

# BALTIC SEA ENVIRONMENT PROCEEDINGS

No. 81

## SECOND ICES/HELCOM WORKSHOP ON QUALITY ASSURANCE OF CHEMICAL ANALYTICAL PROCEDURES FOR THE COMBINE AND PLC-4 PROGRAMMES

21-23 October 1999

Helsinki, Finland



HELSINKI COMMISSION  
Baltic Marine Environment Protection Commission  
2000

HELSINKI COMMISSION

Baltic Marine Environment Protection Commission

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## **1 BACKGROUND, JUSTIFICATION, AND TERMS OF REFERENCE**

As a result of the formation of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC) in the early 1990s, a first workshop on this topic was held in Hamburg in October 1993. The justification for that workshop was, among other things, that it was felt that a more formal approach towards quality assurance within the monitoring activities in the Baltic Sea (what was then called the Baltic Monitoring Programme) was needed. The full report from that meeting has been published in the Baltic Sea Environment Proceedings (No. 58), available from the HELCOM Secretariat in Helsinki.

Since that workshop, SGQAC has met every year and meanwhile has developed the 'Guidelines for Quality Assurance of Chemical Measurements in the Baltic Sea', which contain recommendations and guidance on quality assurance matters in the COMBINE programme. At the SGQAC meeting in 1998, it was realised that a need for a second workshop on quality assurance in the HELCOM area had developed, as it was deemed necessary to properly present the Guidelines to the users, and to create a forum for discussion of their contents.

The suggestion from SGQAC to arrange a second workshop on quality assurance matters was endorsed at the ninth meeting of the HELCOM Environment Committee (EC 9/98, 14/1, Paragraph 5.7).

The following terms of reference, as suggested by SGQAC in its 1998 report (ICES CM 1998/ACME:2), were approved by the ICES Council at the 1998 Annual Science Conference (ICES C.Res. 1998/2:57):

- a) review experience in the use of the Guidelines on Quality Assurance of Chemical Measurements in the Baltic Sea;
- b) exchange views on and experience in the implementation of a quality assurance system and on accreditation for monitoring laboratories;
- c) exchange information about internal and external quality control.

In order to improve the data of the HELCOM Pollution Load Compilation (PLC) programme, a quality assurance programme was established in 1994, before the start of PLC-3. In total, over 300 laboratories participated in the PLC-3 in 1995. The first step was to establish national reference laboratories. Each country established two reference laboratories, one for the analysis of river water and another one for the analysis of wastewater. In the Guidelines for PLC-3, it was recommended that the national reference laboratories educate the personnel of the participating laboratories and conduct the interlaboratory comparisons in their countries.

A first workshop on quality assurance of the PLC programme was held in 1994, in which the personnel of the reference laboratories took part. Furthermore, staff from the national reference laboratories in Estonia, Latvia, Lithuania and Poland participated in the Quality Assurance Workshop (EU-PHARE Programme) in 1995 and the Quality Assurance Workshops (EU-EQUATE Programme) in 1995–1998.

The first invitation to the 1999 workshop was distributed in March 1999, to the contact addresses of EC MON (i.e., COMBINE participants only). When it was discovered that both the COMBINE and the PLC-4 programmes planned on arranging quality assurance related workshops during 1999, it was decided to combine the efforts into one joint workshop. Although there are certain technical differences between the two programmes, there are many common problems concerning more general quality assurance issues, and it was felt that meeting together would create a broader base for discussions and exchange of information. A second invitation, directed to both the contact addresses of EC MON and of TC INPUT (i.e., both COMBINE and PLC-4), and through ICES to the Marine Chemistry Working Group and the Marine Habitat Committee, was distributed during the summer.

Representatives of the Finnish Environment Institute (FEI) in Helsinki kindly offered to host the workshop on their own premises. A list of participants is attached as Annex 1 to this report.

## **2 STRUCTURE OF THE WORKSHOP**

In order to create a forum for both exchange of general information and discussions of a more technical character, the workshop was divided into morning sessions with seminars and afternoon discussions in subgroups. The seminars were given both by participants and by invited experts. As the workshop hosted participants from both the COMBINE and the PLC-4 programmes, with partly different technical problems, the discussions were divided into sub-groups for different topics. The workshop programme is attached as Annex 2 to this report.

### **3 OPENING OF THE WORKSHOP**

The Chair of the Second ICES/HELCOM Workshop on Quality Assurance of Chemical Analytical Procedures for the COMBINE and PLC-4 Programmes (WKQAC) and of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), Dr Mikael Krysell, opened the workshop at 10.00 hrs on Thursday 21 October 1999. The research director of the Finnish Environment Institute, Dr Juha Kämäri, welcomed the participants on behalf of the institute, and gave an introduction to the work carried out there, and how this relates to the topics of the workshop.

Mr Kjell Grip, Environment Secretary of the Helsinki Commission, greeted the participants on behalf of the Commission. He then gave a very informative presentation on the on-going reorganisation of the structure of HELCOM, and explained the implications for the future work.

The Chair then proceeded to go through the practical arrangements, together with the local organizers of the FEI, Irma Mäkinen and Pentti Kangas.

### **4 SEMINARS AND PRESENTATIONS**

The first day was called the 'Guidelines and Analytical Methods Day', and included several seminars on these topics. The morning session mainly dealt with practical arrangements and background presentations, but also a rather extensive presentation of the current QA Guidelines for the COMBINE programme. During the afternoon the PLC-4 participants listened to four seminars on analytical techniques.

The second day, the 'External Quality Control Day', concentrated on topics related to accreditation, external audits and intercomparison exercises. Dr B. Pedersen of the National Environment Research Institute of Denmark (NERI), gave a presentation on intercomparisons of sampling and sample handling as an invited speaker. An important role of the presentations on days 1 and 2 was to form a background for the discussions held in the afternoons.

The third day, 'The Internal Quality Control Day', included seminars on internal QC and audits, and a presentation on measurement uncertainty for chemical laboratories. Dr G. Martin, Chair of the ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea (SGQAB), presented the important work of SGQAB, and suggested several topics on which SGQAB and SGQAC could work more closely together in the future.

Abstracts of the seminars can be found in Annex 3. For more detailed information, the responsible persons can be contacted directly (see list of participants, Annex 1).

### **5 DISCUSSIONS IN RELATION TO THE COMBINE PROGRAMME**

#### **5.1 Hydrography, Thursday (Chair: Mikael Krysell)**

The following topics were discussed:

- HELCOM QA Guidelines
- QA of sampling procedures

Regarding the Guidelines, the subgroup agreed that detailed descriptions of analytical methods are not necessary. Laboratories in the COMBINE programme are not forced to use the same standardised methods for the determination of relevant monitoring parameters, except those which are operationally defined. Instead, home methods can be used provided that their accuracy and comparability has been proven. Therefore, the Guidelines should contain advice and recommendations on the analytical method of choice. To check possible deviations from the recommended COMBINE methods, the Guidelines must contain at least information on the allowable bias and the required precision. Additionally, a chapter on relevant QA measures and on what QA information is to be reported together with the data should be included in the Guidelines.

The subgroup discussion on sampling for the determination of nutrients and hydrographic parameters revealed differences between several steps of the sampling procedures used by the participating laboratories. Therefore, the subgroup stated that there is a strong need to develop detailed Guidelines on sampling in the COMBINE programme, containing advice on necessary QA activities to evaluate the different sampling procedures used by the laboratories. During the discussion, several appropriate QA measures were recommended to be part of a Guideline on sampling for

nutrients and hydrographic parameters. For example, a specifically designed sampling should be carried out at regular intervals (at least during every cruise) to obtain information on different uncertainty components:

- 1) a repeated analysis of sub-samples for an estimation of the analytical precision;
- 2) an analysis of several sub-samples out of one hydrocast bottle to check the precision of sub-sampling; and
- 3) a replicate sampling at the same depth or even replicate casts at the same position for an estimation of the natural variability.

Documentation of the results of these investigations in control charts was recommended by the subgroup. The sampling Guidelines to be developed should also contain advice on:

- how rosette bottles should be fired (automatically or manually, on the way down or on the way up);
- how to take undisturbed bottom water samples including a definition of the term 'bottom water';
- which control charts are appropriate for internal QA of sampling;
- how CTD measurements can be checked manually;
- how field blanks can be used to test the sampling for contamination.

Further points of discussion were:

- the storage of nutrient samples in case they are measured by an auto-analyser equipped with an autosampler;
- sources of pure water on board a ship (it was recommended to carry appropriate amounts of pure water produced in the laboratory);
- comparability of total phosphorus concentrations and reactive soluble phosphate;
- determination of chlorophyll *a* and storage of chlorophyll *a* samples.

### **Recommendations**

The subgroup recommended that the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC):

- a) revise the existing Guidelines in the COMBINE Manual with regard to more detailed information on the QA requirements of the analytical methods; and
- b) develop a technical note on sampling for nutrients and hydrographic parameters including QA measures to obtain information on the reliability of sampling, sub-sampling, and sample preparation procedures.

## **5.2 Contaminants, Thursday (Chair: Uwe Harms)**

### **Validation**

It was highlighted that different strategies might be appropriate for analyses of inorganic and organic determinands, respectively, in order to fulfil the requirements/definitions summarised under the section 'Validation of Analytical Methods' of the QA Guidelines. In particular, it was stressed that information on the selectivity, sensitivity, and limit of detection of methods used for the analysis of organic determinands might be more easily obtained from investigations of real samples (with low contaminant contents) than by the extensive (and partly too theoretically oriented) approaches outlined in the Guidelines.

Furthermore, it should be clarified that validation is undoubtedly essential and required when a new method is introduced. Well-known, tested and established methods certainly need not be subject to the whole validation procedure.

### **Accuracy**

The four systematic errors outlined denote some of the predominant sources that can occur in analytical chemistry. It should be stressed that other sources of systematic errors not mentioned might also have a significant (or even more pronounced) influence on the accuracy of analytical results. The analyst is requested to check and eliminate thoroughly all possible sources of systematic errors.



### ***Certified Reference Materials***

The list of certified reference materials (CRMs) should be updated at regular time intervals. Special demand exists for CRMs adequate for the analysis of PAHs in biota.

Countries in economic transition still have problems purchasing CRMs from the respective organisations (such as BCR). Therefore, the Helsinki Commission should be encouraged to obtain CRMs in greater quantities with appropriate discounts and to sell them to Contracting Parties at reduced prices.

### ***Data Filter in relation to the objectives of COMBINE***

SGQAC should develop an approach to the assessment of the quality of monitoring data, a 'data filter'. Some principles have been described in the scientific literature and might be applied and adjusted respectively to the objectives of the COMBINE programme.

## **5.3 External QC, Friday (Chair: Mikael Krysell)**

### ***External QC in the laboratories***

The participants first studied and commented upon the current section on external QC in the QA Guidelines (Section B6). The following conclusions were drawn from the discussion:

There is a need for a statement on the necessity of regular participation in intercomparison exercises. The Guidelines should state that the participation in QUASIMEME or similar schemes must be mandatory for COMBINE laboratories. During this discussion the lack of intercomparisons for certain standard hydrographic parameters (salinity, oxygen, etc.) was noted, and it was decided that the possibilities for such intercomparisons should be examined by SGQAC.

It was furthermore concluded that the current text is too short to be practical and should be extended to include more useful information and examples.

Finally, the lack of appropriate certified reference materials (CRMs) for nutrients and PAHs was discussed. It would be useful if HELCOM and OSPAR could inform the producers of such materials of the strong need.

### ***Use of intercomparison results***

Two topics were discussed: how intercomparison results are used by the Commissions and how they are used by the laboratories.

First, the need for a standardised procedure for 'data filtration' prior to the periodic assessments was discussed. The conclusion was that a procedure has to be established, so that the external QC information provided by the data producers is used in a correct and generally acceptable way.

The discussion on how the laboratories use the results from intercomparisons resulted in the conclusion that there is a need for a standardised way of reacting to poor results. SGQAC should draft a suggested 'reaction scheme' for inclusion in the Guidelines, such as:

- 1) check calculations and units;
- 2) check control charts;
- 3) check possible interferences/matrices;
- 4) check blank;
- 5) check recovery;
- 6) document conclusions and actions;

With such a well-established procedure, the laboratories would stand a much better chance of explaining poor results and tracing mistakes, which in turn would be very useful for the Commissions when filtering data prior to assessments.

### ***Sampling and sample handling***

Biota, sediments, etc. The need for special training workshops or a video describing the correct procedures for the handling of sediment and biota samples was discussed. WKQAC recommended the production of such videos, and the promotion of existing videos produced as part of the QUASH project.

Hydrography The current section in the QA Guidelines is clearly inadequate and has to be expanded. Among other things, it should contain a section on how QC procedures should be carried out within the COMBINE programme. The following minimum requirements were suggested (detailed requirements will be drafted by SGQAC):

- Every cruise, take double samples from the same hydrographic bottle. This checks the sampling procedure of the laboratory. Results, recorded as the difference between the two double samples, should be plotted in control charts.
- Every year, carry out two casts at the same station and compare the results. This checks the sensitivity for natural variation in the investigated water body.

### ***COMBINE/PLC-4 laboratories***

The future PLC-4 programme will involve 500–800 laboratories. WKQAC strongly recommended that, in order to secure the data quality, the following measures must be taken:

- Strict quality requirements must be set for all parameters, and method requirements must be set for method-dependent analyses.
- A practical way of monitoring the proficiency of all participating laboratories must be developed.

## **6 DISCUSSIONS IN RELATION TO THE PLC-4 PROGRAMME**

### **6.1 Second Project Group Meeting for PLC-4 (Subgroup 1) and the external QC, Friday (Chair: Irma Mäkinen)**

Before the PLC-4 was started, the Project Group was nominated with experts for the three subgroups. Subgroup 1, Chemical Analysis and Quality Assurance, held its second meeting during the workshop, in which 15 experts took part. Experts from Lithuania and Russia did not attend. The items discussed are reported below.

#### *'Analytical Methods and Quality Assurance' Questionnaire*

In the autumn of 1998, a questionnaire on analytical methods and QA was distributed to experts of Subgroup 1 to clarify which improvements had been carried out in the laboratories after their participation in PLC-3. The summary of the results of the questionnaire has not yet been finalised due to late responses from Russia and Sweden. The summary will be finalised before 30 November 1999.

The countries were asked to estimate the number of laboratories participating in PLC-4. The number of participating laboratories seems to be much higher in PLC-4 than it was in PLC-3, because PLC-4 also deals with pollution sources in the catchment area of the Baltic Sea. Poland estimated that several hundred Polish laboratories (~500) will participate in PLC-4. Approximately 250–300 laboratories from other countries will participate, giving a total number of 700–800 laboratories.

#### *PLC-4 Guidelines*

Apparently, the Guidelines are not yet well known in the participating countries. The experts of Subgroup 1 were requested to inform their national laboratories about the existence of the Guidelines.

Some laboratories still use analytical methods that are not recommended in the Guidelines, such as the Nessler method for determination of ammonia and the salicylate method for determination of nitrate. If laboratories use non-recommended methods in PLC-4, they should demonstrate that their methods give results comparable to those of the recommended methods.

National quality requirements have not been set in most countries. In the PLC-4 Guidelines, the countries have been encouraged to start preparing analytical quality requirements. Specific quality requirements are necessary and will be set for the PLC programme in the near future.

### ***External QC***

The reference laboratories have organised intercomparison studies for their national laboratories. Two Estonian and two Latvian reference laboratories have participated or will participate in three intercomparisons organised by the Finnish Environment Institute in 1999. After PLC-3, the national reference laboratories have, in general, participated in many international intercomparisons (e.g., EU/EQUATE, EU/PHARE, NIVA and ITM intercomparisons, AMOS programme).

Because of the large number of participants in PLC-4, WKQAC stressed the importance of national intercomparison studies and also the importance of daily quality control procedures.

### ***Intercomparison study on determination of hydrocarbons***

The clarification of oil inputs is the priority issue in PLC-4, and determination of hydrocarbons is included as a mandatory parameter in PLC-4 on an experimental basis for some larger rivers and point sources. Dr Peter Lepom, from the Federal Environmental Agency of Germany, reported on the organization of an intercomparison study on the determination of hydrocarbons. At present, at least 15 laboratories have registered as participants. Lithuania is not able to participate in the exercise. Russia has confirmed its participation, but it has not sent any response since the distribution of standard solutions.

### ***BOD<sub>5</sub> or BOD<sub>7</sub> determination***

Subgroup 1 was asked to investigate the harmonisation of BOD analysis, as some countries are measuring BOD<sub>5</sub> and other countries BOD<sub>7</sub>. At present, six countries measure BOD<sub>5</sub> (or BOD<sub>2+5</sub>) and three countries (Estonia, Finland, and Sweden) measure BOD<sub>7</sub>. Estonia, Finland, and Sweden have reported that they are not able to change their BOD method in the near future.

### ***Uncertainty of measurements***

In PLC-4, laboratories are asked to report the uncertainty of measurements. Most laboratories carry out estimation of measurement uncertainty using data from internal quality control and method validation procedures. WKQAC was informed that the Danish and Swedish accredited laboratories will be asked to report uncertainty of measurement according to the procedures presented in the EURACHEM Guide (the error budget model) in the near future (2001).

## **7 SUMMARY AND CLOSING OF THE WORKSHOP**

After the last seminar, the Chair summarised the conclusions and recommendations that had emerged during the discussions. After further discussions, the participants agreed on a list of conclusions/recommendations for future work; these are attached as Annex 4 to this report.

The Chair then summarised the outcome of the Workshop, in particular noting the following:

- For the first time, representatives from both the COMBINE and the PLC-4 programmes had come together to discuss quality assurance matters. Both groups benefited greatly from this collaboration.
- The QA Guidelines were less well-known than expected, but were promoted during the Workshop.
- A substantial part of the discussions was devoted to problems related to sampling and sample handling. It is encouraging that this vital part of the analytical chain has been brought to light.
- WKQAC has proposed several good suggestions for the future improvement of QA Guidelines and other important work items for SGQAC and HELCOM.

The Chair thanked all Workshop participants for their valuable contributions, and the host Institute (FEI) for its generous support and for a well-functioning organisation of the Workshop. The Workshop was closed at 12.30 hrs on 23 October 1999.

## ANNEX 1: LIST OF PARTICIPANTS

HELCOM	Grip, Kjell Lääne, Ain	Environment Secretary Technological Secretary
Denmark	Andersen, Kirsten J. Cleeman, Marianne Ferdinand, Hanne Jensen, Dorethe W. Pedersen, Britta Verdier, Charlotte	Water Quality Institute, Hørsholm National Environmental Research Institute, Roskilde National Environmental Research Institute, Roskilde National Environmental Research Institute, Roskilde National Environmental Research Institute, Roskilde National Environmental Research Institute, Roskilde
Estonia	Kraut, Ene Maldre, Tiina Martin, Georg Riipulk, Valli	Estonian Environmental Research Center, Tallinn Tallinn Technical University, Tallinn Estonian Marine Institute, Tallinn Estonian Energy Ltd., Tallinn
Finland	Hahti, Hannu Hartikainen, Eeva-Liisa Huhtala, Sami Kangas, Pentti Knuuttila, Seppo Kotilainen, Helmi Korhonen, Kaija Kämäri, Juha Manninen, Pentti Mäkinen, Irma Pasanen, Jari Pellinen, Jukka Pikkarainen, Anna-Liisa Poutanen, Eeva-Liisa Sarkkinen, Mika Storgård-Envall, Carola Suortti, Anna-Mari Vuolas, Satu	Finnish Institute of Marine Research, Helsinki Finnish Environment Institute, Helsinki Finnish Environment Institute, Helsinki Finnish Environment Institute, Helsinki Finnish Environment Institute, Helsinki Southwest Finland Regional Environment Centre, Turku Finnish Environment Institute, Helsinki Finnish Environment Institute, Helsinki Consulting Engineers Paavo Ristola Ltd., Hollola Finnish Environment Institute, Helsinki Lappi Regional Environment Centre, Rovaniemi Kymi Environmental Laboratory, Ltd., Kouvola Finnish Institute of Marine Research, Helsinki Finnish Institute of Marine Research, Helsinki North Ostrobothnia Regional Environment Centre, Oulu West Finland Regional Environment Centre, Vaasa Finnish Environment Institute, Helsinki Uusimaa Regional Environment Centre, Helsinki
Germany	Harms, Uwe Lepom, Peter Woitke, Peter	Bundesforschungsanstalt für Fischerei Institut für Fischereiökologie, Hamburg Federal Environmental Agency, Berlin Federal Environmental Agency, Berlin
Latvia	Bistrova, Irene Laznik, Mendel Skolmeistere, Rita Vaivada, Maruta	Latvian Hydrometeorological Agency Latvian Hydrometeorological Agency Latvian Environment Data Centre, Jurmala Latvian Environment Data Centre, Jurmala
Poland	Andrzejczak, Włodzimierz Gazda, Krystyna	Voivodship Inspectorate of Environmental Protection, Łódź Voivodship Inspectorate of Environmental Protection, Gdansk
Sweden	Krysell, Mikael Lindevall, Lena	Swedish Meteorological and Hydrographic Institute, Norrköping Swedish University of Agricultural Sciences, Department of Environmental Assessment, Uppsala

## ANNEX 2: WORKSHOP PROGRAMME

### Second ICES/HELCOM Workshop on Quality Assurance of Chemical Analytical Procedures for the COMBINE and PLC-4 Programmes

#### Thursday, October 21: Guidelines and Analytical Method Day

Session Chair: Mikael Krysell

- 10.00–10.15 Welcoming address by FEI and HELCOM (J. Kämäri and K. Grip)  
10.15–10.30 Chair (M. Krysell) opens the meeting  
10.30–11.00 Practical arrangements, presentation of the agenda and the participants  
11.00–11.30 Background: Why are we here (P. Voitke)  
11.30–11.45 Break  
11.45–12.30 Presentation of the QA Guidelines (M. Krysell and E. Lysiak-Pastuszak)

*Lunch 12.30–14.00*

#### COMBINE Participants

- 14.00–15.30 Discussions in subgroups: What has been expected from the QA Guidelines, and have these expectations been fulfilled? What is missing? What is good, what can be improved? A written report expected from each subgroup

Subgroups: Hydrography (Chair: M. Krysell)  
Contaminants (Chair: U. Harms)

- 15.30–16.00 Coffee  
16.00–17.00 Plenary: Conclusions from the discussions

#### PLC-4 Participants (at the Research Laboratory of the FEI)

- 14.00–17.00 Chair: I. Mäkinen  
  
Determination of hydrocarbons in water by gas chromatography with flame ionisation detection (P. Lepom)  
Determination of AOX and TOC (P. Manninen and K. Korhonen)  
Working with Ion Chromatography and Automatic Colourimetric Analysers (K. Korhonen and J. Pasanen)

#### All

- 18.00–21.00 Reception at FEI (8<sup>th</sup> floor) with Poster Session (posters are invited and welcome)

#### Friday, 22 October: The External Quality Control Day

Session chair: Peter Voitke

- 09.00–10.00 Accreditation and external audits (M. Krysell)  
10.00–10.45 Sampling and sample handling intercomparisons (B. Pedersen)  
10.45–11.00 Break  
11.00–11.45 QUASIMEME interlaboratory exercises (M. Krysell and D. Wells)  
11.45–12.30 Quality system for interlaboratory comparisons (I. Mäkinen)

*Lunch 12.30–14.00*

14.00–15.30 Discussions in the COMBINE subgroups: How does the external quality control work in the laboratories? What have we learned during recent years? What more do we want and expect from intercomparison programmes, accreditation, etc.?

Same subgroups and chairs as on Thursday. Written report expected.

Discussions in the PLC subgroup: Expectations on the QA Guidelines? What can be improved in the future? Expectations on interlaboratory comparisons? Problems in organising interlaboratory comparisons? BOD<sub>5</sub> or BOD<sub>7</sub>?

Same subgroup and chair as on Thursday. Written report expected.

15.30–16.00 Coffee

16.00–17.00 Plenary: Summary of discussions

### **Saturday, 23 October: Internal Quality Control Day**

Session Chair: Mikael Krysell

09.00–09.45 Internal quality control (K.J. Andersen)

09.45–10.30 Internal audits of laboratories (A.-L. Pikkarainen)

10.30–10.45 Break

10.45–11.30 Implications of Measurement Uncertainty in Environmental Chemical Analytical Practice (U. Harms)

11.30–12.00 Presentation of the Steering Group on QA of Biological Measurements (G. Martin)

12.00–12.30 Summary of the meeting (Chair)

*Lunch 12.30–14.00*

14.00–17.00 Social programme: A sightseeing trip to the fortress Suomenlinna-Sveaborg by a ferry from the Market Place (15 min)

## ANNEX 3: ABSTRACTS OF CONTRIBUTIONS

### Oral presentations

#### (1) **Background: Why are we here? (P. Voitke)**

Monitoring of physical, chemical, and biological variables has been a well-established function of the Helsinki Convention for a long time. To merge different programmes conducted in the open sea or in coastal waters, the Cooperative Monitoring in the Baltic Sea Environment—COMBINE—was instituted in 1992. It can be estimated that in the COMBINE Programme samples from more than 500 sampling stations are regularly investigated by over 100 laboratories. To meet the requirements of COMBINE, the reliability of all these data is necessary and an appropriate quality assurance system has to be established in every laboratory.

Principally, a quality assurance system of an analytical laboratory can be subdivided into three main parts: the validation of the analytical methods used, the implementation of an in-house or internal quality assurance system, and the participation in external quality assurance measures. The COMBINE Manual depicts in its part B 'General guidelines on quality assurance for monitoring in the Baltic Sea' detailed measures to ensure the quality and comparability of analytical data. As a very first step, the requirements on the accuracy of the analytical results should be determined clearly and unambiguously, so that a suitable analytical procedure can be chosen. To ensure that the analytical procedure is fit for the intended purpose, the method must be examined to determine whether it actually can produce data of the required quality. In other words, a validation of the chosen analytical procedure has to be carried out. In routine monitoring, the use of validated analytical methods is accompanied by a continuous control of their analytical performance. That means that an internal quality control system must be established in order to demonstrate that the stated performance characteristics of the method remain constant. While the use of validated methods and internal quality control ensure accurate results within a laboratory, independent and continuous measures are necessary to demonstrate the comparability of results between different laboratories. Therefore, the participation of laboratories in external quality assessments and proficiency testing schemes is an indispensable part of analytical quality assurance. General features of the three topics—validation, internal and external quality control—were presented together with questions to be discussed during the workshop.

#### (2) **Presentation of the QA Guidelines (M. Krysell and E. Lysiak-Pastuszak)**

The presentation was prepared by E. Lysiak-Pastuszak, but as she was unable to attend the workshop M. Krysell gave the seminar.

In a brief historical review, the work of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea was first presented. The original terms of reference for this Steering Group were to:

- coordinate the development and implementation of a QA programme for laboratories participating in the Baltic Monitoring Programme (now COMBINE);
- give guidance on practical questions relating to QA;
- prepare QA guidelines for the relevant measurements;
- identify relevant reference materials and organise together with the Secretariat the distribution of those materials to laboratories participating in the BMP;
- identify costs associated with QA;
- report annually on progress in QA to the HELCOM Environment Committee and make proposals for action by the Commission.

Given these main tasks, the Steering Group has proposed and implemented QA guidelines for most relevant substance groups, and also for other relevant parts of the QA system of monitoring laboratories. The current guidelines contain the following sections:

### General Sections

- Introduction
- The quality system
- Specifying analytical requirements
- Validation of analytical methods

- Routine quality control
- External quality control
- Definitions
- References

#### Annexes

- Principal components of a quality manual
- Examples of reference materials for internal quality control
- Validation of an established analytical method
- Quality Audit – areas of particular importance to a chemistry laboratory
- General remarks on sampling
- Technical notes on the determination of nutrients
- Technical notes on the determination of organic and inorganic contaminants in biota
- Technical notes on the determination of trace metals in sea water
- Problems related to chemical analysis of anoxic waters
- Technical notes on the determination of total mercury in marine biota by cold vapour atomic absorption spectrometry

New developments are technical notes on PCBs and OCPs, PAHs, and hydrographic parameters.

The complete and most updated version of the guidelines is found on the HELCOM web page ([www.helcom.fi/ec.html](http://www.helcom.fi/ec.html)).

#### **(3) Determination of hydrocarbons in water by gas chromatography with flame ionisation detection (Peter Lepom)**

A detailed summary of the ISO/DIS 9377 Water Quality—Determination of hydrocarbon oil index—Part 4: method using solvent extraction and gas chromatography was given and results of a German national round robin test and the recently performed international interlaboratory study were presented. The proposed draft method allows the quantitative determination of hydrocarbons in water by capillary gas chromatography at concentrations above 100 µg l<sup>-1</sup> and covers a wide range of aliphatic, alicyclic and aromatic compounds of interest. The gas chromatographic procedure provides a lot of additional information with regard to the boiling range and the qualitative composition of the contamination. Preliminary results of two interlaboratory studies showed acceptable accuracy with relative reproducibility standard deviations between about 20 % and 40 %, depending on the hydrocarbon concentration and the amount of interfering compounds in the sample. The recoveries were between about 80 % and 100 % for most samples. If considerable concentrations of surfactants are in the samples, recoveries can decline to 70 % or less. Within PLC-4 the parameter 'Oil' is to be measured for the first time using this method. Prior to starting the measuring campaign, an intercomparison study with participants from all HELCOM countries is planned. Up to now, 15 laboratories from Denmark, Estonia, Germany, Finland, Latvia, Poland, Russia, and Sweden have promised their participation. Results of this exercise can be expected to be available in April 2000.

#### **(4) Determination of AOX and TOC (P. Manninen and K. Korhonen)**

##### Determination of activated carbon adsorbable organically bound halogens (AOX)

###### *Samples*

Surface waters, municipal waste waters, waste waters from pulp and paper industry.

###### *Principle*

The sum of organically bound chlorine, bromine and iodine – not fluorine – expressed as chloride.

Acidification of the water sample with HNO<sub>3</sub> (pH < 2)

Adsorption onto activated carbon by shaking or by column adsorption.

Removing inorganic halides by rinsing the carbon with acidified NO<sub>3</sub><sup>-</sup> solution

Combustion of the carbon in an oxygen stream (950°C)



Adsorption of the hydrogen halides  
Determination of the halide ions by microcolourmetric titration

Expression of the results as the mass concentration of chloride  
Working range 10 – 300 µg l<sup>-1</sup>

*Interferences*

Active chlorine – add sodium sulphate  
Inorganic bromine and iodine compounds  
Insoluble inorganic halides  
Living cells  
High chloride concentrations (Cl<sup>-</sup> / AOX > 10 000)

*Reference*

EN 1485

Determination of total organic carbon (TOC)

*Samples*

Surface waters, coastal waters, municipal waste waters, waste waters from pulp and paper industry

*Principle*

TOC is a measure of the carbon content of dissolved or undissolved organic matter in water.

Oxidation of organic carbon in water to CO<sub>2</sub> by combustion. CO<sub>2</sub> is determined by a IR-detector. Inorganic carbon is removed by acidification and purging or is determined separately.

*Interferences*

The total inorganic carbon should be less than the TOC.

Purgeable organic substances (e.g., benzene) may partly escape upon stripping.

Samples containing particles:

- the instrument should be suitable for measuring particles at least of a size 100 µm;
- check of the homogenisation is necessary by using a test suspension.

*Reference*

EN 1484

**(5) Working with Ion Chromatography and Automatic Colourimetric Analysers (K. Korhonen and J. Pasanen)**

Working with ion chromatography

*Samples*

Ground waters, surface waters and rain waters

*Principle*

Anions are separated using an anion exchanger as a separation column, carbonate solution as an eluant, and a conductivity detector combined with a suppressor device as a detector. Chloride, nitrate and sulphate are mainly determined.

In general, the uncertainty of the measurement is ≤ 10 %.

*Interferences*

Separation performance of column depends on, e.g., column material and type of eluants. Use only those separating columns that yield a baseline-resolved separation of all the components to be measured. The peak resolution should not fall below R = 1.3.

### *Reference*

EN ISO 10403-1

### Automatic Colourimetric Analysers/the FIA Method for determination of nitrate and nitrite nitrogen

#### *Samples*

Surface waters, coastal waters, municipal waste waters

#### *Principle*

The sample is fed into a continuously flowing buffer solution by means of an injection valve. Nitrate in the sample is reduced with metallic cadmium to nitrite. Then, a phosphoric acid reagent is admixed. Nitrite and nitrate are diazotized and coupled with N-(1 naphthyl)-ethylendiamine to form a red colour.

#### *Interferences*

Particles: larger particles (> 0.1 mm) can be removed by membrane filtration.

Self-absorption: compensation by measuring also the signal of the sample without the admixture of the reagent.

A pH of 6.5 to 7.5 not reached after the admixture of the buffer solution: treatment of the sample with bases or acids before the measurement.

### *Reference*

EN ISO 13395

## **(6) Accreditation and external audits (M. Krysell)**

The presentation was based upon the experience the author had gained as quality manager of an accredited laboratory and as auditor of other laboratories for the Swedish accreditation body, SWEDAC. The main aim of the seminar was to show the workshop participants how to prepare for an external audit, what the auditors look for, and how to benefit from the results of the audit.

### There are many good reasons for seeking formal accreditation

- It is a good way of (internally) raising funds
- It is a way to make the staff feel the importance of your QA work
- It provides you with a clear goal for your QA work
- It improves your reputation
- Customers may even demand it

It is always important to remember that accreditation never proves that your data are correct!

### The role of the external auditor is:

- To think of things you never thought of
- To give you a good reason (pressure) to improve
- To help you interpret the ISO 45001 standard, which is not always easy
- To informally disseminate experiences

### **How do you use the external audit for your own purposes?**

- Make sure the auditors spot the weaknesses you want them to spot (can be used to support pleas for funding new equipment, etc.!!)
- If your colleagues do not want to follow your intentions, make sure the external auditor supports you
- Try to get hints
- Do not hide things, start a useful discussion instead
- Do not accept everything the auditor says. Argumentation is always possible

## **Does accreditation improve your laboratory?**

Not automatically, but if you want to improve, it is a very good tool!

### **(7) Sampling and sample handling intercomparisons (B. Pedersen)**

#### **Introduction**

Monitoring data of good quality are needed to make a realistic assessment of the state of the marine environment. This requires that the data from different national and international monitoring programmes are comparable. The comparability of the chemical measurements made by the laboratories can be assessed through their participation in various proficiency testing schemes, e.g., QUASIMEME. It is equally important, however, to ensure that any differences in the sampling and sample-handling procedures and in a normalisation procedure of the data do not introduce major errors to the results. Testing the comparability of the pre-treatment processes is, however, more demanding than just testing the comparability of the chemical measurements. The question is also how you best can study it: through interlaboratory or within-laboratory studies, with some special test material or in a completely different way? Only a few exercises have, therefore, been performed where the variance due to differences in the sampling and sample handling procedures has been tested.

In 1996, the four-year EU-QUASH (Quality Assurance of Sampling and Sample Handling) project started, focusing on the pre-treatment processes. The project is led by the FRS Marine Laboratory in Aberdeen (Dr D. Wells) and the main aims of the project are to:

- estimate the uncertainty associated with sampling and sample manipulation prior to analysis;
- develop procedures for quality assessment and quality control of sample handling;
- improve the reliability on data on co-factors from sampling to analysis;
- provide QA/QC information and practice to all EU marine laboratories and information and recommendations concerning sampling, sample handling and co-factors to monitoring organisations (OSPAR, HELCOM and MEDPOL) as well as to European Accreditation Bodies.

The QUASH project is especially dealing with the following areas:

- 1) Sampling and preservation of nutrients in sea water;
- 2) Sample handling of biological tissues;
- 3) Lipid and water as co-factors in biota;
- 4) Sample handling and co-factors in relation to normalisation procedures for sediments.

Only results from the first two areas will be presented.

#### **Sampling and preservation of nutrients in sea water**

This special part of the QUASH project, which is led by S. Carlberg and M. Krysell (SMHI, Sweden), concentrates on problems related to the sampling and sample handling of sea water for nutrient determination. Results from a practical exercise, where different sub-sampling and preservation techniques were tested, showed that:

- The choice of bottle material and the bottle cleaning process as applied by the participants caused no major problems for determination of nutrients. Minor contamination of the samples did however occur, presumably due to an inadequate cleaning procedure. This is especially true for nitrate/nitrite, phosphate and ammonia.
- Contamination of the sample can also occur in the filtering process. This is especially pronounced for ammonia, but filtering can also create problems for phosphate.
- Each laboratory has to perform a thorough test on the preservation of ammonia in sea water from its own waters as no method for preservation can be recommended. For the other nutrients (nitrate/nitrite/phosphate/silicate), freezing of the samples for preservation seems to be the most promising of the techniques investigated.

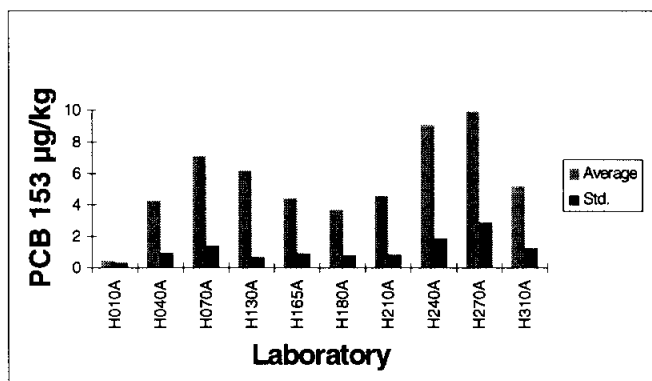
More details about this part of the QUASH project are given in Carlberg *et al.*, 1997.

#### **Sample handling of biological tissues**

This part of the QUASH project, which is led by NERI, Denmark, focuses on the interlaboratory variance of the sample handling procedures for biological samples prior to the analysis of organic compounds and trace elements. Preliminary results from an interlaboratory study, where the samples used were whole fish (frozen herring from the Baltic), indicate

that not only differences in the chemical analysis but also in the dissection procedures can contribute to the between-laboratory variance, see Figure 1. A closer investigation of the data is however needed before any firm conclusions can be drawn.

**Figure 1.** Between-laboratory variance in the determination of the concentration of PCB 153 ( $\mu\text{g kg}^{-1}$  ww) in herring.



## Conclusion

Our knowledge concerning errors due to the sampling and sample handling procedures in relation to marine monitoring has been much improved through the QUASH project. The findings also highlight the importance that these processes are included/tested in future interlaboratory studies in order to ensure comparable results in different national and international monitoring programmes.

## References

Carlberg, S., Krysell, M., de Armas, J., and Escanez, J. 1999. Practical workshop on sampling and preservation of Nutrients in Sea Water. Report from EU-QUASH.

### (8) The QUASIMEME interlaboratory exercises (M. Krysell and D. Wells)

M. Krysell presented a review of the QUASIMEME project and the exercises, which had mainly been prepared by D. Wells, project manager of the QUASIMEME and QUASH projects.

#### Short historical background:

- Started in December 1992 as an EU-sponsored project
- The launch workshop was held in February 1993
- First project ended in March 1996 (with the Crieff Workshop)
- QUASIMEME II started as a subscription scheme
- In 1999: 180 laboratories from 26 countries subscribed to samples
- 17 different samples and 5 development exercises are currently running.

#### Review of results

- Many parameters show improvement in laboratory performance over the years, but some (e.g., *p,p'*-DDT in biota) still do not give acceptable results.
- The nutrients are generally under control, but there are laboratories that constantly perform badly
- It is clear (and not surprising) that the variance increases considerably at low concentrations
- Replicate samples, dispatched in different rounds, indicate that rather many laboratories have problems with their long-term performance
- More than 50 % of extreme data are simple errors, mainly miscalculations or wrong units
- New laboratories joining QUASIMEME usually require a couple of rounds to 'settle in'

- It is important for all laboratories to look at their long-term performance, which can be done by, e.g., plotting Z-scores in a control chart. It is very possible to have a Z-score less than 2 in every round but still have a positive or negative long-term bias.

## **(9) Quality system for interlaboratory comparisons (I. Mäkinen)**

### **A short background**

Several guidelines for carrying out interlaboratory comparisons have been published in recent years, e.g., ISO/IEC Guide 43-1 (1996), ILAC requirements for the Competence of Providers of Proficiency Testing Schemes (1998). The purpose of the guidelines is to provide harmonised principles for organising interlaboratory comparisons and to describe the factors which should be taken into account in organising interlaboratory comparisons. The Finnish Environment Institute has prepared a quality system based on the above-mentioned guidelines and it has demonstrated at the assessment made by FINAS in 1999 that the quality system meets the requirements presented in the above-mentioned guidelines.

### **Quality system for organising interlaboratory comparisons**

In the quality system for organising interlaboratory comparisons, the guidelines have been prepared as follows:

- guideline for general organisation and management (e.g., managerial personnel, technical personnel, responsibilities and authority of all personnel, tasks of the external advisory group, tasks of the internal planning group, collaborators, registration of clients and client feedbacks, corrective actions, internal audits, reviews);
- guideline for general technical operation (preparation and testing of samples);
- guideline for participating in interlaboratory comparisons;
- guideline for treatment of the data and reporting of the results;
- guidelines for preparation of the samples for determination of different analytes (e.g., nutrients, metals from water, metals from solid samples).

### **Testing of sample material**

Testing of the samples is one of the most important steps in preparation of the samples. Homogeneity, stability, possible damage in transit, and the effects of ambient conditions should be considered. Also, testing of cleanness of the sample bottles is necessary, in particular before distribution of a water sample.

### **Treatment of the data**

In the evaluation of data, the following steps are common to all interlaboratory comparisons:

- Determination of the assigned value: The assigned value should be as 'true' as possible and it can be estimated, e.g., by formulation from a known concentration, by use of data obtained by a special method, by use of a consensus value produced by a group of experts or referee laboratories (mean, median), or by use of a consensus value based on the results obtained by the participants (after rejection of outliers). Where appropriate, the uncertainty of assigned values should be determined.
- Calculation of performance statistics and evaluation of performance: The results need to be transformed into a performance statistic, to allow comparison with defined goals. For the commonly used calculation of Z scores, it is necessary to select a variability, which should meet the requirements of the comparison.
- The organiser of the interlaboratory comparisons should be able to monitor the performance of the participants over time. Also, comparison of different analytical methods used by the participants should be included in the treatment of the data.

### **References**

ISO/IEC Guide 43-1. 1996. Proficiency testing by interlaboratory comparisons - Part 1: Development and operation of proficiency testing schemes.

ILAC requirements for the Competence of Providers of Proficiency Testing Schemes, 1998.

Lawn, R.E., Thompson, M., Walker R.F. 1997. Proficiency Testing in Analytical Chemistry. The Royal Society of Chemistry, Cambridge (available from the British Library).

**(10) Internal quality control (K.J. Andersen)**

(Abstract not available.)

**(11) Internal audits of laboratories (A.-L. Pikkarainen)**

The importance of quality audits when implementing a quality system has been taken into account in the Manual for Marine Monitoring in the COMBINE Programme of HELCOM. Guidelines for laboratories on how to establish a programme for internal audits and management reviews were presented in relation to standard EN 45001 (General criteria for the operation of testing laboratories), ISO/IEC Guide 25 (General requirements for the competence of calibration and testing laboratories) and EAL-G3 (Internal audits and management review for laboratories). These documents have been accepted at the international level. Some national guidance is also available—recommendations for internal audits and management reviews published by the Finnish Accreditation Service (FINAS, which is Finland's national accreditation body) are examples. Internal audits of laboratories are closely related to the standards EN 45001 and ISO/IEC Guide 25.

Official definitions for the most common terms—quality audit, quality auditor, management review—were highlighted in relation to international standard 'Quality management and quality assurance. Vocabulary (ISO 8402:1994)'. An example of an audit programme was presented as well as objectives, organisation, planning, implementation and reporting of internal audits. The connection between internal audits and management review was explained. Special attention was also paid to the quality audit annex (B-4) of the Manual for Marine Monitoring in the COMBINE Programme of HELCOM as well as to common audit procedures implemented in the Finnish Institute of Marine Research.

Some useful documents and links available on the Internet

<http://www.helcom.fi> (for example 'COMBINE manual' and 'PLC manual')

<http://www.european-accreditation.org> (EAL-G3)

<http://www.vtt.fi/ket/eurachem> (EURACHEM publications)

<http://www.mikes.fi> (for example scope of accreditation for accredited laboratories in Finland)

**(12) Implications of Measurement Uncertainty in Environmental Chemical Analytical Practice (U. Harms)**

A short description of the concept of uncertainty, which is presented in detail in the ISO 'Guide to the Expression of Uncertainty in Measurement' (ISO, 1993), was given. It was further demonstrated by means of an example taken from environmental chemical analytical practice (analysis of lead in the liver of Baltic cod), showing how different steps of an analytical system contribute to the uncertainty of the overall analytical result.

In practice, only a small number of possible sources of uncertainty will make a significant contribution to the final uncertainty of a measurement result. Components that are more than 3 to 4 times smaller than the largest component can usually be ignored. However, all possible sources need to be identified and the size of the associated component estimated, but only the largest components need to be evaluated in detail.

The following conclusions were drawn:

Evaluation of uncertainty is quite clearly connected with a substantial amount of work, but the rewards from doing so will be high:

- Standard uncertainty is a universal parameter, since it is applicable to all kinds of measurements, and it is internally consistent, since it is derivable from the components that contribute to it.
- The user of the result is enabled to make an objective assessment of the reliability that can be placed in its value.

- The uncertainty of the bias needs to be included in the uncertainty budget (combined uncertainty) whether or not the bias is significant.
- The uncertainty of the bias is dominated by the uncertainty of the assigned value of the CRM used in a trueness experiment. Therefore, the selection of an adequate CRM with a low uncertainty is of advantage.

Uncertainty in environmental analysis presents some unique features which differ from those common to other fields of analysis:

- The measurand is usually the true value of the analyte concentration in the environmental target material rather than the test portion subjected to analysis. This means that the analyst is involved with sampling/sub-sampling uncertainty right from the planning phase.
- When heterogeneous material has to be analysed, the uncertainties associated with sampling and sub-sampling, respectively, can be high and can contribute substantially to the combined uncertainty.

**(13) Presentation of the ICES/HELCOM Steering Group on QA of Biological Measurements in the Baltic Sea (G. Martin)**

SGQAB was established in 1992 with the aim to coordinate the activities related to the QA of biological parameters measured in the HELCOM BMP programme.

The list of biological parameters, which are dealt with in SGQAB activities, covers the following items in the present COMBINE programme:

- chlorophyll *a*;
- phytoplankton primary production;
- phytoplankton species composition;
- mesozooplankton;
- zoobenthos;
- phytobenthos (NEW);
- coastal fish (NEW).

The last two parameters have been included in the COMBINE programme starting in 1998.

During the last 6–7 years, SGQAB has mainly dealt with the following items:

- establishment of a QA system for HELCOM laboratories;
- harmonising the sampling and determination methodology;
- organising QA workshops for different parameters;
- development of the COMBINE Manual concerning QA chapters and technical annexes;
- developing QA procedures and guidelines for new parameters in the HELCOM monitoring programme (phytobenthos, coastal fish).

At the present time, the work is organised mainly through different HELCOM Projects and ICES Working Groups. In 1999 there are two currently running HELCOM projects directly related to QA of phytoplankton and zoobenthos parameters.

Current SGQAB activities include:

- updating of taxonomic lists;
- organising regular ring tests and intercalibration exercises;
- updating the COMBINE Manual;
- review of new biological data reporting formats developed by ICES;
- developing data quality criteria for HELCOM Periodic Assessments;
- coordination of other QA activities.

## Possible cooperation with SGQAC

SGQAB is very interested in closer cooperation with relevant working groups. At present, SGQAB has a good cooperation with ICES/OSPAR SGQAE. During the last two years, SGQAB and SGQAE have held joint sessions during their meetings. The same experience is enjoyed in past relations between SGQAB and SGQAC which could be utilised again in the future. The main interests from the SGQAB side for cooperation with SGQAC include:

- primary production measurements;
- chlorophyll *a* determination;
- implementation of general QA policy by participating laboratories.

## Posters

### (1) **Simple water sampling is not that simple (M. Krysell)**

The aim of this experiment was to show the significance of the uncertainties and problems involved in marine water sampling, compared to the uncertainty in the final data originating from the analytical step. Though the results may not be directly transferable to any kind of environmental sampling, they hint at difficulties obtained whenever the whole body of interest cannot be investigated, but measurements have to be carried out on small fractions of the whole truth.

Water was sampled with several standard samplers from the same depth using a rosette, and the total data uncertainty obtained for each parameter was fractionated into uncertainty contributions from the actual sampling, the sub-sampling and storage process, and the analysis. The water was analysed for salinity, oxygen and nutrients. The results showed that, even in seemingly homogeneous water bodies, the sampling process often contributes with the major part of the total data uncertainty. Consequently, there appears to be no reason for sharpening the analytical performance of our laboratory further, but there may well be reason to question the sampling strategy currently employed in most marine monitoring programmes. It also has to be underlined, again and again, how important it is to include the sampling process in the quality system of any marine laboratory.

### (2) **The Baltic QUASH meeting (M. Krysell)**

In the QUASH (Quality Assurance of Sampling and Sample Handling) project, information from the international meetings should be distributed on the national level in national meetings. When the Swedish national nutrients meeting was planned, it was decided to extend it into a regional Baltic meeting. This way, we could provide the meeting with a much broader basis for discussions, while disseminating information to the countries around the Baltic Sea that are not yet members of the EU. The meeting was held at SMHI in Göteborg, Sweden, and was attended by 15 participants from Sweden, Russia, Latvia, Lithuania, and Poland. Apart from a general presentation of the project, and of earlier activities and findings, the meeting programme included both presentations of sampling experiences by the participants, and a practical exercise.

In the practical exercise, water for nutrient determinations was sampled from a carboy in the laboratory by the participants, both using their best possible practice and, in contrast, while performing activities that were suspected to compromise the integrity of the samples. The results from the experiment show that it is hard to destroy the samples during the sub-sampling. The only activity which was clearly inappropriate, was to allow the water sample to pass over the fingers of the person performing the sub-sampling.



#### ANNEX 4: RECOMMENDATIONS ADOPTED BY THE PARTICIPANTS

The following recommendations were adopted by WKQAC participants:

Recommendation	Action
Salinity and oxygen (and hydrogen sulphide, if possible) should be included in future intercomparison exercises	Chair to approach QUASIMEME or other competent bodies to promote the inclusion of these compounds in the exercises
A data filter for objective classification of monitoring data prior to assessments should be produced and implemented	SGQAC to take initiatives, together with suitable ICES working groups
The possibility of buying large amounts of CRMs at discount prices for distribution to monitoring laboratories (primarily in countries in economic transition) should be investigated	HELCOM MONAS to coordinate
Specified quality requirements for the laboratory performance are needed	HELCOM MONAS to coordinate actions for both COMBINE and PLC-4
Fish dissection is still a problem—to overcome this, either a workshop should be arranged or a video produced	HELCOM MONAS
There is a need for a better definition of 'bottom water' with regard to the maximum allowable distance to the sea floor	HELCOM MONAS
The QA Guidelines for COMBINE and PLC have to be promoted in the HELCOM News and by targeted e-mails to persons on the appropriate HELCOM contact lists	HELCOM Environment Secretary
HELCOM should approach the appropriate body in the EU system to ask for the production of suitable CRMs	HELCOM Environment Secretary
Persons responsible for QA matters in the COMBINE and PLC-4 programmes should meet more regularly to discuss common problems	HELCOM
<p>Certain parts of the QA Guidelines for COMBINE need to be updated:</p> <p>Sampling part 3 extended to include:</p> <ul style="list-style-type: none"> <li>• Minimum regular QC procedure</li> <li>• Field blanks procedure</li> </ul> <p>External QC part extended to include:</p> <ul style="list-style-type: none"> <li>• Frequency requirement</li> <li>• 'Reaction scheme' if the internal control fails</li> </ul> <p>Validation note needs updating:</p> <ul style="list-style-type: none"> <li>• LOD definition (two ways according to GUM: real sample matrix at low concentration or blank without matrix)</li> <li>• Different procedure for old and new method (less extensive for established method)</li> </ul> <p>Accuracy definition: sources for error of bias lacking</p> <ul style="list-style-type: none"> <li>• List of CRMs incomplete</li> </ul> <p>Section on Measurement Uncertainty should be added as soon as possible</p>	SGQAC

## BALTIC SEA ENVIRONMENT PROCEEDINGS

- No. 1 JOINT ACTIVITIES OF THE BALTIC SEA STATES WITHIN THE FRAMEWORK OF THE CONVENTION ON THE PROTECTION OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA 1974-1978  
(1979)\*
- No. 2 REPORT OF THE INTERIM COMMISSION (IC) TO THE BALTIC MARINE ENVIRONMENT PROTECTION COMMISSION  
(1981)\*
- No. 3 ACTIVITIES OF THE COMMISSION 1980  
- Report on the activities of the Baltic Marine Environment Protection Commission during 1980  
- HELCOM Recommendations passed during 1980  
(1981)\*
- No. 4 BALTIC MARINE ENVIRONMENT BIBLIOGRAPHY 1970-1979  
(1981)\*
- No. 5A ASSESSMENT OF THE EFFECTS OF POLLUTION ON THE NATURAL RESOURCES OF THE BALTIC SEA, 1980  
PART A-1: OVERALL CONCLUSIONS  
(1981)\*
- No. 5B ASSESSMENT OF THE EFFECTS OF POLLUTION ON THE NATURAL RESOURCES OF THE BALTIC SEA, 1980  
PART A-1: OVERALL CONCLUSIONS  
PART A-2: SUMMARY OF RESULTS  
PART B: SCIENTIFIC MATERIAL  
(1981)
- No. 6 WORKSHOP ON THE ANALYSIS OF HYDROCARBONS IN SEAWATER  
Institut für Meereskunde an der Universität Kiel, Department of Marine Chemistry, March 23 -April 3, 1981  
(1982)
- No. 7 ACTIVITIES OF THE COMMISSION 1981  
- Report of the activities of the Baltic Marine Environment Protection Commission during 1981 including the Third Meeting of the Commission held in Helsinki 16-19 February 1982  
- HELCOM Recommendations passed during 1981 and 1982  
(1982)
- No. 8 ACTIVITIES OF THE COMMISSION 1982  
- Report of the activities of the Baltic Marine Environment Protection Commission during 1982 including the Fourth Meeting of the Commission held in Helsinki 1-3 February 1983  
- HELCOM Recommendations passed during 1982 and 1983  
(1983)
- No. 9 SECOND BIOLOGICAL INTERCALIBRATION WORKSHOP  
Marine Pollution Laboratory and Marine Division of the National Agency of Environmental Protection, Denmark, August 17-20, 1982, Rønne, Denmark  
(1983)
- No. 10 TEN YEARS AFTER THE SIGNING OF THE HELSINKI CONVENTION  
National Statements by the Contracting Parties on the Achievements in Implementing the Goals of the Convention on the Protection of the Marine Environment of the Baltic Sea Area (1984)
- No. 11 STUDIES ON SHIP CASUALTIES IN THE BALTIC SEA 1979-1981  
Helsinki University of Technology, Ship Hydrodynamics Laboratory, Otaniemi, Finland  
P. Tuovinen, V. Kostilainen and A. Hämäläinen  
(1984)
- No. 12 GUIDELINES FOR THE BALTIC MONITORING PROGRAMME FOR THE SECOND STAGE  
(1984)\*

\*) out of print

\*\*) in print

- No. 13      ACTIVITIES OF THE COMMISSION 1983  
 - Report of the activities of the Baltic Marine Environment Protection Commission during 1983 including the Fifth Meeting of the Commission held in Helsinki 13-16 March 1984  
 - HELCOM Recommendations passed during 1983 and 1984 (1984)
- No. 14      SEMINAR ON REVIEW OF PROGRESS MADE IN WATER PROTECTION MEASURES  
 17-21 October 1983, Espoo, Finland  
 (1985)
- No. 15      ACTIVITIES OF THE COMMISSION 1984  
 - Report of the activities of the Baltic Marine Environment Protection Commission during 1984 including the Sixth Meeting of the Commission held in Helsinki 12-15 March 1985  
 - HELCOM Recommendations passed during 1984 and 1985 (1985)
- No. 16      WATER BALANCE OF THE BALTIC SEA  
 A Regional Cooperation Project of the Baltic Sea States;  
 International Summary Report  
 (1986)
- No. 17A     FIRST PERIODIC ASSESSMENT OF THE STATE OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA, 1980-1985; GENERAL CONCLUSIONS  
 (1986)
- No. 17B     FIRST PERIODIC ASSESSMENT OF THE STATE OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA, 1980-1985; BACKGROUND DOCUMENT  
 (1987)
- No. 18      ACTIVITIES OF THE COMMISSION 1985  
 - Report of the activities of the Baltic Marine Environment Protection Commission during 1985 including the Seventh Meeting of the Commission held in Helsinki 11-14 February 1986  
 - HELCOM Recommendations passed during 1986 (1986)\*
- No. 19      BALTIC SEA MONITORING SYMPOSIUM  
 Tallinn, USSR, 10-15 March 1986  
 (1986)
- No. 20      FIRST BALTIC SEA POLLUTION LOAD COMPILATION  
 (1987)
- No. 21      SEMINAR ON REGULATIONS CONTAINED IN ANNEX II OF MARPOL 73/78 AND REGULATION 5 OF ANNEX IV OF THE HELSINKI CONVENTION  
 National Swedish Administration of Shipping and Navigation;  
 17-18 November 1986, Norrköping, Sweden  
 (1987)
- No. 22      SEMINAR ON OIL POLLUTION QUESTIONS  
 19-20 November 1986, Norrköping, Sweden  
 (1987)
- No. 23      ACTIVITIES OF THE COMMISSION 1986  
 - Report on the activities of the Baltic Marine Environment Protection Commission during 1986 including the Eighth Meeting of the Commission held in Helsinki 24-27 February 1987  
 - HELCOM Recommendations passed during 1987 (1987)\*
- No. 24      PROGRESS REPORTS ON CADMIUM, MERCURY, COPPER AND ZINC  
 (1987)
- No. 25      SEMINAR ON WASTEWATER TREATMENT IN URBAN AREAS  
 7-9 September 1986, Visby, Sweden  
 (1987)

\*) out of print  
 \*\*) in print

- No. 26      ACTIVITIES OF THE COMMISSION 1987  
 - Report on the activities of the Baltic Marine Environment Protection Commission during 1987 including the Ninth Meeting of the Commission held in Helsinki 15-19 February 1988  
 - HELCOM Recommendations passed during 1988 (1988)
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- No. 27B      GUIDELINES FOR THE BALTIC MONITORING PROGRAMME FOR THE THIRD STAGE; PART B. PHYSICAL AND CHEMICAL DETERMINANDS IN SEA WATER (1988)
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- No. 27D      GUIDELINES FOR THE BALTIC MONITORING PROGRAMME FOR THE THIRD STAGE; PART D. BIOLOGICAL DETERMINANDS (1988)
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- No. 30      SECOND SEMINAR ON WASTEWATER TREATMENT IN URBAN AREAS  
 6-8 September 1987, Visby, Sweden (1989)
- No. 31      THREE YEARS OBSERVATIONS OF THE LEVELS OF SOME RADIONUCLIDES IN THE BALTIC SEA AFTER THE CHERNOBYL ACCIDENT  
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 29 May 1989, Rostock-Warnemünde, German Democratic Republic (1989)
- No. 32      DEPOSITION OF AIRBORNE POLLUTANTS TO THE BALTIC SEA AREA 1983-1985 AND 1986 (1989)
- No. 33      ACTIVITIES OF THE COMMISSION 1989  
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- No. 34      STUDY OF THE RISK FOR ACCIDENTS AND THE RELATED ENVIRONMENTAL HAZARDS FROM THE TRANSPORTATION OF CHEMICALS BY TANKERS IN THE BALTIC SEA AREA (1990)
- No. 35A      SECOND PERIODIC ASSESSMENT OF THE STATE OF THE MARINE ENVIRONMENT OF THE BALTIC SEA, 1984-1988; GENERAL CONCLUSIONS (1990)
- No. 35B      SECOND PERIODIC ASSESSMENT OF THE STATE OF THE MARINE ENVIRONMENT OF THE BALTIC SEA, 1984-1988; BACKGROUND DOCUMENT (1990)
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- No. 39      AIRBORNE POLLUTION LOAD TO THE BALTIC SEA 1986-1990 (1991)
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- No. 41      INTERCALIBRATIONS AND INTERCOMPARISONS OF MEASUREMENT METHODS FOR AIRBORNE POLLUTANTS (1992)
- No. 42      ACTIVITIES OF THE COMMISSION 1991  
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