because different authors are never exactly comparing 'like with like'.

The potential for variability of temporal and spatial numbers and species composition in seawater is clearly immense but there are two popular approaches to the problem; these are refrigeration and poisoning.

10.4.2.1 Refrigeration

a. Freezing - is the method of choice of many workers, but several important details require attention.

i. Bottles should be frozen, stored and thawed, in an upright position, and they should not be completely filled.

The reason for these recommendations is that during the freezing process the last few millilitres to freeze will have a very different composition from the original sample, and if the bottle is completely filled the expansion of the sample due to the formation of ice will cause liquid to be expressed from the bottle past the closure. As this liquid will have an unrepresentative composition, the integrity of the sample will be lost.

ii. Dissolved silicate is reported to polymerise/crystallise during the freezing process and several authors warn that when samples are thawed prior to analysis, sufficient time must be allowed for de-polymerisation/re-dissolution.

b. Non-Frozen Refrigeration - is recommended by some workers, particularly below 4 °C but the majority appear to find frozen storage more convincing, for example, Kremling and Wenck (ref 10) showed that storage at 4 °C was totally inadequate for samples of unfiltered Atlantic water.

10.4.2.2 Poisoning

An alternative approach, particularly where refrigeration is not possible, is the addition of chemicals with the intention of poisoning the species responsible for consuming the nutrients to be determined.

Of the various chemicals that have been investigated, only two can claim any measure of popularity; these are, chloroform, and mercuric chloride.

a. Chloroform

The heterogeneous nature of the addition of a small globule of chloroform, producing a saturated solution of the toxic agent with virtually no alteration of the sample's composition, is a very attractive feature. The volatility of chloroform is however, a disadvantage that has already been discussed in the context of preservation of standard solutions.

b. Mercuric Chloride

The use of mercuric chloride in this or a similar context dates from at least 1931 when Ibanez (ref 11) described its use thus:-

'The bactericidal action of mercuric chloride prevents the troublesome activity of micro-organisms present in seawater whilst its very small dissociation constant (a = 0.013) is without effect on the pH'.

Ibanez used four drops of a saturated solution per 100 ml of sample, which is very approximately 100 µg mercuric chloride per ml of sample, depending on the effect of ambient temperature on saturation concentration.

Several authors have reported the use of mercuric chloride at a variety of (predominantly lower) concentrations but over the years it seems to have lost favour, no doubt due to the concurrent increase in interest in the determination of mercury in seawater at nanogram per litre levels, and the perceived contamination problems.

10.5 Contamination

In general, nutrient concentrations in unpolluted seawater are seldom greater than a few micromoles per litre. Consequently, from the analytical chemist's viewpoint they should be regarded as trace components.

Contamination has been briefly mentioned elsewhere in the text where applicable, but its wider implications must be appreciated. Sources of contamination may be internal, equipment, atmospheric, the analyst, or any combination of these.

a. Internal - suspended material, organic or inorganic small enough to survive filtration, may contribute chemically or physically (or both) to the Absorbance signal.

b. Equipment - surfaces that come into contact with the sample may contaminate it if not sufficiently clean.

c. Atmospheric - ammonia is a particular problem. Laboratory air is a notorious source of ammonia contamination, even in the total absence of smoking, stored ammonia solutions, and ammonia-producing chemical operations.

d. The analyst - direct finger contact with the sample or indirect via equipment surfaces and the atmosphere (particularly ammonia and urea).

Much of this kind of information cannot be found in text-books but tends to be accumulated slowly and painfully from practical experience.

Kerouel and Aminot's systematic study of these effects appears to be the only one of its kind, and their findings are worth re-stating here.

Bearing in mind the relativities of their normal concentrations in seawater, they ranked nutrients in decreasing order of contamination risk, thus: urea>nitrate>ammonia>phosphate>nitrite

10.6 Intercalibration

In the absence of readily available Reference Materials, analysts have had to rely on their own resources.

Because of problems due to biological activity in seawater, and the uncertainties associated with preservation and storage techniques, the widespread distribution and exchange of 'real' samples between laboratories has been generally considered impractical.

Certified standard solutions are commercially available (ref 12) but many laboratories consider them too expensive for routine use. These solutions of nutrients are supplied in a sodium chloride matrix of stated nominal salinity and they can give the analyst a measure of confidence in the accuracy of his techniques. Though it may be said that they are 'not quite the real thing', use of these solutions should be encouraged because the credibility of results is considerably enhanced if the measurement technique has been validated by the simultaneous successful analysis of appropriate certified solutions.

There have been successful intercomparison/intercalibration (I/C) exercises in the past based on the use of materials of this kind.

A well designed I/C exercise should not simply come to an end with the listing of results, but should find ways of helping the poorer performers to improve. To aid in this process, it is immensely valuable to the organisers to have detailed information from the participants on the manner by which they obtained their results, as this can often be much more revealing than the results themselves. I/C exercises offer opportunities for workers to communicate with each other and this helps to improve understanding of and control over the various processes that complicate the task of measuring nutrient concentrations.

It goes without saying that since techniques, equipment, standards, and analysts, all change with time, the skills of a given laboratory will also be subject to change and should be tested by formal intercomparisons at regular intervals, not just once.

At their best, I/C exercises are an ideal means for laboratories lacking experience and expertise to be helped by acknowledged experts; alternatively, it is reassuring for a laboratory to be aware that even if their efforts may not assess the *true* concentrations of nutrients in seawater their results can still be comparable with those of other leading laboratories in the field.

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